# Effect of phenyl ring substitution on J-aggregate formation ability of novel bisazomethine dyes in vapour-deposited films

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**Abstract**

Bisazomethine dyes, which are synthesized using diaminomaleonitrile and aminobenzaldehydes, exhibit red fluorescence in solution and in the solid state. Several bisazomethine dyes are known to form J-aggregates in vapour-deposited films. In this work, novel bisazomethine dyes were synthesized and the effect of phenyl ring substitution on the J-aggregate formation in vapour-deposited films was examined. The optical properties of the dyes were examined in solution and in the solid state through molecular orbital calculations. Four derivatives were found to form J-aggregates in vapour-deposited films as determined from the shape of the spectrum and the absorption edge.

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## 1. Introduction

In recent years, organic molecular materials have gained considerable importance from the viewpoint of their applications in optoelectronics: these materials can be used to fabricate optoelectronic devices such as organic light-emitting diodes, organic thin-film transistors, and organic solar cells [1-9]. Devices fabricated using organic molecular materials are expected to be lightweight and flexible; moreover, the fabrication process is environmentally friendly [10-12]. Many studies have focused on the development of novel organic molecular materials for the abovementioned applications [13, 14] with the aim of obtaining devices with high performance characteristics. However, it is difficult to design the solid-state structure of organic molecules with the desired properties. This is because very little is known about the crystallization phenomena of organic molecules.

Molecular aggregates have attracted considerable attention as potential candidates for improving the characteristics of optoelectronic devices, with the most well-known example of molecular aggregates being J-aggregates. J-aggregates are characterized by sharp red-shifted absorption and strong photoluminescence with respect to the corresponding molecular electronic states [15-22]. These characteristic features are attributed to the excitonic interaction within the aggregates [23]. Scheibe [24] and Khun [25] reported plausible low-dimensional molecular arrangements of J-aggregates. Kato experimentally demonstrated that merocyanine J-aggregates have a brick-wall arrangement in a LB-film and that the electronic states of the film can be interpreted on the basis of exciton interaction [17].

In this study, we have synthesized bisazomethine dyes by using diaminomaleonitrile and benzaldehydes. Crystal structure studies on some bisazomethine dyes [26-28] have revealed that this dye system has a potential to form J-aggregates [20, 22, 29]. The spectra of several bisazomethine dyes in vapour-deposited films were remarkably different from those of their solutions; the spectra in the former case showed a sharp absorption band in the long-wavelength region [30, 31]. For *N, N*′-bis[4-(*N, N*-diethylamino)benzylidene]-diaminomaleonitrile (DE2), this band was assigned to J-aggregates [31]. J-

aggregate films of DE2, however, also include a non-aggregate solid phase corresponding to the single crystal phase [26]. This phase mixing was thought to be the cause of the weak fluorescence of J-aggregate films of DE2 [32]. In a previous study, we examined the photovoltaic properties of J-aggregate films of DE2; although we did not find an apparent contribution of J-aggregates in the photocurrent action spectra of the films, we found that the films are a potential photocarrier-generating material comparable to metal phthalocyanines [33]. Thus, it may be possible to improve the solid state properties of this dye system by using a pure J-aggregate solid film. This report describes the effect of phenyl ring substitution on J-aggregate formation in vapour-deposited films. The dyes were synthesized by the reaction of diaminomaleonitrile with 4-(dimethylamino)-2-alkoxybenzaldehydes (**1a–7a**) and 4-(diethylamino)-2-alkoxybenzaldehydes (**8a–14a**). The UV-Vis absorption and fluorescent properties of the synthesized dyes were investigated in solution as well as in vapour-deposited films. The electronic states of the dyes were characterized by molecular orbital calculations.

## 2. Experimental

### 2.1 Materials and equipment

3-(Dimethylamino)phenol (97%) and 4-(diethylamino)salicylaldehyde (98%) were purchased from Sigma-Aldrich Co. Alkylbromides (98%) and diaminomaleonitrile (98%) were obtained from Wako Pure Chem. Ind., Ltd. and Nacalai Tesque Inc., respectively. Wakogel C-300 (silica gel) was used for the column chromatography. The $^1$H NMR spectra were recorded on an EX 270 MHz NMR instrument (Jeol Ltd.) and a DRX 300 MHz NMR instrument (Bruker Co.) with TMS as the internal standard. The elemental analyses were recorded on a Vario EL III elemental analyzer (Elementar Co.). The IR spectra were recorded using a PerkinElmer Spectrum BX FTIR system spectrophotometer. The absorption spectra

of the bisazomethine dyes and those of their vapour-deposited films were determined using a PerkinElmer Lambda 20 UV-Vis spectrophotometer and a PerkinElmer Lambda 750 UV-Vis spectrophotometer, respectively. Fluorescence spectra measurements were performed on a LS 45 spectrofluorimeter (PerkinElmer) equipped with a xenon discharge lamp and 1-cm quartz cells. The fluorescence spectra of the vapour-deposited films were recorded using a LS 55 spectrofluorimeter (PerkinElmer). The concentration of the solutions used for absorption and fluorescence measurements was ca. $1.0 \times 10^{-5}$ M. Thermal analysis of the synthesized dyes was carried out by using a MEL-TEMP electrothermal melting point apparatus without corrections. Thin films of the synthesized novel bisazomethine dyes were vapour-deposited onto a glass substrate using vacuum deposition equipment (ULVAC VPC-060) under vacuum conditions of ca. $3.0 \times 10^{-2}$ Pa. All measurements were taken at room temperature at approximately 298 K.

