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Effect of alkoxy side chain length on the solid-state fluorescence behaviour of bisazomethine dyes possessing a dipropylamino terminal group

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Abstract: A study was conducted on the optical properties of alkoxy-substituted bisazomethine dyes possessing a dipropylamino terminal group in solution and the solid state. All of the derivatives had similar optical properties in chloroform solution, showing weak fluorescence quantum yield of 5%. In the solid state, the fluorescence behaviour was found to be dependent on the length of the alkoxy side chain. The solid-state fluorescence intensity of the derivatives with the short alkoxy side chains (methoxy, propoxy, and butoxy) was rather low compared to that of the other derivatives in the near-infrared region. However, in the case of the derivatives with the ethoxy side chain the red solid-state fluorescence quantum efficiency improved to 13% at around 700 nm. On the other hand, the derivatives with the middle (pentyloxy to octyloxy) to long (dodecyloxy, hexadecyloxy, and eicosanoxy) alkoxy side chains emitted at around 680 nm, producing enhanced red fluorescence compared to that of the chloroform solution. In particular, the derivative with the hexyloxy side chain showed the highest fluorescence quantum efficiency of over 20% in the solid state. To determine the influence of the alkoxy side chain length on the observed solid-state fluorescence

behaviour, X-ray structure analysis was carried out focusing on the molecular arrangement of bisazomethine dyes in crystals. The crystal structures were analysed based on the molecular arrangements of their geometrical characteristics. The result indicated that their solid-state fluorescence depends on the relative positional relationship of the neighbouring molecules and the intermolecular distance resulting from the alkoxy side chain length.

Keywords: Bisazomethine dye, Substituent effects, Crystal structure, Solid-state fluorescence, Near-infrared fluorescence

1. Introduction

Recently, organic fluorescent materials have attracted considerable interest because of their extensive and direct applications in organic semiconducting devices [1–3]. In particular, the enhanced fluorescence of π -conjugated organic materials is essential for the development of optoelectronic devices such as organic light-emitting diodes (OLEDs) [4–6]. However, organic materials that fluoresce in dilute solutions cannot efficiently fluoresce in the solid state because of the aggregation-caused quenching (ACQ) effect. The ACQ effect results from strong intermolecular π - π interactions caused by molecular aggregation [7, 8]. Fluorescence quenching in the solid state hindered the development of a near-infrared fluorophore, which has an extended π conjugated system, reducing the HOMO-LUMO energy gap. Consequently, this system facilitates increased intermolecular interactions in the tightly packed crystalline state or amorphous solid phase such as a thin film, leading to a weak emission or non-emission [9–18].

Solid-state optical properties, including fluorescence quenching, are considered to be strongly correlated with the molecular arrangement and packing pattern [19-26]. Jaggregate is a typical example, exhibiting a sharp red-shifted absorption band with strong resonance fluorescence, based on its unique electronic states derived from the characteristic low-dimensional molecular arrangement [27–29]. Some interesting results regarding the effect of substitution have been reported with bisazomethine (BAM) dyes, which can form J-aggregates in vapour-deposited films [30, 31]. In the vapourdeposited films, however, it is difficult to determine the effect of molecular arrangement and packing pattern on the intermolecular interactions and, consequently, the resulting optical and electronic properties [27, 28, 32]. Moreover, enhancement of the fluorescence intensity by molecular design of pure J-aggregate formation in the crystalline state remains to be a challenge [33, 34]. To design efficient solid-state organic materials, fluorescence quenching of the fluorophore must be prevented by controlling the molecular arrangement. A common method to obtain improved fluorescent intensity in the solid state is the introduction of substituent groups to fluorophores [23, 35–40]. The length of the substituted alkoxy chain can particularly affect the molecular arrangement and the three-dimensional aggregation of molecules, adjusting light emission in the solid state [24, 34, 41–43].

We studied BAM dyes forming J-aggregates in vapour-deposited films [30, 31, 44– 51], and observed that the fluorescence properties of some derivatives drastically changed with the length of the alkoxy side chain in the crystalline state. Herein, we report the absorption and emission properties for a range of alkoxy-substituted BAM dyes possessing a dipropylamino terminal group (Fig. 1), in solution and the solid state. X-ray structure analysis was carried out to determine the effect of molecular arrangement on the solid-state optical properties. The observed difference in the solidstate fluorescence behaviour of the BAM dyes was interpreted in the context of their molecular arrangements in the crystalline state.

<Insert Fig. 1>

2. Experimental

2.1. Materials and instruments

3-Aminophenol (98.5%), alkyl bromides (98%), alkyl iodides (98%), and phosphoryl chloride (99%) were obtained from Tokyo Chemical Industry (TCI) Co. Diaminomaleonitrile (98%) was purchased from Wako Pure Chem. Ind. Ltd. Wako silica gel C-300 (45–75 µm) was used for the column chromatography. ¹H-NMR spectra were recorded on a DRX 300 MHz NMR instrument (Bruker Co.) with TMS as the internal standard. Elemental analyses of carbon, hydrogen, and nitrogen were performed with a CHNOS Elemental Analyzer Vario ELIII Elemental (Elementar Co.). The IR spectra were collected with a PerkinElmer Spectrum BX FTIR system spectrophotometer. Melting point (T_m) was measured by differential scanning calorimetry (DSC) on a Rigaku ThermoPlus DSC 8230 at a heating rate of 10 °C/min under an air flow rate of 10 mL/min. UV-Vis absorption spectra were obtained with a Perkin Elmer Lambda 750 UV-Vis spectrometer and fluorescence spectra were collected on a Jasco FP-8500 spectrofluorometer using solution concentrations of 1.0×10^{-5} M. For the solid-state optical properties, the absorption and fluorescence spectra were measured using an optical waveguide SIS-50 surface/interface spectrometer (SIC Co.) and a Jasco FP-8500 spectrofluorometer, respectively. The fluorescence quantum efficiency ($\Phi_{\rm F}$) was estimated by using a Jasco FP-8500 spectrofluorometer. All of the optical measurements were performed in triplicate at room temperature.

