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Alkyl substituent effects on J- or H-aggregate formation of bisazomethine dyes

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ABSTRACT

Bisazomethine dyes with terminal alkyl substituents of different chain lengths (BAR: $R = 1, 2, 3, 4, 5$ and 6) were synthesized and deposited on a glass substrate to investigate the effect of the alkyl chain length on aggregate formation. Methyl- and ethyl-substituted bisazomethine dyes (BA1 and BA2) formed J-aggregates in thin films (ca. 50 nm), whereas, propyl-, butyl-, pentyl- and hexyl-substituted derivatives (BA3, BA4, BA5 and BA6) formed H-aggregates in thin films (ca. 50 nm). The aggregate formation of the BARs changed drastically between ethyl- and propyl-substituents (BA2/BA3). However, no remarkable changes were observed in the surface morphologies of BA2 and BA3 films. It is suggested that the critical determinant of aggregate formation of BAR is the molecular packing in the film, which depends on the chain length of the terminal alkyl substituent.

1. Introduction

Organic molecules can form crystals or aggregates, in which the visible absorption bands in the solid state are generally split or shifted from those of the monomeric molecules. Dye aggregates have played important roles in both fundamental science and technological applications such as optical memory, organic solar cells and organic light-emitting diodes [1–3]. In general, they are classified into two types, H- and J-aggregates [4–6]. H-aggregates adopt face-to-face stacking structures, which are characterized by a blue-shift in the absorption band. H-aggregates can effectively contribute to the photocurrent in Schottky-type photovoltaic cells where thin films are sandwiched between two different types of metal electrodes [7]. J-aggregates are characterized by a sharp absorption band (J-band) with red-shifted from that of isolated molecules and have attracted much attention for both fundamental studies and their large optical non-linearity and ultra-fast response time for nonlinear optical materials. The specific structure of the J-aggregates is a head-to-tail stacking between adjacent molecules. Intriguingly, most studies on J- or H-aggregates described them as compounds with dipole moments [8–10] and ionic features [11,12]. Thus, J-aggregate formation is irrelevant to polar and/or ionic dyes. However, Matsumoto et al. found that large and homogeneous films of J-aggregates can be formed in vapor-deposited films of *N,N′*-bis[(4-(*N,N*-diethylamino)benzylidene]diaminofumaronitrile (BA2), even though it is a non-polar (and non-ionic) dye. The packing structure of BA2 is consistent with the J-aggregate films consisting of a stable single crystal phase and a metastable crystalline phase [13]. BA2 also forms J-aggregates in vapor-deposited films depending on the film thickness (>100 nm), despite its symmetric and non-ionic molecular structure. The J-aggregate film was extremely stable such that no significant change in absorption spectra was observed even after one year at ambient conditions or after thermal treatment at 375 K for 1 h. However, despite enormous effort, sufficient understanding of the substituent effects on aggregate formations has not yet been obtained. Therefore, studies on the controlling dye aggregate formation and the formation mechanism of these aggregates in thin films are of great importance for practical applications as well as for basic research of assembled dye molecules. Recently, some interesting results have been reported by Kim et al. regarding the effect of phenyl substitution on the J-aggregation of bisazomethine dyes [14]. The absorption spectra of these dyes showed a variety of spectral changes in the visible region and some of the synthesized dyes were found to form J-aggregates in vapor-deposited films. Therefore, bisazomethine dyes are excellent candidates for the further

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study of the correlation between substituent effects and the aggregation mechanism.

In this study, based on the spectroscopic evidence, the influence of the chain length of the terminal substituent on the aggregate formation was determined in order to understand the mechanism of J- and H-aggregate formation, and to guide the design of novel J- and H-aggregate organic dyes.