## 2.2 Molecular orbital calculations

The molecular structure for the calculation of the electronic states of a molecule was optimized by using the AM1 Hamiltonian [34]. Theoretical absorption properties were obtained by the INDO/S Hamiltonian [35, 36] on the basis of the optimized molecular structure. 257 configuration interactions were taken into account. All the calculations were performed with a CAChe 5.2 program package [37].

## 2.3 Synthesis and characterization

Novel bisazomethine dyes were synthesized according to a previously described method [38, 39], and their chemical structure was confirmed by ^{1}H NMR, IR, and elemental analysis. The synthetic procedure is illustrated in Scheme 1.

*2.3.1 4-(Dimethylamino)salicylaldehyde, 4-(dimethylamino)-2-alkoxybenzaldehydes 1a–7a and 4-(diethylamino)-2-alkoxybenzaldehydes 8a–14a*

4-(Dimethylamino)salicylaldehyde was synthesized by the reported procedure [40]. To the mixture of 3-(dimethylamino)phenol 20 mmol (2.75 g) and 10 ml *N, N*-dimethylformamide was dropwise added 42 mmol phosphorus oxychloride (3.46 g) at 0 °C while stirring. The resulting mixture was stirred at 80 °C for 16 h. After 16 h, the reaction was cooled to room temperature and the mixture was quenched into 150 ml ice water. The formed precipitate solution was adjusted to the neutral pH condition using 4M sodium hydroxide solution. The solid was filtered and purified by column chromatography by eluting with ethyl acetate/ *n*-hexane (ethyl acetate:*n*-hexane = 1:3 v/v). The yellow solid was obtained after recrystalization with *n*-hexane. Yield: 61.2% (2.02 g); M.p. 78–79 °C. ^{1}H NMR (300 MHZ, CDCl$_3$): δ10.73 (s, 1H, CHO), δ8.64 (s, 1H, OH), δ6.38~6.43 (t, *J* = 8.8 Hz, 1H, aromatic), δ5.40~5.44 (dd, *J* = 6.6 and 2.3 Hz, 1H, aromatic), δ5.21~4.22 (d, *J* = 2.3 Hz, 1H, aromatic), δ2.17~2.19 (d, *J* = 5.0 Hz, 6H, NMe$_2$); IR (KBr): 1646 (C=O) cm$^{-1}$.

A mixture of 10 mmol 4-(dimethylamino)salicylaldehyde (1.66 g) (or 4-(diethylamino)salicylaldehyde (1.94 g)) and 20 mmol potassium carbonate (2.76 g) was dissolved in 30 ml dry DMF. To this mixture was added 30 mmol alkyl bromide and the mixture was refluxed for 8 h at 50 °C. 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) and recrystallization with *n*-hexane. These bright brown compounds **1a–14a** were found to melt around 30–32 °C. To obtain **2a** and **9a**, 10 mmol of copper (I) oxide (1.43 g) was added as a catalyst and the reaction conditions were changed to 5 h and 100 °C. **1a** [41-43], Yield:

87.6% (2.24 g); $^1$H NMR (300 MHz, CDCl$_3$): δ10.21 (s, 1H, CHO), δ7.68~7.71 (d, $J$ = 8.8 Hz, 1H, aromatic), δ7.27~7.40 (m, 5H, O-Bz), δ6.29 (d, $J$ = 1.5 Hz, 1H, aromatic), δ6.26 (d, $J$ = 1.5Hz, 1H, aromatic), δ5.11 (s, 2H, O-Bz), δ2.99 (s, 6H, NMe$_2$); IR (KBr): 1651 (C=O) cm$^{-1}$. **2a** [44-46], Yield: 33.2% (0.80 g); $^1$H NMR (300 MHz, CDCl$_3$): δ10.10~10.11 (s, 1H, CHO), δ7.76~7.79 (d, $J$ = 8.8 Hz, 1H, aromatic), δ7.27~7.34 (m, 2H, O-Ph), δ6.97~7.09 (m, 3H, O-Ph), δ6.43~6.47 (dd, $J$ = 6.4 and 2.4 Hz, 1H, aromatic), δ5.99~6.00 (d, $J$ = 2.5 Hz, 1H, aromatic), δ2.92 (s, 6H, NMe$_2$); IR (KBr): 1664 (C=O) cm$^{-1}$. **3a**, Yield: 68.1% (1.22 g); $^1$H NMR (270 MHz, CDCl$_3$): δ10.15 (s, 1H, CHO), δ7.69~72 (d, $J$ = 8.1 Hz, 1H, aromatic), δ6.27~6.31 (dd, $J$ = 8.1 and 2.7 Hz, 1H, aromatic), δ6.01~6.02 (s, 1H, aromatic), δ3.89 (s, 3H, O-Me), δ3.07 (s, 6H, NMe$_2$); IR (KBr): 1656 (C=O) cm$^{-1}$. **4a**, Yield: 52.6% (1.09 g); $^1$H NMR (270 MHz, CDCl$_3$): δ10.23 (s, 1H, CHO), δ7.72~75 (d, $J$ = 8.1 Hz, 1H, aromatic), δ6.28~6.32 (dd, $J$ = 8.1 and 2.7 Hz, 1H, aromatic), δ6.03~6.04 (d, $J$ = 2.7 Hz, 1H, aromatic), δ3.99~4.03 (t, $J$ = 5.4 Hz, 2H, O-Pr), δ3.07 (s, 6H, NMe$_2$), δ1.80~1.93 (m, 2H, O-Pr), δ1.04~1.10 (t, $J$ = 5.4 Hz, 3H, O-Pr); IR (KBr): 1660 (C=O) cm$^{-1}$. **5a**, Yield: 64.9% (1.44 g); $^1$H NMR (270 MHz, CDCl$_3$): δ10.21 (s, 1H, CHO), δ7.70~7.74 (d, $J$ = 8.9 Hz, 1H, aromatic), δ6.26~6.30 (m, 1H, aromatic), δ6.02~6.03 (d, $J$ = 2.1 Hz, 1H, aromatic), δ4.02~4.07 (t, $J$ = 6.2 Hz, 2H, O-Bu), δ3.06 (s, 6H, NMe$_2$), δ1.77~1.87 (m, 2H, O-Bu), δ1.45~1.59 (m, 2H, O-Bu), δ0.96~1.01 (t, $J$ = 7.3 Hz, 3H, O-Bu); IR (KBr): 1660 (C=O) cm$^{-1}$. **6a**, Yield: 67.6% (1.59 g); $^1$H NMR (300 MHz, DMSO-d$_6$): δ10.05 (s, 1H, CHO), δ7.49~7.52 (d, $J$ = 8.8 Hz, 1H, aromatic), δ6.34~6.37 (dd, $J$ = 9.0 and 1.5 Hz, 1H, aromatic), δ6.17~6.18 (d, $J$ = 2.2 Hz, 1H, aromatic), δ4.06~4.11 (t, $J$ = 6.4 Hz, 2H, O-Pen), δ3.04 (s, 6H, NMe$_2$), δ1.74~1.79 (m, 2H, O-Pen), δ1.34~1.39 (m, 4H, O-Pen), δ0.87~0.92 (t, $J$ = 7.0 Hz, 3H, O-Pen); IR (KBr): 1661 (C=O) cm$^{-1}$. **7a**, Yield: 56.1% (1.71 g); $^1$H NMR (300 MHz, DMSO-d$_6$): δ10.05 (s, 1H, CHO), δ7.49~7.52 (d, $J$ = 8.8 Hz, 1H, aromatic), δ6.33~6.36 (d, $J$ = 8.8 Hz, 1H, aromatic), δ6.16~6.17 (d, $J$ = 2.3 Hz, 1H, aromatic), δ4.06~4.10 (t, $J$ = 6.4 Hz, 2H, O-Dec), δ3.04 (s, 6H, NMe$_2$), δ1.72~1.77 (m, 2H, O-Dec), δ1.24~1.43 (m, 14H, O-Dec), δ0.82~0.86 (t, $J$ = 6.4 Hz, 3H, O-Dec); IR (KBr): 1664 (C=O) cm$^{-1}$. **8a**, Yield: 35.0% (0.99 g); $^1$H NMR (270 MHz, CDCl$_3$): δ10.23 (s, 1H,

CHO), δ7.71~7.74 (d, $J$ = 8.8 Hz, 1H, aromatic), δ7.24~7.45 (m, 5H, O-Bz), δ6.12~6.32 (d, $J$ = 8.2 Hz, 2H, aromatic), δ5.16 (s, 2H, O-Bz), δ3.31~3.39 (q, $J$ = 7.2 Hz, 4H, NEt$_2$), δ1.06~1.23 (m, 6H, NEt$_2$); IR (KBr): 1644 (C=O) cm$^{-1}$. **9a**, Yield: 30.0% (0.81 g); $^1$H NMR (300 MHz, CDCl$_3$): δ10.13 (s, 1H, CHO), δ7.80~7.83 (d, $J$ = 8.8 Hz, 1H, aromatic), δ7.33~7.38 (m, 2H, O-Ph), δ7.03~7.14 (m, 3H, O-Ph), δ6.47~6.50 (d, $J$ = 9.0 Hz, 1H, aromatic), δ6.02~6.03 (d, $J$ = 2.0 Hz, 1H, aromatic), δ3.28~3.35 (q, $J$ = 7.1 Hz, 4H, NEt$_2$), δ1.10~1.14 (t, $J$ = 6.9 Hz, 6H, NEt$_2$); IR (KBr): 1658 (C=O) cm$^{-1}$. **10a**, Yield: 84.8% (1.76 g); $^1$H NMR (300 MHz, CDCl$_3$): δ10.11~10.12 (s, 1H, CHO), δ7.68~7.71 (d, $J$ = 8.8 Hz, 1H, aromatic), δ6.26~6.29 (dd, $J$ = 7.1 and 1.6 Hz, 1H, aromatic), δ6.02~6.03 (d, $J$ = 2.4 Hz, 1H, aromatic), δ3.88 (s, 3H, O-Me), δ3.39~3.46 (q, $J$ = 7.1 Hz, 4H, NEt$_2$), δ1.15~1.24 (t, $J$ = 7.0 Hz, 6H, NEt$_2$); IR (KBr): 1645 (C=O) cm$^{-1}$. **11a**, Yield: 84.9% (1.88 g); $^1$H NMR (270 MHz, CDCl$_3$): δ10.17 (s, 1H, CHO), δ7.69~7.72 (d, $J$ = 8.9 Hz, 1H, aromatic), δ6.25~6.28 (m, 1H, aromatic), δ6.01~6.02 (d, $J$ = 2.4 Hz, 1H, aromatic), δ4.06~4.14 (q, $J$ = 7.0 Hz, 2H, O-Et), δ3.37~3.45 (q, $J$ = 7.0 Hz, 4H, NEt$_2$), δ1.43~1.48 (t, $J$ = 7.0 Hz, 3H, O-Et), δ1.18~1.23 (t, $J$ = 7.0 Hz, 6H, NEt$_2$); IR (KBr): 1652 (C=O) cm$^{-1}$. **12a**, Yield: 77.3% (1.82 g); $^1$H NMR (300 MHz, CDCl$_3$): δ10.19 (s, 1H, CHO), δ7.70~7.73 (d, $J$ = 9.0 Hz, 1H, aromatic), δ6.25~6.29 (dd, $J$ = 7.3 and 1.7 Hz, 1H, aromatic), δ6.01 (d, $J$ = 2.2 Hz, 1H, aromatic), δ3.97~4.01 (t, $J$ = 6.4 Hz, 2H, O-Pr), δ3.38~3.45 (q, $J$ = 7.1 Hz, 4H, NEt$_2$), δ1.80~1.92 (m, 2H, O-Po), δ1.19~1.24 (t, $J$ = 7.1 Hz, 6H, NEt$_2$), δ1.10~1.14 (t, $J$ = 7.4 Hz, 3H, O-Pr); IR (KBr): 1655 (C=O) cm$^{-1}$. **13a**, Yield: 72.9% (1.92 g); $^1$H NMR (270 MHz, CDCl$_3$): δ10.19 (s, 1H, CHO), δ7.69~7.72 (d, $J$ = 8.1 Hz, 1H, aromatic), δ6.24~6.28 (dd, $J$ = 5.4 and 2.7 Hz, 1H, aromatic), δ6.01~6.02 (d, $J$ = 2.7 Hz, 1H, aromatic), δ4.00~4.05 (t, $J$ = 6.7 Hz, 2H, O-Pen), δ3.37~3.45 (q, $J$ = 8.1 Hz, 4H, NEt$_2$), δ1.78~1.88 (m, 2H, O-Pen), δ1.38~1.51 (m, 4H, O-Pen), δ1.19~1.24 (t, $J$ = 6.7 Hz, 6H, NEt$_2$), δ0.91~0.95 (t, $J$ = 6.7 Hz, 3H, O-Pen); IR (KBr): 1661 (C=O) cm$^{-1}$. **14a**, Yield: 55.7% (1.86 g); $^1$H NMR (270 MHz, CDCl$_3$): δ10.18 (s, 1H, CHO), δ7.70~7.73 (d, $J$ = 8.1 Hz, 1H, aromatic), δ6.25~6.29 (m, 1H, aromatic), δ6.01~6.02 (d, $J$ = 2.7 Hz, 1H, aromatic), δ4.00~4.05 (t, $J$ = 6.7 Hz, 2H, O-Dec), δ3.38~3.46 (q, $J$ = 8.1 Hz, 4H, NEt$_2$), δ1.78~1.88 (m, 2H, O-Dec), 1.11~1.51 (m,