2.2. Synthesis and characterisation

Novel BAM dyes were synthesised according to a previously described method [30], and their chemical structures were confirmed by nuclear magnetic resonance spectroscopy (¹H-NMR), Fourier transform infrared spectroscopy (FT-IR), and elemental analysis (EA). The synthetic route is illustrated in Fig. 1. 3-(Dipropylamino)phenol [52] and 4-(Dipropylamino)salicylaldehyde [53] were synthesised according to previously reported methods.

2.2.1. 4-(Dipropylamino)-2-alkoxybenzaldehyde (DP1a–DP20a)

A mixture of 4-(Dipropylamino)salicylaldehyde (0.66 g, 3 mmol) and potassium carbonate (0.9 g, 6 mmol) was dissolved in 15 mL of dry DMF. The alkyl halide (9 mmol) was added to the mixture and then the subsequent mixture was refluxed at 60 °C for 8h. The reaction mixture was cooled to room temperature and filtered to remove potassium carbonate. The mixture was then poured into ice water and extracted with ethyl acetate. The combined organic layer was washed with water and brine and dried over magnesium sulphate. The solvent was evaporated under reduced pressure and then purified by column chromatography by eluting with ethyl acetate/*n*-hexane (ethyl acetate : *n*-hexane=1 : 3 v/v). **DP1a**, Yield: 89% (0.63 g); ¹H-NMR (300 MHz, CDCl₃): δ (ppm): 10.16 (*s*, 1H), 7.71 (*d*, 1H, *J*= 9 Hz), 6.25 (*dd*, 1H, *J*= 6 Hz and *J*= 3 Hz), 6.01 (*d*, 1H, *J*= 3 Hz), 4.10 (*s*, 3H), 3.31 (*t*, 4H, *J*= 9 Hz), 1.62 (*m*, 4H), 0.98 (*t*, 6H, *J*= 9 Hz); IR(KBr): 1657 (C=O) cm⁻¹. **DP2a**, Yield: 83% (0.62 g); ¹H-NMR (300 MHz, CDCl₃): δ

(ppm): 10.16 (s, 1H), 7.70 (d, 1H, J= 9 Hz), 6.25 (dd, 1H, J= 6 Hz and J= 3 Hz), 6.00 (*d*, 1H, *J*= 3 Hz), 4.10 (*q*, 2H, *J*= 9 Hz), 3.30 (*t*, 4H, *J*= 9 Hz), 1.66 (*m*, 4H), 1.46 (*t*, 3H, J=9 Hz), 0.93 (t, 6H, J=9 Hz); IR(KBr): 1657 (C=O) cm⁻¹. **DP3a**, Yield: 68% (0.54 g); ¹H-NMR (300 MHz, CDCl₃): δ (ppm): 10.19 (s, 1H), 7.71 (d, 1H, J= 9 Hz), 6.25 (dd, 1H, J = 6 Hz and J = 3 Hz), 6.00 (d, 1H, J = 3 Hz), 3.98 (t, 2H, J = 9 Hz), 3.30 (t, 4H, J = 9Hz), 1.90 (*m*, 2H), 1.69 (*m*, 4H), 1.09 (*t*, 3H, *J*= 9 Hz), 0.93 (*t*, 6H, *J*= 9 Hz); IR(KBr): 1662 (C=O) cm⁻¹. **DP4a**, Yield: 81% (0.67 g); ¹H-NMR (300 MHz, CDCl₃): δ (ppm): 10.17 (s, 1H), 7.69 (d, 1H, J=9 Hz), 6.24 (dd, 1H, J=6 Hz and J=3 Hz), 6.00 (d, 1H, J= 3 Hz), 4.03 (t, 2H, J= 9 Hz) 3.30 (t, 4H, J= 9 Hz), 1.84 (m, 2H), 1.72 (m, 4H), 1.54 (m, 2H), 1.01 (t, 3H, J=9 Hz), 0.98 (t, 6H, J=9 Hz); IR(KBr): 1656 (C=O) cm⁻¹. DP5a,Yield: 78% (0.68 g); ¹H-NMR (300 MHz, CDCl₃): δ (ppm): 10.18 (s, 1H), 7.70 (d, 1H, J= 9 Hz), 6.24 (dd, 1H, J= 6 Hz and J= 3 Hz), 6.00 (d, 1H, J= 3 Hz), 4.02 (t, 2H, J= 9 Hz), 3.30 (t, 4H, J= 9 Hz), 1.85 (m, 2H), 1.65 (m, 4H), 1.59–1.40 (m, 4H), 0.98–0.91 (t, 9H, J=9 Hz); IR(KBr): 1661 (C=O) cm⁻¹. **DP6a**, Yield: 83% (0.76 g); ¹H-NMR (300 MHz, CDCl₃): δ (ppm): 10.17 (s, 1H), 7.70 (d, 1H, J= 9 Hz), 6.24 (dd, 1H, J= 6 Hz and J=3 Hz), 6.00 (d, 1H, J=3 Hz), 4.02 (t, 2H, J=9 Hz), 3.30 (t, 4H, J=9 Hz), 1.84 (m, 2H), 1.69 (*m*, 4H), 1.54–1.34 (*m*, 6H), 0.98–0.88 (*t*, 9H, *J*= 9 Hz); IR(KBr): 1666 (C=O) cm⁻¹. **DP7a**, Yield: 75% (0.71 g); ¹H-NMR (300 MHz, CDCl₃): δ (ppm): 10.18 (s, 1H), 7.71 (d, 1H, J = 9 Hz) 6.24 (dd, 1H, J = 6 Hz and J = 3 Hz), 5.99 (d, 1H, J = 3 Hz), 4.02 (t, 2H, J= 9 Hz), 3.30 (t, 4H, J= 9 Hz), 1.87–1.44 (m, 14H), 1.30 (t, 3H, J= 9 Hz), 0.95 (t, 6H, J=9 Hz); IR(KBr): 1667 (C=O) cm⁻¹. **DP8a**, Yield: 78% (0.78 g); ¹H-NMR (300 MHz, CDCl₃): δ (ppm): 10.18 (s, 1H), 7.71 (d, 1H, J= 9 Hz), 6.24 (dd, 1H, J= 6 Hz and *J*= 3 Hz), 5.99 (*d*, 1H, *J*= 3 Hz), 4.04 (*t*, 2H, *J*= 9 Hz), 3.30 (*t*, 4H, *J*= 9 Hz), 1.87–1.44 (m, 16H), 1.30 (t, 3H, J= 9 Hz), 0.96 (t, 6H, J= 9 Hz); IR(KBr): 1651 (C=O) cm⁻¹. **DP12a**, Yield: 62% (0.72 g); ¹H-NMR (300 MHz, CDCl₃): δ (ppm): 10.18 (*s*, 1H), 7.70 (*d*, 1H, *J*= 9 Hz), 6.24 (*dd*, 1H, *J*= 6 Hz and *J*= 3 Hz), 5.99 (*d*, 1H, *J*= 3 Hz), 4.01 (*t*, 2H, *J*= 9 Hz), 3.30 (*t*, 4H, *J*= 9 Hz), 1.87–1.24 (*m*, 27H), 0.93 (*t*, 6H, *J*= 9 Hz); IR(KBr): 1668 (C=O) cm⁻¹. **DP16a**, Yield: 63% (0.84 g); ¹H-NMR (300 MHz, CDCl₃): δ (ppm): 10.18 (*s*, 1H), 7.71 (*d*, 1H, *J*= 9 Hz), 6.26 (*dd*, 1H, *J*= 6 Hz and *J*= 3 Hz), 5.99 (*d*, 1H, *J*= 3 Hz), 4.01 (*t*, 2H, *J*= 9 Hz), 3.30 (*t*, 4H, *J*= 9 Hz), 1.85–1.45 (*m*, 35H), 0.93 (*t*, 6H, *J*= 9 Hz); IR(KBr): 1668 (C=O) cm⁻¹. **DP20a**, Yield: 80% (1.21 g); ¹H-NMR (300 MHz, CDCl₃): δ (ppm): 10.18 (*s*, 1H), 7.71 (*d*, 1H, *J*= 9 Hz), 6.25 (*dd*, 1H, *J*= 6 Hz and *J*= 3 Hz), 5.99 (*d*, 1H, *J*= 9 Hz), 4.01 (*t*, 2H, *J*= 9 Hz), 3.30 (*t*, 4H, *J*= 9 Hz), 6.25 (*dd*, 1H, *J*= 6 Hz and *J*= 3 Hz), 5.99 (*d*, 1H, *J*= 9 Hz), 4.01 (*t*, 2H, *J*= 9 Hz), 3.30 (*t*, 4H, *J*= 9 Hz), 6.25 (*dd*, 1H, *J*= 6 Hz and *J*= 3 Hz), 5.99 (*d*, 1H, *J*= 9 Hz), 4.01 (*t*, 2H, *J*= 9 Hz), 1.85–1.46 (*m*, 43H), 0.93 (*t*, 6H, *J*= 9 Hz); IR(KBr): 1668 (C=O) cm⁻¹.