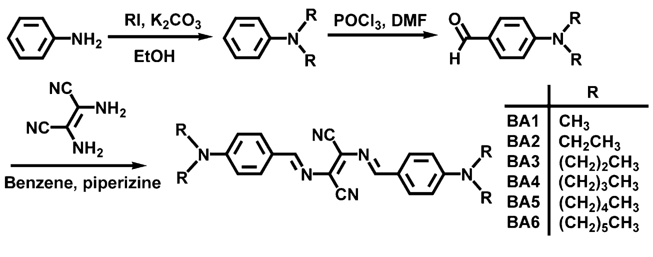
2. Experimental

Bisazomethine dyes (BA) with different alkyl chain lengths were synthesized. BAs with different alkyl chains are abbreviated as BAR where $R = 1, 2, 3, 4, 5$ and 6 to represent methyl-, ethyl-, propyl-, butyl-, pentyl- and hexyl-substituents, respectively. The synthetic procedure of BA dyes is shown in Scheme 1. BA1 and BA2 were synthesized from *p-N,N*-dialkylaminobenzaldehyde, BA3 and BA4 were synthesized from *N,N*-dialkylaniline, and BA5 and BA6 were synthesized from aniline. *p-N,N*-Dimethyl- and *p-N,N*-diethylaminobenzaldehyde were purchased from Nacalai Tesque, Inc. *N,N*-Dipropyl- and *N,N*-dibutylaniline were purchased from Tokyo Kasei Co., Ltd. They were used without further purification. The chemical structures of the synthesized compounds were characterized using ^{1}H NMR [Bruker Advance500, $CDCl_3$ solvent, tetramethylsilane (TMS) internal standard], FT-IR (Jasco FT/IR-600 plus) and TOF-MS (PerSeptive Biosystems Mariner) spectroscopies. Melting points (mp) were determined using a melting point apparatus (Yanaco MP-500P) with a digital thermometer. UV–visible absorption and photoluminescence (PL) spectra were recorded on JASCO V-670 and Hitachi F-2500 spectrophotometers, respectively. Measurements of absorption and PL spectra in solution were performed in a quartz cell with a path length of 1 cm. The films were prepared on a glass substrate from a quartz crucible heated by a tungsten filament in a vacuum of 10^{-4} Pa. The deposition rate was 5 nm/s and the substrate temperature was maintained at 40 °C. The film thickness was controlled at 50 nm. The morphologies of the films were characterized using an atomic force microscope (AFM, SPI-3700, Seiko Instruments).

3. Synthesis

3.1. N,N-dialkylanilines

A mixture of fresh aniline (21.5 mmol), iodoalkane (4.51 mmol), and K_2CO_3 (4.51 mmol) in EtOH (20 mL) was refluxed at 75 °C for 18 h. The suspension was filtered, and the resulting solid was washed with CH_2Cl_2. The filtered solution was extracted with water, and the organic layer was dried over anhydrous $MgSO_4$ and concentrated in vacuo. Purification by column chromatography on silica gel (eluent: $CHCl_3$) produced an oil. Products with different alkyl chains (pentyl and hexyl) were synthesized using the same procedure. Specific details for each compound are given below.



Scheme 1. Synthetic procedure for BAR.

3.1.1. N,N-dipentylaniline

70.3% yield. Product: yellow oil. FT-IR (cm^{-1}): 3986, 3647, 3412, 3093, 3061, 3024, 2958, 2873, 2735, 2649, 2596, 2495, 2470, 2449, 2390, 2358, 2264, 2186, 1909, 1806, 1752, 1714, 1607, 1569, 1539, 1519, 1505, 1464, 1432, 1494, 1386, 1357, 1316, 1288, 1255, 1231, 1213, 1185, 1148, 1116, 1040, 998, 987, 963, 886, 858, 815, 743, 724, 690. TOF-MS calcd (found): m/z 233.3 (233.4) [M+]. ^{1}H NMR (500 MHz, $CDCl_3$): δ 0.91 (t, 6H, $J = 6.9$ Hz, CH_3), 1.21–1.37 [m, 8H, $(CH_2)_2$], 1.38 (sextet, 4H, $J = 7.0$, $\underline{CH_2}CH_3$), 3.35 (t, 4H, $J = 8.0$, NCH_2), 6.60 (d, 2H, $J = 7.0$ Hz, 2,6Ph), 6.62 (t, 1H, $J = 7.5$ Hz, 4Ph), 7.18 (t, 2H, $J = 7.5$ Hz, 3,5Ph).

3.1.2. N,N-dihexylaniline

74.3% yield. Product: yellow oil. FT-IR (cm^{-1}): 3986, 3647, 3412, 3093, 3061, 3024, 2958, 2873, 2735, 2649, 2596, 2495, 2470, 2449, 2390, 2358, 2264, 2186, 1909, 1806, 1752, 1714, 1607, 1569, 1539, 1519, 1505, 1464, 1432, 1494, 1386, 1357, 1316, 1288, 1255, 1231, 1213, 1185, 1148, 1116, 1040, 998, 987, 963, 886, 858, 815, 743, 724, 690. TOF-MS calcd (found): m/z 262.3 (262.2) [M+]. ^{1}H NMR (500 MHz, $CDCl_3$): δ 0.91 (t, 6H, $J = 6.9$ Hz, CH_3), 1.22–1.39 [m, 12H, $(CH_2)_3$], 3.35 (t, 4H, $J = 8.0$, NCH_2), 6.60 (d, 2H, $J = 7.0$ Hz, 2,6Ph), 6.62 (d, 1H, $J = 7.5$ Hz, 4Ph), 7.18 (t, 2H, $J = 7.5$ Hz, 3,5Ph).