20H, O-Den and NEt$_2$), δ0.86~0.91 (t, $J$ = 5.4 Hz, 3H, O-Dec); IR (KBr): 1661 (C=O) cm$^{-1}$.

### 2.3.2 Bisazomethine dyes 1b–14b

To 15 ml of benzene was added a mixture of 0.5 mmol diaminomaleonitrile (0.06 g) and 1.0 mmol of the prepared 4-(dimethylamino)-2-alkoxybenzaldehydes (or 4-(diethylamino)-2-alkoxybenzaldehydes); the resulting mixture was stirred. Piperidine was added dropwise during the reaction. Reflux was continued for 8 h with a Dean-Stark trap. After 8 h, 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. The purple solids were obtained after recrytallization from chloroform except for dyes **7b** and **14b** which gave red solids. **1b**, Yield: 62.0% (0.18 g); M.p. 310–311 °C. Anal. Calcd for C$_{36}$H$_{34}$N$_6$O$_2$: C, 74.20; H, 5.88; N, 14.42. Found: C, 74.12; H, 5.78; N, 14.13. $^1$H NMR (300 MHz, CDCl$_3$): δ9.15 (s, 2H, CH=N), δ8.14~8.17 (d, $J$ = 9.0 Hz, 2H, aromatic), δ7.37~7.48 (m, 10H, O-Bz), δ6.34~6.38 (dd, $J$ = 6.4 and 2.5 Hz, 2H, aromatic), δ6.08~6.09 (d, $J$ = 2.3 Hz, 2H, aromatic), δ5.22 (s, 4H, O-Bz), δ3.05 (s, 12H, NMe$_2$); IR (KBr): 2208 (C≡N) cm$^{-1}$, 1615 (CH=N) cm$^{-1}$. **2b**, Yield: 64.3% (0.18 g); M.p. 312–313 °C. Anal. Calcd for C$_{34}$H$_{30}$N$_6$O$_2$: C, 73.63; H, 5.45; N, 15.15. Found: C, 72.79; H, 5.39; N, 15.0. $^1$H NMR (270 MHz, CDCl$_3$): δ9.01~9.06 (s, 2H, CH=N), δ8.20~8.23 (d, $J$ = 9.1 Hz, 2H, aromatic), δ7.32~7.38 (m, 4H, O-Ph), δ7.07~7.16 (m, 6H, O-Ph), δ6.55~6.60 (dd, $J$ = 7.0 and 2.2 Hz, 2H, aromatic), δ6.12~6.13 (d, $J$ = 2.4 Hz, 2H, aromatic), δ2.98~3.08 (m, 12H, NMe$_2$); IR (KBr): 2207 (C≡N) cm$^{-1}$, 1612 (CH=N) cm$^{-1}$. **3b**, Yield: 70.9% (0.15 g); M.p. 318–320 °C. Anal. Calcd for C$_{24}$H$_{26}$N$_6$O$_2$: C, 66.96; H, 6.09; N, 19.52. Found: C, 66.89; H, 6.08; N, 19.50. $^1$H NMR (270 MHz, CDCl$_3$): δ9.03 (s, 2H, CH=N), δ8.12~8.15 (d, $J$ = 8.9 Hz, 2H, aromatic), δ6.38 (dd, $J$ = 7.1 and 2.1 Hz, 2H, aromatic), δ6.04~6.05 (d, $J$ = 2.0 Hz, 2H, aromatic), δ3.90 (s, 6H, O-Me), δ3.11 (s, 12H, NMe$_2$); IR (KBr): 2203 (C≡N) cm$^{-1}$, 1608 (CH=N) cm$^{-1}$. **4b**, Yield: 46.5% (0.11 g); M.p. 320–321 °C. Anal. Calcd