2.2.2. BAM dyes (**DP1b–DP20b**)

A mixture of diaminomaleonitrile (0.11 g, 1 mmol) and 2 mmol of the prepared 4-(Dipropylamino)-2-alkoxybenzaldehyde were added to 20 mL of benzene; the resulting mixture was stirred. Piperidine was added dropwise for a total of 5–6 drops during the reaction. Reflux was continued at 70 °C for 8h with a Dean-Stark trap. After 8h, the reaction mixture was cooled to room temperature. The precipitated crude product was filtered and washed with methanol. The product was then purified by column chromatography using chloroform to get purple or red compounds. **DP1b**, Yield: 12% (0.07 g); M.p. 253–254 °C. ¹H-NMR (300 MHz, CDCl₃): δ (ppm): 8.99 (*s*, 2H), 8.11 (*d*, 2H, *J*= 9 Hz), 6.32 (*dd*, 2H, *J*= 6 Hz and *J*= 3 Hz), 6.01 (*d*, 2H, *J*= 3 Hz), 3.88 (*s*, 6H), 3.33 (*t*, 8H, *J*= 9 Hz), 1.68 (*m*, 8H), 0.96 (*q*, 12H, *J*= 9 Hz); EA: Found: C, 70.40; H, 7.97; N, 12.70. Calc. For C₃₂H₄₂N₆O₂: C, 70.82; H, 7.80; N, 15.49; O, 4.89; IR(KBr): 2205 (C=N) cm⁻¹, 1615 (CH=N) cm⁻¹. **DP2b**, Yield: 19% (0.11 g); M.p. 250–251 °C.

