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Liquid Crystallinity of 2-Acyl-7-[*p*-(alkoxy)benzylideneamino]fluorenes

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The liquid crystallinity of the title compounds was studied in order to design a stable liquid crystal used at low temperature. The Schiff base derived from 1- or 3-fluoreneamine scarcely shows liquid crystallinity. The propionyl group is effective for lowering the melting point of the mesophase compared to the acetyl group in a series of the title substances. The liquid crystallinity of the title compounds was compared with that of biphenyl homologues. A mesophase of the title substances was observed over a wider range of temperatures than in the case of biphenyl derivatives in a series of propionyl groups.

Fluorene, one of polycyclic aromatic hydrocarbons (PAHs), has been reported[1—4] to be a core in the field of liquid crystals.[5] The structural characteristic of fluorene compared to biphenyl is the existence of a 9-methylene group. This results in the two six-membered aromatic rings being fixed to each other in a same plane, and each of the 2- and 7-substituents deviating by an angle of 12° from the axis of the central 4a–4b bond. The structure of fluorene is both a merit and a demerit concerning the liquid crystallinity in comparison with the liquid crystal derived from biphenyl.[6]

In the molecular design of a liquid crystal, the merit of fluorene compared to that of biphenyl is delocalization of π-electrons over the biphenyl moiety due to the coplanarity of the molecule. This is expected to increase the thermal stability of the mesophase, because of increasing polarity of the core part. A structural demerit of fluorene is that the methylene group, itself, increases the width of the molecule. In addition, the substituents at the 2- and 7-positions are not situated mutually linear, and the molecule is thus a "banana shape".[7,8] These decrease the thermal stability of the mesophase.

In a comparison of 2-[*p*-(alkoxy)benzylideneamino]fluorenes[9] with 4-[*p*-(alkoxy)benzylideneamino]biphenyls,[9] the melting point of the former is lower than that of the latter, and the clearing point of the former is higher than that of the latter when the carbon number of alkoxy group is 1—10, 12, 16, or 18. Therefore, the thermal stability of the mesophase of fluorene derivatives is better than that of biphenyl homologues.

Based on the above consideration, the present paper deals with the liquid crystallinity of 2-acyl-7-[*p*-(alkoxy)benzylideneamino]fluorenes to design a stable liquid crystal used at a wide range of temperatures, as a part of our continuous studies on the synthesis and characterization of PAHs.[10] The introduction of an acyl group to 2-[*p*-(alkoxy)benzylideneamino]fluorenes is expected to increase the polarity of the molecule and to act favorably for thermal stability of the mesophase. The acyl group, having a long carbon chain, should result in a lowering of the melting point. Regarding these viewpoints, this paper concerns the following three points. The first is related to the properties of regio-isomers of 2-acyl-7-[*p*-(alkoxy)benzylideneamino]fluorene. The Schiff base attached to the 1- or 3-position of fluorene scarcely shows liquid crystallinity. The second is the effect of the acyl group of 2-acyl-7-[*p*-(alkoxy)benzylideneamino]fluorene, and states that the propionyl group is effective to lower the melting point. The last is a comparison of the liquid crystallinity of fluorene derivatives with that of biphenyl homologues. The mesophase of the fluorene derivatives was observed over a wider range of temperatures than that of biphenyl derivatives in the case of a propionyl group being attached.

Results and Discussion

The Schiff base was obtained by the reaction of the corresponding fluoreneamine and *p*-alkoxybenzaldehyde in the presence of catalytic amounts of acetic acid in a refluxing ethanol. The thermal behavior was determined at the second heating and cooling process using a polarized microscope and a DSC, as is summarized in Table 1.

2-[*p*-(Octyloxy)benzylideneamino]fluorene (**1**) has been known to be a liquid crystal.[9] The regio-isomers on the fluorene ring system of **1**, or the 1-(**2**) and 3-Schiff bases (**3**), and those 7-acetyl derivatives (**4**, **5**, and **6**) (Scheme 1) were synthesized. In the case of the 4-Schiff base, the substituent is considered to be not in a same plane with the fluorene moiety and to show no liquid crystallinity.

Compound **1** shows two mesophases (smectic and nematic), but the acetyl derivative, **4**, shows only a smectic phase over a wide range of temperatures. Compound **5** has two mesophases, in contrast with **2**, which shows no mesophase. The 3-Schiff bases, **3** and **6**, show a mesophase monotropically during the cooling process.

The structure of these Schiff bases must be considered upon the conformation of the fluoreneamine and the geometry of the Schiff double bond. Four kinds of structures, (*s*-

Table 1. Phase-Transition Temperature of Compd **1—33**[a]

Compd	Phase-transition temp/°C	Compd	Phase-transition temp/°C
1[b]	C-117.5–S-165.5–N-189.5–I	**18**	C-128–S-234–I
2	C-62–I	**19**	C-120–S-233–I
3	C-100.6–(M-51.7)–I	**20**	C-125–S-218–I
4	C-144–S-273–I	**21**	C-129–S-219–I
5	C-113.4–S-115.9–N-118.7–I	**22**[b]	C-132–S-146–N-168.5–I
6	C-123.3–(M-90.4)–I	**23**[b]	C-142.5–S-155.5–N-164–I
7[b]	C-125–S-149.5–N-198.5–I	**24**[b]	C-140–S-157.4–N-159.5–I
8[b]	C-115–S-170.5–N-181–I	**25**	C-189–S-291–I
9	C-110–S-164.5–I	**26**	C-185–S-288–I
10	C-146–S-267–I	**27**	C-174–S-279–I
11	C-140–S-273–I	**28**	C-115–S-248–I
12	C-133–S-260–I	**29**	C-104–M_1-220–M_2-241–I
13	C-137–S-285–I	**30**	C-95–S-235–I
14	C-131–S-275–I	**31**	C-102–S-235–I
15	C-120–S-273–I	**32**	C-94–S-224–I
16	C-115–S-249–I	**33**	C-85–S-218–I
17	C-121–S-236–I		

a) C: crystal state; S: smectic phase; N: nematic phase; M:mesophase; I: isotropic state. ( ): monotropic transition at cooling process. b) See Ref. 9.