for $C_{28}H_{34}N_6O_2$: C, 69.11; H, 7.04; N, 17.27. Found: C, 68.86; H, 7.03; N, 17.17. ^{1}H NMR (270 MHz, CDCl$_3$): δ9.03 (s, 2H, CH=N), δ8.12~8.15 (d, $J$ = 8.1 Hz, 2H, aromatic), δ6.38 (s, 2H, aromatic), δ6.04~6.05 (d, $J$ = 2.7 Hz, 2H, aromatic), δ3.97~4.02 (t, $J$ = 6.7 Hz, 4H, O-Pr), δ3.11 (s, 12H, NMe$_2$), δ1.86~1.93 (m, 4H, O-Pr), δ1.07~1.12 (t, $J$ = 6.8 Hz, 6H, O-Pr); IR (KBr): 2202 (C≡N) cm$^{-1}$, 1611 (CH=N) cm$^{-1}$. **5b**, Yield: 60.4% (0.16 g); M.p. 300–302 °C. Anal. Calcd for $C_{30}H_{38}N_6O_2$: C, 70.01; H, 7.44; N, 16.33. Found: C, 70.12; H, 7.48; N, 16.31. ^{1}H NMR (270 MHz, CDCl$_3$): δ9.04 (s, 2H, CH=N), δ8.11~8.14 (d, $J$ = 8.2 Hz, 2H, aromatic), δ6.33~6.37 (dd, $J$ = 7.0 and 2.2 Hz, 2H, aromatic), δ6.04~6.05 (d, $J$ = 2.4 Hz, 2H, aromatic), δ4.03~4.08 (t, $J$ = 6.5 Hz, 4H, O-Bu), δ3.09 (s, 12H, NMe$_2$), δ1.81~1.91 (m, 4H, O-Bu), δ1.48~1.61 (m, 4H, O-Bu), δ0.98~1.03 (t, $J$ = 7.3 Hz, 6H, O-Bu); IR (KBr): 2202 (C≡N) cm$^{-1}$, 1613 (CH=N) cm$^{-1}$. **6b**, Yield: 72.5% (0.20 g); M.p. 287–289 °C. Anal. Calcd for $C_{32}H_{42}N_6O_2$: C, 70.82; H, 7.80; N, 15.49. Found: C, 70.42; H, 7.70; N, 15.49. ^{1}H NMR (270 MHz, CDCl$_3$): δ9.02 (s, 2H, CH=N), δ8.09~8.12 (d, $J$ = 8.1 Hz, 2H, aromatic), δ6.31~6.35 (dd, $J$ = 7.1 and 2.7 Hz, 2H, aromatic), δ6.03~6.04 (d, $J$ = 2.7 Hz, 2H, aromatic), δ4.01~4.05 (t, $J$ = 5.4 Hz, 4H, O-Pen), δ3.09 (s, 12H, NMe$_2$), δ1.81~1.90 (m, 4H, O-Pen), δ1.37~1.56 (m, 8H, O-Pen), δ0.93~0.97 (t, $J$ = 5.4 Hz, 6H, O-Pen); IR (KBr): 2202 (C≡N) cm$^{-1}$, 1616 (CH=N) cm$^{-1}$. **7b**, Yield: 50.6% (0.17 g); M.p. 210–211 °C. Anal. Calcd for $C_{42}H_{62}N_6O_2$: C, 73.86; H, 9.15; N, 12.30. Found: C, 73.41; H, 9.46; N, 12.37. ^{1}H NMR (300 MHz, CDCl$_3$): δ9.05 (s, 2H, CH=N), δ8.11~8.14 (d, $J$ = 9.0 Hz, 2H, aromatic), δ6.34~6.37 (d, $J$ = 9.0 Hz, 2H, aromatic), δ6.04~6.05 (d, $J$ = 2.4 Hz, 2H, aromatic), δ4.02~4.06 (t, $J$ = 6.6 Hz, 4H, O-Dec), δ3.11 (s, 12H, NMe$_2$), δ1.71~1.81 (m, 4H, O-Dec), δ1.20~1.42 (m, 28H, O-Dec), δ0.85~0.90 (t, $J$ = 6.6 Hz, 6H, O-Dec); IR (KBr): 2204 (C≡N) cm$^{-1}$, 1618 (CH=N) cm$^{-1}$. **8b**, Yield: 40.1% (0.13 g); M.p. 283–285 °C. Anal. Calcd for $C_{40}H_{42}N_6O_2$: C, 75.21; H, 6.63; N, 13.16: Found; C, 74.77; H, 6.61; N, 13.08. ^{1}H NMR (300 MHz, CDCl$_3$): δ9.13 (s, 2H, CH=N), δ8.12~8.16 (d, $J$ = 9.0 Hz, 2H, aromatic), δ7.19~7.48 (m, 10H, O-Bz), δ6.37 (s, 2H, aromatic), δ6.06 (s, 2H, aromatic), δ5.10~5.22 (s, 4H, O-Bz), δ3.32~3.39 (q, $J$ = 6.0 Hz, 8H, Net$_2$), δ1.06~1.20 (m, 12H, Net$_2$); IR (KBr): 2203 (C≡N) cm$^{-1}$, 1612 (CH=N) cm$^{-1}$. **9b**, Yield: 53.5%