¹H-NMR (300 MHz, CDCl₃): δ (ppm): 9.00 (s, 2H), 8.11 (d, 2H, J= 9 Hz), 6.31 (dd, 2H, J= 6 Hz and J= 3 Hz), 6.02 (d, 2H, J= 3 Hz), 4.10 (q, 4H, J= 9 Hz), 3.32 (t, 8H, J= 9 Hz), 1.67 (*m*, 8H), 1.49 (*t*, 6H, *J*= 9 Hz), 0.96 (*t*, 12H, *J*= 9 Hz); EA: Found: C, 71.97; H, 8.72; N, 13.41. Calc. For C₃₄H₄₆N₆O₂: C, 71.55; H, 8.12; N, 14.72; O, 5.61; IR(KBr): 2204 (C=N) cm⁻¹, 1615 (CH=N) cm⁻¹. **DP3b**, Yield: 13% (0.08 g); M.p. 224–225 °C. ¹H-NMR (300 MHz, CDCl₃): δ (ppm): 9.02 (s, 2H), 8.11 (d, 2H, J= 9 Hz), 6.32 (dd, 2H, J= 6 Hz and J= 3 Hz), 6.02 (d, 2H, J= 3 Hz), 3.99 (t, 4H, J= 9 Hz), 3.32 (t, 8H, J= 9 Hz), 1.92 (*m*, 4H), 1.70 (*m*, 8H), 1.09 (*t*, 6H, J= 9 Hz), 0.91 (*t*, 12H, J= 9 Hz); EA: Found: C, 62.16; H, 7.14; N, 11.66. Calc. For C₃₇H₅₁N₆O₂Cl₃: C, 61.88; H, 7.16; N, 11.70; O, 4.46; IR(KBr): 2205 (C=N) cm⁻¹, 1612 (CH=N) cm⁻¹. **DP4b**, Yield: 6% (0.04) g); M.p. 215–216 °C. ¹H-NMR (300 MHz, CDCl₃): δ (ppm): 9.01 (s, 2H), 8.10 (d, 2H, J= 9 Hz), 6.32 (dd, 2H, J= 6 Hz and J= 3 Hz), 6.02 (d, 2H, J= 3 Hz), 4.03 (t, 4H, J= 9 Hz), 3.32 (t, 8H, J= 9 Hz), 1.85 (m, 64H), 1.68 (m, 8H), 1.31 (m, 4H), 1.01 (t, 6H, J= 9 Hz), 0.91 (t, 12H, J= 9 Hz); EA: Found: C, 73.73; H, 9.43; N, 10.27. Calc. For $C_{38}H_{54}N_6O_2$: C, 72.81; H, 8.68; N, 13.41; O, 5.10; IR(KBr): 2208 (C=N) cm⁻¹, 1614 (CH=N) cm⁻¹. **DP5b**, Yield: 48% (0.31 g); M.p. 217–218 °C. ¹H-NMR (300 MHz, CDCl₃): δ (ppm): 9.01 (s, 2H), 8.09 (d, 2H, J= 9 Hz), 6.31 (dd, 2H, J= 6 Hz and J= 3 Hz), 6.01 (*d*, 2H, J= 3 Hz), 4.02 (*t*, 4H, J= 9 Hz), 3.32 (*t*, 8H, J= 9 Hz), 1.86 (*m*, 4H), 1.69 (*m*, 8H), 1.53–1.37 (*m*, 8H), 1.01 (*t*, 6H, J= 9 Hz), 0.95 (*t*, 12H, J= 9 Hz); EA: Found: C, 72.18; H, 8.93; N, 12.76. Calc. For C₄₀H₅₈N₆O₂: C, 73.36; H, 8.93; N, 12.83; O, 4.89; IR(KBr): 2205 (C \equiv N) cm⁻¹, 1613 (CH=N) cm⁻¹. **DP6b**, Yield: 51% (0.35 g); M.p. 203–204 °C. ¹H-NMR (300 MHz, CDCl₃): δ (ppm): 9.01 (s, 2H), 8.10 (d, 2H, J= 9) Hz), 6.31 (dd, 2H, J = 6 Hz and J = 3 Hz), 6.01 (d, 2H, J = 3 Hz), 4.02 (t, 4H, J = 9 Hz), 3.32 (t, 8H, J = 9 Hz), 1.86 (m, 4H), 1.67 (m, 8H), 1.54-1.35 (m, 12H), 0.99-0.89 (t, 1.10) (t

18H, J= 9 Hz); EA: Found: C, 72.07; H, 9.10; N, 12.04. Calc. For C₄₂H₆₂N₆O₂: C, 73.86; H, 9.15; N, 12.30; O, 4.69; IR(KBr): 2204 (C=N) cm⁻¹, 1612 (CH=N) cm⁻¹. **DP7b**, Yield: 11% (0.08 g); M.p. 174–175 °C. ¹H-NMR (300 MHz, CDCl₃): δ (ppm): 9.01 (s, 2H), 8.11 (d, 2H, J= 9 Hz), 6.30 (dd, 2H, J= 6 Hz and J= 3 Hz), 6.01 (d, 2H, J= 3 Hz) 4.02 (*t*, 4H, *J*= 9 Hz), 3.33 (*t*, 8H, *J*= 9 Hz), 1.86 (*m*, 4H), 1.66 (*m*, 8H), 1.51–1.23 (*m*, 16H), 0.99–0.89 (*t*, 18H, *J*= 9 Hz); EA: Found: C, 64.10; H, 8.36; N, 9.81. Calc. For $C_{45}H_{67}N_6O_2Cl_3$: C, 65.09; H, 8.13; N, 10.12; O, 3.85; IR(KBr): 2203 (C=N) cm⁻¹, 1612 (CH=N) cm⁻¹. **DP8b**, Yield: 30% (0.22 g); M.p. 160–161 °C. ¹H-NMR (300 MHz, CDCl₃): δ (ppm): 9.01 (s, 2H), 8.11 (d, 2H, J= 9 Hz), 6.31 (dd, 2H, J= 6 Hz and J= 3 Hz), 6.01 (*d*, 2H, J= 3 Hz), 4.02 (*t*, 4H, J= 9 Hz), 3.32 (*t*, 8H, J= 9 Hz), 1.86 (*m*, 4H), 1.65 (m, 8H), 1.52–1.30 (m, 20H), 1.09–0.86 (t, 18H, J= 9 Hz); EA: Found: C, 74.17; H, 9.66; N, 12.29. Calc. For C₄₆H₇₀N₆O₂: C, 74.75; H, 9.55; N, 11.37; O, 4.33; IR(KBr): 2204 (C=N) cm⁻¹, 1613 (CH=N) cm⁻¹. **DP12b**, Yield: 6% (0.05 g); M.p. 134–135 °C. ¹H-NMR (300 MHz, CDCl₃): δ (ppm): 9.00 (s, 2H), 8.11 (d, 2H, J= 9 Hz), 6.32 (dd, 2H, J= 6 Hz and J= 3 Hz), 6.01 (d, 2H, J= 3 Hz), 4.01 (t, 4H, J= 9 Hz), 3.32 (t, 8H, J= 9Hz), 1.83 (*m*, 4H), 1.68 (*m*, 8H), 1.50–1.12 (*m*, 36H), 1.06–0.85 (*t*, 18H, *J*= 9 Hz); EA: Found: C, 75.00; H, 9.83; N, 9.62. Calc. For C₅₄H₈₆N₆O₂: C, 76.19; H, 10.18; N, 9.87; O, 3.76; IR(KBr): 2203 (C=N) cm⁻¹, 1614 (CH=N) cm⁻¹. **DP16b**, Yield: 8% (0.08 g); M.p. 115–116 °C. ¹H-NMR (300 MHz, CDCl₃): δ (ppm): 9.00 (s, 2H), 8.09 (d, 2H, J= 9 Hz), 6.31 (*dd*, 2H, J= 6 Hz and J= 3 Hz), 6.01 (*d*, 2H, J= 3 Hz), 4.02 (*t*, 4H, J= 9 Hz), 3.32 (t, 8H, J= 9 Hz) 1.96 (m, 4H), 1.68 (m, 8H), 1.50-1.26 (m, 52H), 1.03-0.86 (t, 5H), 1.03-0.86 (t, 5H)18H, J= 9 Hz); EA: Found: C, 72.30; H, 10.16; N, 8.18. Calc. For $C_{62}H_{102}N_6O_2$: C, 77.29; H, 10.67; N, 8.72; O, 3.32; IR(KBr): 2205 (C=N) cm⁻¹, 1610 (CH=N) cm⁻¹. **DP20b**, Yield: 2% (0.02 g); M.p. 108–109 °C. ¹H-NMR (300 MHz, CDCl₃): δ (ppm): 9.00 (*s*, 2H), 8.11 (*d*, 2H, J= 9 Hz), 6.31 (*dd*, 2H, J= 6 Hz and J= 3 Hz), 6.01 (*d*, 2H, J= 3 Hz), 4.01 (*t*, 4H, J= 9 Hz), 3.32 (*t*, 8H, J= 9 Hz), 1.85 (*m*, 4H), 1.65 (*m*, 8H), 1.50– 1.25 (*m*, 68H), 1.06–0.86 (*t*, 18H, J= 9 Hz); EA: Found: C, 77.59; H, 11.19; N, 7.75. Calc. For C₇₀H₁₁₈N₆O₂: C, 78.16; H, 11.06; N,7.81; O, 2.97; IR(KBr): 2205 (C=N) cm⁻¹, 1610 (CH=N) cm⁻¹.