3.2. p-N,N-dialkylaminobenzaldehydes

$POCl_3$ (22 mmol) was slowly added to anhydrous DMF (18.4 mmol) in an ice bath (−10 °C) for 30 min. To this reaction mixture *N,N*-dialkylaniline (18.4 mmol) was added, and the resulting mixture was carefully heated at 60 °C for 2 h. After hydrolysis for 2 h under vigorous stirring at r.t. using an aqueous solution of 2 N NaOH, the crude product was extracted with EtOAc. The organic layer was dried over anhydrous $MgSO_4$ and evaporated in vacuo before purification by column chromatography in silica gel (eluent: $CHCl_3$) to produce an oil. This synthetic procedure was carried out according to the Vilsmeier–Haack reaction [15]. Intermediates with different alkyl chains (propyl, butyl, pentyl and hexyl) were synthesized using the same procedure. Specific details for each compound are given below.

3.2.1. p-N,N-dipropylaminobenzaldehyde

13.2% yield. Product: colorless oil. FT-IR (cm^{-1}), 2904, 2814, 2795, 2730, 2713, 2695, 1608, 1567, 1537, 1516, 1435, 1405, 1384, 1354, 1315, 1294, 1265, 1241, 1186, 1143, 1120, 1100, 1034, 976, 816, 797, 765, 749. TOF-MS calcd (found): m/z 205.3 (206.2) [M+]. ^{1}H NMR (500 MHz, $CDCl_3$): δ 0.96 (t, 6H, $J = 7.5$ Hz, CH_3), 1.65 (sextet, 4H, $J = 8.0$ Hz, $\underline{CH_2}CH_3$), 3.32 (t, 4H, $J = 8.0$ Hz, NCH_2), 6.64 (d, 2H, $J = 9.0$ Hz, 3Ph), 7.70 (d, 2H, $J = 8.5$ Hz, 2Ph), 9.70 (s, 1H, CHO).

3.2.2. p-N,N-dibutylaminobenzaldehyde

10.1% yield. Product: colorless oil. FT-IR (cm^{-1}), 2904, 2814, 2795, 2730, 2713, 2695, 1609, 1570, 1540, 1518, 1434, 1403, 1388, 1356, 1314, 1286, 1263, 1223, 1186, 1147, 1122, 1107, 1017, 926, 813, 757, 727, 634. FAB-MS calcd (found): m/z 233.4 (233.2) [M+]. ^{1}H NMR (500 MHz, $CDCl_3$): δ 0.91 (t, 6H, $J = 7.0$ Hz, CH_3), 1.59 (sextet, 4H, $J = 7.5$ Hz, $\underline{CH_2}CH_3$), 1.66 (quintet, 4H, $J = 7.0$ Hz, $NCH_2\underline{CH_2}$), 3.20 (t, 2H, $J = 7.5$, NCH_2), 6.66 (d, 2H, $J = 9.0$ Hz, 3Ph), 7.70 (d, 2H, $J = 9.0$ Hz, 2Ph), 9.70 (s, 1H, CHO).

3.2.3. p-N,N-dipentylaminobenzaldehyde

52.0% yield. Product: colorless oil. FT-IR (cm^{-1}), 2904, 2814, 2795, 2730, 2713, 2695, 1607, 1569, 1539, 1519, 1505, 1464, 1432, 1494, 1386, 1357, 1316, 1288, 1255, 1231, 1213, 1185, 1148, 1116, 1040, 998, 987, 963, 886, 858, 815, 743, 724, 690. FAB-MS calcd (found): m/z 289.2 (289.2) [M+]. ^{1}H NMR (500 MHz, $CDCl_3$): δ 0.91 (t, 6H, $J = 7.0$ Hz, CH_3), 1.21–1.35 [m, 8H, $(CH_2)_2$], 1.59 (sextet, 4H,