(0.16 g); M.p. 310–312 °C. Anal. Calcd for $C_{38}H_{38}N_6O_2$: C, 74.73; H, 6.27; N, 13.76: Found; C, 74.31; H, 6.24; N, 13.65. ^{1}H NMR (300 MHz, CDCl$_3$): δ8.98 (s, 2H, CH=N), δ8.19~8.22 (d, $J$ = 9.0 Hz, 2H, aromatic), δ7.33~7.40 (m, 4H, O-Ph), δ7.04~7.16 (m, 6H, O-Ph), δ6.53~6.56 (d, $J$ = 8.8 Hz, 2H, aromatic), δ6.07 (s, 2H, aromatic), δ3.28~3.35 (q, $J$ = 7.1 Hz, 8H, NEt$_2$), δ1.10~1.15 (t, $J$ = 7.1 Hz, 12H, NEt$_2$); IR (KBr): 2208 (C≡N) cm$^{-1}$, 1613 (CH=N) cm$^{-1}$. **10b**, Yield: 72.2% (0.18 g); M.p. 285–287 °C. Anal. Calcd for $C_{28}H_{34}N_6O_2$: C, 69.11; H, 7.04; N, 17.27: Found; C, 69.08; H, 7.07; N, 17.26. ^{1}H NMR (270 MHz, CDCl$_3$): δ8.99 (s, 2H, CH=N), δ8.10~8.13 (d, $J$ = 9.2 Hz, 2H, aromatic), δ6.32~6.36 (dd, $J$ = 7.0 and 2.2 Hz, 2H, aromatic), δ6.03~6.04 (d, $J$ = 2.2 Hz, 2H, aromatic), δ3.88 (s, 6H, O-Me), δ3.41~3.49 (q, $J$ = 7.0 Hz, 8H, NEt$_2$), δ1.21~1.26 (t, $J$ = 7.3 Hz, 12H, NEt$_2$); IR (KBr): 2201 (C≡N) cm$^{-1}$, 1610 (CH=N) cm$^{-1}$. **11b**, Yield: 71.7% (0.18 g); M.p. 258–259 °C. Anal. Calcd for $C_{30}H_{38}N_6O_2$: C, 70.01; H, 7.44; N, 16.33: Found; C, 69.78; H, 7.44; N, 16.27. ^{1}H NMR (300 MHz, CDCl$_3$): δ9.01 (s, 2H, CH=N), δ8.10~8.13 (d, $J$ = 9.0 Hz, 2H, aromatic), δ6.33~6.36 (dd, $J$ = 9.0 and 2.1 Hz, 2H, aromatic), δ6.03~6.04 (d, $J$ = 3.0 Hz, 2H, aromatic), δ4.08~4.15 (dd, $J$ = 9.0 and 6.0 Hz, 4H, O-Et), δ3.40~3.47 (q, $J$ = 6.0 Hz, 8H, NEt$_2$), δ1.47~1.51 (t, $J$ = 6.0 Hz, 6H, O-Et), δ1.21~1.25 (t, $J$ = 6.0 Hz, 12H, NEt$_2$); IR (KBr): 2203 (C≡N) cm$^{-1}$, 1609 (CH=N) cm$^{-1}$. **12b**, Yield: 71.8% (0.19 g); M.p. 302–304 °C. Anal. Calcd for $C_{32}H_{42}N_6O_2$: C, 70.82; H, 7.80; N, 15.49: Found; C, 70.02; H, 7.72; N, 15.12. ^{1}H NMR (300 MHz, CDCl$_3$): δ9.02 (s, 2H, CH=N), δ8.09~8.12 (d, $J$ = 9.0 Hz, 2H, aromatic), δ6.32~6.36 (dd, $J$ = 7.2 and 2.1 Hz, 2H, aromatic), δ6.03 (d, $J$ = 2.3 Hz, 2H, aromatic), δ3.97~4.02 (t, $J$ = 6.5 Hz, 4H, O-Pr), δ3.40~3.47 (q, $J$ = 7.2 Hz, 8H, NEt$_2$), δ1.86~1.93 (m, 4H, O-Pr), δ1.20~1.25 (t, $J$ = 7.1 Hz, 12H, NEt$_2$), δ1.07~1.12 (t, $J$ = 7.3 Hz, 6H, O-Pr); IR (KBr): 2201 (C≡N) cm$^{-1}$, 1612 (CH=N) cm$^{-1}$. **13b**, Yield: 60.8% (0.18 g); M.p. 270–271 °C. Anal. Calcd for $C_{36}H_{50}N_6O_2$: C, 72.21; H, 8.42; N, 14.03: Found; C, 71.92; H, 8.41; N, 13.94. ^{1}H NMR (270 MHz, CDCl$_3$): δ9.02 (s, 2H, CH=N), δ8.09~8.13 (d, $J$ = 9.5 Hz, 2H, aromatic), δ6.31~6.35 (dd, $J$ = 5.4 and 2.7 Hz, 2H, aromatic), δ6.03~6.04 (d, $J$ = 2.7 Hz, 2H, aromatic), δ4.01~4.05 (t, $J$ = 5.4 Hz, 4H, O-Pen), δ3.40~3.47 (dd, $J$ = 8.1 and 5.4 Hz, 8H, NEt$_2$), δ1.56~1.90 (m, 4H, O-Pen), δ1.37~1.56