2.3. Crystallography

X-ray diffraction experiments were performed on a Rigaku RAXIS-RAPID imaging plate diffractometer with a graphite-monochromatic CuKa radiation at room temperature (296 K) for **DP2b**, **DP5b**, and **DP8b** (40 kV and 30 mA). Single crystal Xray diffraction data were recorded on a Rigaku AFC-7R Mercury 70 imaging plate diffractometer equipped with a graphite-monochromatic MoKa radiation at 223.2 K for **DP3b**, **DP4b**, **DP6b**, **DP16b**, and **DP20b** (50 kV and 80 mA) and at 93 K for **DP7b** and **DP12b** (50 kV and 100 mA). The structure was solved by direct method of SIR2011 [54] and refined by full-matrix least-squares techniques. Non-hydrogen atoms were anisotropically refined. Hydrogen atoms were located at the calculated positions and refined using the riding model. All of the calculations were performed using the CrystalStructure 4.2.1 crystallographic software package [55]. The crystal structure was visualised using Mercury 3.6 [56]. All of the suitable crystals were obtained through a solvent-diffusion method. Chloroform was used as a good solvent and *n*-hexane for **DP1b–DP8b** and methanol for **DP12b–DP20b** were used as a poor solvent to grow crystals, respectively.

3. Results and discussion

3.1. Optical properties

The synthesised BAM dyes were soluble in chloroform solution $(1.0\times10^{-5} \text{ M})$. UV-Vis absorption and fluorescence spectra in chloroform are illustrated in Fig. 2. Their optical characteristics are summarised in Table 1. **DP1b–DP20b** showed a similar absorption band characterised by an absorption maximum (λ_{max}) at 558 nm and a small shoulder around 520 nm with a molar extinction coefficient (e_{max}) in the range of 1.1- 1.2×10^{5} . The λ_{max} with large e_{max} values for the BAM dyes are due to the intramolecular charge transfer (ICT) of the π -conjugate push-pull system from the arylamine moiety as the donor to the central dicyanoethylene moiety as the acceptor [30, 57]. All of the derivatives exhibited a sharp fluorescence band with the maximum fluorescence (F_{max}) in the range of 609–612 nm. In addition, the fluorescence quantum yield was low and similar ($\Phi_{\rm F} < 0.05$) for all the dyes. Excitation spectra for the observed F_{max} were in good agreement with the absorption spectra (Fig. S1 (a)). No remarkable difference in the optical properties was found in chloroform solution. In the present series of BAM dyes, the length of alkoxy substituents did not lead to large alterations of absorption and fluorescence spectra in chloroform solution.

<Insert Fig. 2>

As shown in Fig. 3, the absorption and fluorescence properties of all the BAM dyes were also measured in the crystalline state. Their optical properties in the crystalline state are summarised in Table 1. None of the derivatives exhibited any significant difference in the absorption band, with an absorption maximum at around 610 nm, which is red-shifted compared to that in chloroform solution. Significant differences were observed in the fluorescence behaviour of the dyes in the crystalline state, as shown in Fig. 3 (b) and Table 1. The derivatives with short alkoxy side chains (**DP1b**– **DP4b**) exhibited slightly red-shifted fluorescence spectra with F_{max} of about 700 nm. In particular, the derivatives with short alkoxy side chains with the exception of **DP2b** had a relatively lower $\Phi_{\rm F}$ (of about 5%) compared to that of the other derivatives. **DP2b** exhibited the enhanced near-infrared solid-state fluorescence with $\Phi_{\rm F}$ of 13%. The derivatives with short side chains might have dissimilarities in their intermolecular interactions, weakening the emission. In the case of the derivatives with longer alkoxy side chains (**DP5b–DP20b**), however, F_{max} of the fluorescence spectra was observed in the range of 680-690 nm producing a stronger fluorescence intensity of over 12% greater than that of solution. These results suggest that the length of the side chain could decrease intermolecular interactions, leading to enhanced fluorescence in the solid state. Therefore, a particular length of the side chain in this dye system could give the most favoured packing structure with minimised intermolecular interactions in the solid state. There is no significant difference of excitation spectra for the observed F_{max} in the crystalline state (Fig. S1 (b)). As listed in Table 1, DP6b with its hexyloxy side chain exhibited the highest $\Phi_{\rm F}$ of 20% in the present series. These dyes have the potential to be used as near-infrared fluorescent materials, which usually suffer from low quantum efficiencies [11, 13]. On the other hand, there was little difference in its λ_{max} in the solid state, which was red-shifted compared to that in solution. The length of the side chain affects fluorescence behaviour in the solid state, whereas it does not significantly modify absorption spectra based on interactions such as excitonic interactions [38, 58].

<Insert Table 1>

3.2. Crystal structures

In order to interpret the fluorescence behaviour of **DP2b–DP20b** in the solid state, Xray structure analysis was carried out. The crystallographic data are summarised in Table 2. A suitable single crystal of **DP1b** for the analysis was not obtained. The core of the BAM dyes corresponding to the π -conjugated push-pull system is almost planar and has a crystallographic centre of symmetry in the crystal. Moreover, the substituted side chains, except for the hexyloxy side chain in **DP6b**, adopt a trans-zigzag conformation. There is no critical short contact between the stacked molecules of all BAM dye derivatives (Table S1). Intermolecular distance and slip angles were measured between the closest stacked molecules to investigate the relationship between molecular arrangement and the length of the alkoxy side chain. The slip angles were calculated in two directions: along the long molecular axis as viewed from the side of the π conjugated part from the terminal arylamine moiety to the other terminal arylamine moiety, and along the short molecular axis as viewed from the side of the π -conjugated part from the central dicyanoethylene moiety to the other central dicyanoethylene moiety. This geometrical examination allowed us to divide the crystal structures into three groups. DP2b, DP4b, DP5b, DP6b, DP8b, and DP12b with short and middle lengths of the alkoxy side chain are in Group 1; **DP16b** and **DP20b** with long lengths of the alkoxy side chain belong to Group 2; and DP3b and DP7b with solvated crystals are assigned to Group 3 (Table S2). The most remarkable structural difference between Groups 1 and 2 was found in the slip angle along the short molecular axis. Molecules are stacked with this slip angle in the range of 56–58° in Group 1, whereas a larger slippage of about 80° along this direction was found in the derivatives in Group 2. The π -conjugated part of molecules in Group 2 overlapped more by the enlarged slip angle along the short molecular axis compared to that in Group 1. The intermolecular distance in Group 2 is under 3.41 Å, which is smaller than that in Group 1 members except for **DP4b**. In the case of the derivatives of Group 3, these structural features are similar to those of Group 1 unless the chloroform solvent is included in the crystal. Interestingly, the molecules in all the groups were stacked with similar small slip angles in the range of 25–30° along the long molecular axis forming a staircase arrangement [28, 33]. This structural feature can be regarded as one of structural components for J-type aggregates causing enhanced fluorescence compared to those of the monomer [27, 28].

The molecules of **DP4b** in Group 1 are π - π stacked in a layer parallel to the *ac* plane (Fig. 4 (a)). The intermolecular distance is the shortest length of 3.35 Å in the present series (Fig. 4 (b)). The slip angles are calculated to be 27° along the long molecular axis and 56° along the short molecular axis. The short intermolecular distance of **DP4b** between the π -conjugated molecules might have the potential to form tight molecular packing in the crystalline state leading to stronger intermolecular interactions as a short intermolecular distance between π -conjugated molecules has been known to correlate with significant intermolecular interactions in solid-state fluorescence quenching [13, 20, 26, 35]. The strong intermolecular interactions between the π -conjugated molecules could lead to the weakened fluorescence of the chromophore [36, 37]. This result agrees with the relatively low fluorescence quantum yield of **DP4b** compared to that of the other derivatives in the solid state. Fig. 5 depicts the molecular arrangement of **DP5b**. The crystal system of **DP5b** is different from the others as it belongs to a monoclinic system with $P2_1/c$ space group. However, its molecular arrangement is categorised as Group 1. As shown in Fig. 5, the molecules are stacked along the *c* axis with an

intermolecular distance of 3.47 Å. They form two-dimensional staircase arrangements with slip angles of 27° and 57° along the long and short molecular axes, respectively. The only structural difference from the other derivatives in Group 1 is that the two-dimensional staircase layers do not align in a completely parallel way as indicated in Fig. 5 (a). This result suggests that the influence of the small difference in the interlayer alignment is negligible for the purposes of fluorescence quenching in the solid state of these dyes. Fig. 6 shows the molecular arrangement of **DP2b** (Fig. S2), **DP8b** (Fig. S3) and **DP12b** (Fig. S4) is similar to that of **DP6b** as listed in Table S2. The molecules are arranged in parallel with an intermolecular distance of 3.48 Å. The two types of small slip angles are 28° along the long molecular axis and 58° along the short molecular axis (Fig. 6 (b)). The derivatives in Group 1 have similar molecular arrangements. An almost similar fluorescence behaviour of the derivatives in this Group could be interpreted by this structural similarity, except for **DP4b** having a relatively small fluorescence quantum yield correlated with its short intermolecular distance.