(m, 8H, O-Pen), δ1.20~1.25 (t, $J$ = 5.4 Hz, 12H, NEt$_2$), δ0.93~0.98 (t, $J$ = 5.4 Hz, 6H, O-Pen); IR (KBr):

2201 (C≡N) cm$^{-1}$, 1614 (CH=N) cm$^{-1}$. **14b**, Yield: 58.9% (0.22 g); M.p. 192–194 °C. Anal. Calcd for

C$_{46}$H$_{70}$N$_6$O$_2$: C, 74.75; H, 9.55; N, 11.37: Found; C, 74.88; H, 9.59; N, 11.37. $^1$H NMR (270 MHz,

CDCl$_3$): δ9.01 (s, 2H, CH=N), δ8.09~8.13 (d, $J$ = 8.1 Hz, 2H, aromatic), δ6.32~6.36 (dd, $J$ = 5.4 and 2.7

Hz, 2H, aromatic), δ6.03~6.04 (d, $J$ = 2.7 Hz, 2H, aromatic), δ4.00~4.05 (t, $J$ = 5.4 Hz, 4H, O-Dec),

δ3.40~3.47 (q, $J$ = 5.4 Hz, 8H, NEt$_2$), δ1.81~1.91 (m, 4H, O-Dec), δ1.20~1.52 (m, 40H, O-Dec and NEt$_2$),

δ0.85~0.90 (t, $J$ = 5.4 Hz, 6H, O-Dec); IR (KBr): 2207 (C≡N) cm$^{-1}$, 1609 (CH=N) cm$^{-1}$.

## 3. Results and Discussion

Several reports on the crystal structure of bisazomethine dyes have revealed that their crystal structure is characterized by a two-dimensional (2-D) molecular stacking layer in which molecules are π-π stacked in a staircase arrangement with small slip angles along the long molecular axis [26, 28]. The 2-D layers are aligned along the short molecular axis such that they form a crystal structure. The observed 2-D molecular stacking layer feature indicated that the bisazomethine dye system has the potential to form J-aggregates and, indeed, DE2 was found to form J-aggregates in vapour-deposited films [31], although those films were composed of J-aggregates and a single crystalline phase.

With respect to the molecular arrangement along the short molecular axis, the cyano group, the substituents on the phenyl ring, and the alkyl substituents on the amino group are related by the spacing between the adjacent 2-D stacking layers. This spacing between the neighbouring layers is regarded as one of the important parameters for obtaining pure J-aggregate solid films, because J-aggregates are considered to have a low-dimensional electronic state. Among the different substituents, phenyl ring substitution was examined in this study. 4-(Dimethylamino)- and 4-(diethylamino)-2-alkoxybenzaldehydes **1a–14a** were reacted with diaminomaleonitrile to yield bisazomethine dyes **1b–14b**,

respectively, to obtain J-aggregates in the solid state. The active amino groups of diaminomaleonitrile can readily react with the aldehyde group to afford azomethine linkages. All the prepared novel bisazomethine dyes were obtained in yields of 40–78%.

[Scheme 1]

The UV-Vis absorption and fluorescence spectra of **1b–7b** and **8b–14b** in chloroform are shown in Figs. 1 (a) and (b), respectively. All the synthesized bisazomethine dyes show strong absorption around 550 nm with a very large molar extinction coefficient of about 120000 to 150000, which confirms the symmetrical strong intramolecular charge-transfer chromophoric system of the bisazomethine dye molecule [39]. All the absorption bands have a small shoulder around 520 nm, and no significant difference was observed in their spectral shape. Dyes **1b–7b** exhibit a sharp fluorescent band around 595 nm. Dyes **8b–14b** also show a sharp fluorescent band but the spectral region is slightly shifted to the long-wavelength region. Thus, these derivatives can be used as a fluorescent material for a red emitter, although their quantum efficiency is very low. All the dyes showed a Stokes shift of about 45 nm. These experimental data clearly indicate that the substitution in the amino groups as well as in the alkoxy groups on the phenyl ring exerts no considerable influence on the electronic states in the visible region.

[Figure 1]

To gain further insight into the electronic states of these bisazomethine dyes, their molecular geometry and absorption characteristics were computed. The optimized molecular geometry for **1b** and **8b** is illustrated in Figs. 2 (a) and (b), respectively. The molecule has an almost planar π-conjugation from the terminal amino group to the central dicyanoethylene moiety. This molecular conformation implies that a strong intramolecular charge-transfer exists in this chromophoric system upon excitation. The absorption corresponding to the visible absorption was estimated on the basis of configuration interactions. The calculation result is listed in Table 1. A strong absorption was observed for all dyes whose oscillator strengths ranged from 1.9 to 2.0. We found no significant difference in the calculated

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absorption energy. This result is in good agreement with the absorption characteristics shown in Fig. 1. The major component of this transition is the HOMO-LUMO transition. The HOMO was found to consist of amino nitrogen atoms including phenyl carbons and the central ethylene moiety. The LUMO is mainly distributed over the azomethine and dicyanoethylene moieties. The transition dipole was found to be oriented along the long molecular axis parallel to the direction from the amino nitrogen to its conjugated cyano nitrogen. This reflects exactly the conjugation of π-electrons between the terminal amino donors and the central cyano groups. A cross-conjugation through the central ethylene moiety is also suggested and this is considered the reason for the very large oscillator strength of these bisazomethine dyes.