<Insert Fig. 4> <Insert Fig. 5> <Insert Fig. 6>

The crystal structure of **DP16b** in Group 2 is shown in Fig. 7. The structure of **DP20b** is isomorphic with **DP16b** (Table S2 and Fig. S5). The intermolecular distance is 3.40 Å for **DP16b** and 3.41 Å for **DP20b**. The two slip angles along the long and short molecular axes are 25° and 81° for **DP16b** and 25° and 80° for **DP20b**,

respectively. The conformation of the long alkoxy side chain is not horizontal to the planar core plane with a typical zigzag conformation. There is no significant difference in the optical properties of the derivatives in Group 2. In the view along the long molecular axis, the molecules of **DP16b** and **DP20b** are also aligned in the head-to-tail arrangement like Group 1. However, Group 2 dyes have a tendency to form different molecular pairs along the short molecular axis from those of Group 1. The long side chain causes a molecule to be closer to neighbouring molecules with large slip angles of about 80° along the short molecular axis. The small intermolecular distance and enlarged slip angle along the short molecular axis of the longer side chains lead to further overlapping of the π -conjugated part of molecules, resulting in an increase in intermolecular interactions. The long side chain may cause an increase in intermolecular interactions in the fluorescence intensity of **DP16b** and **DP20b** compared to those of the derivatives in Group 1 (with the exception of **DP4b**).

<Insert Fig. 7>

In the solvated crystal of **DP3b** and **DP7b** in Group 3, the chloroform molecules are arranged between the two-dimensional layers, as illustrated in Fig. 8 (a). These solvated crystals have two unsymmetrical half-molecular units. In the solvated crystal of **DP3b**, these two different molecular units are almost planar and are stacked in a parallel fashion, thereby forming the staircase arrangement as recognised in the derivatives of Groups 1 and 2. Two intermolecular distances were identified in the crystal of **DP3b**, because of two different unsymmetrical units. They are 3.45 Å and 3.52 Å. The slip angle is calculated to be 26–28° and 56° along the long and short molecular axes,

respectively. In the solvated crystal of **DP7b**, two different molecular units are slightly distorted. The molecules in this solvated crystal also form the staircase arrangement with two different intermolecular distances. The molecules of **DP7b** are packed in almost parallel with intermolecular distance of 3.33 Å and 3.48 Å. The slip angle is measured as 27–29° and 50–53° along the long and short molecular axes, respectively (Fig. S6 and Table S2). From this structural perspective, it seems that there would be no significant difference in fluorescence behaviour of these two solvated crystals. However, fluorescent characteristics of two derivatives are not the same. Powder X-ray measurement for the ground sample of **DP3b** showed that there was no structural change of its solvate by grinding, whereas we found that a slight structural change occurred by the grinding process in the **DP7b** solvate. This may cause their different fluorescence behaviour.

<Insert Fig. 8>

<Insert Table 2>

4. Conclusions

Eleven novel BAM dyes possessing a dipropyl terminal amino group with different alkoxy side chains on the phenyl ring were synthesised and their optical properties were investigated. All the synthesised BAM dyes exhibited similar absorption and fluorescence behaviour in chloroform solution. Further, there was no significant difference in the absorption spectra among the derivatives in the crystalline state. On the other hand, the dyes exhibited red-shifted fluorescence spectra, with enhanced fluorescence quantum efficiency in the crystalline state compared to that in the chloroform solution. The difference in the solid-state fluorescence behaviour was found

to be dependent on the length of the alkoxy side chains. The BAM dyes were grouped by analysing their molecular arrangement in their crystal structure. The derivatives in the same group showed similar fluorescence behaviour because of their structural similarities with the exceptions of **DP3b**, **DP4b**, and **DP7b**. **DP3b** and **DP7b** belong to the same group – a solvated crystal – but exhibit dissimilar fluorescence behaviour in the solid state. Low solid-state fluorescence quantum yield of **DP4b** is correlated with its closed intermolecular distance. The present result suggests that the solid-state fluorescence of BAM dyes is influenced by the molecular arrangement dependent on the alkoxy side chain length in the crystalline state.

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Figure captions

Fig. 1 The synthetic route and chemical structures of novel bisazomethine dyes.

Fig. 2 Normalised (a) absorption and (b) fluorescence spectra for **DP1b–DP20b** in chloroform solution; the concentrations of 1.0×10^{-5} M for each derivative.

Fig. 3 Normalised (a) absorption and (b) fluorescence spectra for **DP1b–DP20b** in the crystalline state.

Fig. 4 Crystal structure of **DP4b** viewed from three directions: (a) top view, (b) side view along the long molecular axis, and (c) side view along the short molecular axis.

Fig. 5 Crystal structure of **DP5b** viewed from three directions: (a) top view, (b) side view along the long molecular axis, and (c) side view along the short molecular axis.

Fig. 6 Crystal structure of **DP6b** viewed from three directions: (a) top view, (b) side view along the long molecular axis, and (c) side view along the short molecular axis.

Fig. 7 Crystal structure of **DP16b** viewed from three directions: (a) top view, (b) side view along the long molecular axis, and (c) side view along the short molecular axis.

Fig. 8 Crystal structure of **DP3b** solvate viewed from three directions: (a) top view, (b) side view along the long molecular axis, and (c) side view along the short molecular axis.

Table captions

 Table 1 Absorption and fluorescence properties in chloroform solution and in the crystalline state.

 Table 2 Summary of crystallographic data.

Dye		In chl	oroform solu		In crystalline state				$\Lambda^{1} (nm)^{g}$	$\Lambda E(nm)^h$	
	λ_{\max} (nm)	$\varepsilon_{\rm max} \times 10^{-5}$	$F_{\rm max} ({\rm nm})^a$	$\Phi_{\mathrm{F}}\left(\% ight)^{b}$	$SS(nm)^c$	λ_{\max} (nm)	$F_{\max} (\mathrm{nm})^d$	$\Phi_{\mathrm{F}}\left(\% ight)^{e}$	$SS (nm)^{f}$	$\Delta \lambda$ (IIIII)	$\Delta I'$ (IIIII)
DP1b	558	1.11	611	3.1	53	608	702	4.1	94	50	91
DP2b	558	1.12	610	3.4	52	607	697	12.9	90	49	87
DP3b	558	1.12	609	4.7	51	609	696	5.3	87	51	87
DP4b	558	1.11	611	4.8	53	610	694	5.0	84	52	83
DP5b	558	1.11	611	4.3	53	609	688	13.7	79	51	77
DP6b	558	1.12	610	4.0	52	609	687	20.1	78	51	77
DP7b	558	1.11	612	4.3	54	608	680	17.1	72	50	68
DP8b	558	1.12	612	3.1	54	609	679	16.6	70	51	67
DP12b	558	1.12	610	4.3	52	610	687	13.7	77	52	77
DP16b	558	1.12	610	3.9	52	610	689	12.8	79	52	79
DP20b	558	1.12	611	3.0	53	609	682	11.9	72	51	71

Table 1 Absorption and fluorescence properties in chloroform solution and in the crystalline state.

Cor

 ${}^{a}F_{\text{max}}$ (solution) excited at 558 nm.

 ${}^{b}\Phi_{\rm F}$: Fluorescence quantum yield in solution.

^{*c*}SS : Stokes shift, F_{max} - λ_{max} in chloroform solution.

 ${}^{d}F_{\text{max}}$ (the crystalline state) excited at 610 nm.

 ${}^{e}\Phi_{\rm F}$: Fluorescence quantum yield in a crystalline state.

^{*f}SS* : Stokes shift, F_{max} - λ_{max} in a crystalline state.</sup>

^{*g*}Δλ (nm) : λ_{max} (the crystalline state) - λ_{max} (solution).

 ${}^{h}\Delta F$ (nm) : F_{max} (the crystalline state) - F_{max} (solution).

Crystal data	DP2b	DP3b	DP4b	DP5b	DP6b	DP7b	DP8b	DP12b	DP16b	DP20b
Formula	$C_{34}H_{46}N_6O_2$	$C_{37}H_{51}N_6O_2Cl_3$	$C_{38}H_{54}N_6O_2$	$C_{40}H_{58}N_6O_2$	$C_{42}H_{62}N_6O_2$	$C_{45}H_{67}N_6O_2Cl_3$	$C_{46}H_{70}N_6O_2$	$C_{54}H_{86}N_6O_2$	$C_{62}H_{102}N_6O_2$	$C_{70}H_{118}N_6O_2$
Formula weight	570.78	718.21	626.88	654.94	682.99	830.42	739.10	851.31	963.53	1075.74
Crystal system	<i>P</i> -1	<i>P</i> -1	<i>P</i> -1	$P2_{1}/c$	<i>P</i> -1	<i>P</i> -1	<i>P</i> -1	<i>P</i> -1	<i>P</i> -1	<i>P</i> -1
Space group	trclinic	trclinic	trclinic	monoclinic	trclinic	trelinic	trelinic	trclinic	trclinic	trclinic
Temperature, K	296	223.2	223.2	296	223.2	93	296	93	223.2	223.2
<i>a</i> , Å	8.6273(2)	8.843(2)	8.550(7)	8.7836(2)	8.794(9)	10.756(3)	8.4180(2)	8.538(7)	8.343(2)	8.339(5)
b, Å	9.0502(2)	13.289(3)	9.149(9)	25.0075(6)	8.879(8)	13.803(3)	9.4288(2)	8.996(8)	11.267(3)	11.259(6)
<i>c</i> , Å	13.3357(3)	17.726(4)	12.90(1)	9.0627(2)	13.32(1)	16.943(4)	15.4182(4)	17.08(2)	17.408(6)	19.91(1)
α , deg	73.833(1)	73.521(5)	87.48(4)	90	79.54(6)	101.927(5)	95.911(1)	76.91(4)	83.234(9)	76.83(2)
eta , deg	86.587(1)	77.317(8)	72.02(4)	103.622(1)	85.63(4)	91.835(3)	97.431(1)	77.83(5)	84.48(1)	87.47(3)
γ, deg	75.355(1)	88.466(8)	74.27(4)	90	78.57(5)	91.153(4)	105.153(1)	75.35(6)	70.471(9)	70.16(2)
Ζ	1	2	1	2	1	2	1	1	1	1
V, Å ³	967.51(4)	1947.3(8)	923.0(2)	1934.68(8)	1001.0(2)	2459.0(1)	1159.27(5)	1220.0(2)	1528.7(8)	1711.0(2)
$d_{\rm calc}, {\rm g/cm}^3$	0.980	1.225	1.128	1.124	1.132	1.121	1.059	1.159	1.047	1.044
<i>F</i> (000)	308.00	764.00	340.00	712.00	372.00	892.00	404.00	468.00	532.00	596.00
μ , mm ⁻¹	0.490	0.274	0.071	0.546	0.070	0.225	0.503	0.070	0.063	0.062
No. of reflns measured	8231	16992	5899	17158	1039	16120	10750	1234	9946	10784
No. of unique reflns	3290	10133	3170	3503	337	8524	3957	413	5276	5599
No. of parameters	190	437	208	217	226	505	239	299	316	352
$\mathbf{D} / \mathbf{w} \mathbf{D}$	0.0866/	0.0805/	0.0792/	0.0892/	0.0806/	0.0665/	0.0694/	0.1033/	0.0779/	0.0880/
\mathbf{K}_1 / $\mathbf{W}\mathbf{K}_2$	0.1972	0.1753	0.2385	0.2052	0.1630	0.1327	0.1465	0.2246	0.1573	0.1671
GOF	1.000	1.000	1.000	1.000	1.000	1.000	1.000	1.000	1.000	1.000
CCDC	1485364	1485365	1485366	1485371	1485372	1485373	1485374	1485375	1485376	1485377

 Table 2 Summary of crystallographic data.













(c)









(c)











(c)























(c)

Effect of alkoxy side chain length on the solid-state fluorescence behaviour of bisazomethine dyes possessing a dipropylamino terminal group

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Highlights

- · Alkoxy-substituted bisazomethine dyes with a dipropylamino group were synthesised.
- \cdot The derivatives exhibited near-infrared fluorescence in a crystalline state.
- · Fluorescence intensity of the derivatives was enhanced in a crystalline state.
- Fluorescence behaviour in solids are dependent on the length of alkoxy substituents.
- · Solid-state fluorescence behaviour was correlated with molecular arrangement.

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