[Figure 2]

[Table 1]

These experimental results clearly indicate that for all the prepared bisazomethine dyes in a solution, there is little effect of the substituents on the optical properties of the dyes in the visible region. This, of course, is attributed to the small electronic effect of the substituents on the π-conjugation of the chromophoric system. These novel bisazomethine dyes, however, exhibit a significant spectral change in solid films. Figs. 3 and 4 show the absorption and fluorescent spectra of **1b–7b** and **8b–14b**, respectively, in a vapour-deposited film. These spectral characteristics are summarized in Table 2, along with the spectral characteristics in a chloroform solution. The spectral shift between the solution and the films is also listed.

[Figure 3]

[Figure 4]

[Table 2]

The shape of the absorption bands of **3b** and **10b** is noteworthy. They are characterized by a broad band over the visible region with a sharp peak around 650 nm. The shift between the peaks of the solution spectra and film spectra is 103 nm in the case of both dyes. This spectral change is quite similar to that of

DE2 [31], which shows a sharp peak—that was assigned to J-aggregates—in the long-wavelength region in vapour-deposited films. Thus, J-aggregates are considered to form in these films; to obtain pure J-aggregate films, the preparation conditions of the films will have to be examined. In the case of other dyes, both band broadening and bathochromic spectral shifts in the absorption spectra were observed. The degree of bathochromic shift is dependent on the alkyl chain length of the alkoxy substituents on the phenyl rings. The methoxy group (**3b** and **10b**) showed the largest shift in absorption, and the spectral shift decreased with increasing chain length in both series. The decyloxy group (**7b** and **14b**) showed the shortest spectral shift. The alkoxy substituents were introduced to modulate the spacing between the 2-D stacking molecular layers. They also have an influence on the geometry of the molecular stacking in the 2-D layer. This observation may thus reflect some structural variety in molecular arrangement in the solid state. However, the dye films showed a simple fluorescence band around 620–690 nm in the solid state. The shape of the peak was slightly different from that in the solution. There were no significant differences in the spectral shifts for the dyes except for **1b** and **8b**. Among all the dyes, **1b** and **8b** showed quite an unusual absorption band with two distinct absorption maxima around 450 nm and 600 nm. A theory to explain this phenomenon was proposed: during vacuum deposition, both dyes are thermally decomposed to give mono-substituted azomethine dyes, which show the hypsochromic absorption band. This theory was experimentally confirmed by preparing the corresponding monoazomethine dyes and their vapour-deposited films. These bisazomethine dyes showed significant spectral difference in the solid state, despite their molecules having almost similar electronic states. Therefore, the spectral shift is correlated with the solid-state structure; the spectral shift is considered to depend on the alkoxy substituents on the phenyl ring.

The absorption bands for **3b**, **9b**, **10b**, and **11b** in vapour-deposited films are illustrated in Fig. 5, along with their absorption spectra in chloroform solution. As mentioned above, the shape of the spectra of **3b** and **10b** was very similar to that of DE2 in vapour-deposited films and their peaks around 650 nm

can be ascribed to J-aggregate formation. In addition to these two dyes, **9b** and **11b** exhibited a tendency to form J-aggregates in vapour-deposited films. In their film absorption bands, the absorption spectrum increases very sharply around the absorption edge in the long-wavelength region. In the solution spectrum, the bisazomethine dyes generally exhibit a well-defined peak as well as a relatively small Stokes shift of about 1400 cm$^{-1}$. This suggests that the major absorption peak can be assigned to the 0-0 transition. In the case of **9b** and **11b**, the rise in the absorption edge in the longer wavelength region was steeper in the case of the film absorption spectra than in the case of the solution spectra. This implies that a pure electronic transition in the longer-wavelength region, namely, J-aggregate absorption, is incorporated in the film absorption spectra. Among all dyes, four dyes—**3b**, **9b**, **10b**, and **11b**—were considered to form J-aggregates in vapour-deposited films, on the basis of the shape of the absorption spectrum and absorption edge.

[Figure 5]

For an exact interpretation of these spectral changes and to achieve our final goal of obtaining pure J-aggregate solid films, the preparation conditions of the films will have to be examined and the optical properties of the dyes will have to be characterized on the basis of the solid-state structure. Crystal structure analysis of these dyes is thus very important and the results will be reported elsewhere.


**4. Conclusions**


In an attempt to prepare pure J-aggregate solid films, we investigated the effect of phenyl ring substitution in bisazomethine chromophoric systems, synthesized using diaminomaleonitrile and aminobenzaldehydes, with alkoxy groups. In chloroform solution, all the synthesized bisazomethine dyes exhibited almost similar optical properties, namely, strong absorption around 550 nm and weak red fluorescence around 590 nm. Molecular orbital calculations confirmed the strong intramolecular charge-

transfer property of the synthesized dyes and the calculation result was in good agreement with their solution properties. In the case of vapour-deposited films, the absorption spectra of the dyes showed a variety of spectral changes in the visible region. Four of the synthesized derivatives were found to form J-aggregates in vapour-deposited films, as determined from the shape of the spectrum and the absorption edge. Further investigation of the observed spectral changes, which involves crystal structure analysis of all the dyes, is underway. In addition, to obtain pure J-aggregate solid films, the various preparation conditions of the films and other combinations of substituents will be examined.

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**Captions**

Scheme 1

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