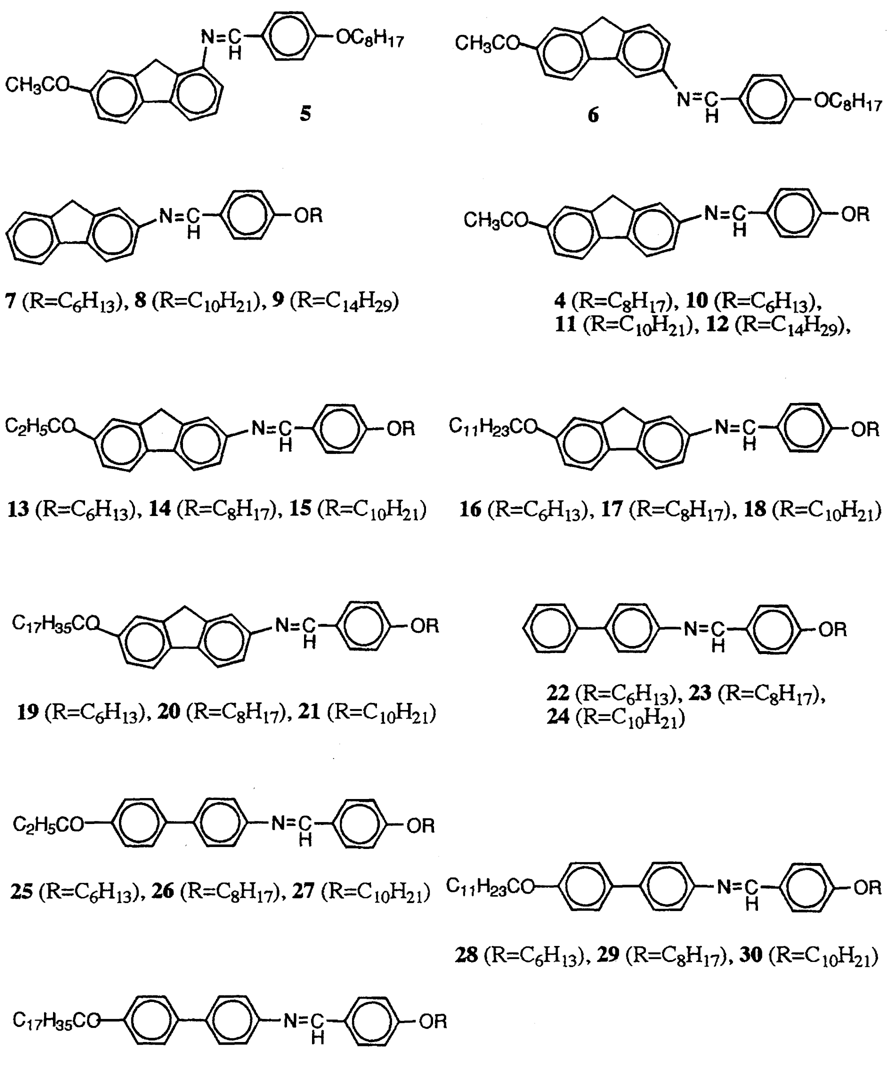
trans/*E*, *s*-*cis*/*E*, *s*-*trans*/*Z*, and *s*-*cis*/*Z*) are possible by assuming that the molecule is a plane, as shown in Fig. 1 for **1**. The NOE differential spectra of **1**, **2**, and **3** were measured in a $CDCl_3$ solution at room temperature (Fig. 2). The geometry of the Schiff double bond of **1**, **2**, and **3** is *E*, not *Z*, because that NOE was observed between the hydrogen of the azomethine group and that of the fluorene moiety.

In the case of **2**, 5.2% and 0.3% of NOE were observed between the azomethine hydrogen and the 2-hydrogen of fluorene moiety and between the azomethine hydrogen and the 9-hydrogen of fluorene part, respectively. This indicates that the preferential structure of **2** is *s*-*trans*/*E*, in spite of the 9-hydrogen not being in the same plane as the Schiff structure, and being apart from the azomethine hydrogen compared to the case of the 2-hydrogen. This explanation is agreeable to a calculation based on the molecular model: *s*-*Trans*/*E* form is more stable (1.2 kcal mol^{-1}) than the isomeric *s*-*cis*/*E*. Similarly, the *s*-*Cis*/*E* structure is predominant in the cases of **1** and **3**: *s*-*cis*/*E* is more stable (0.2 kcal mol^{-1} for **1** and 0.3 kcal mol^{-1} for **3**) than *s*-*trans*/*E*. The mesophase as a liquid crystal is considered to be aggregation of stable molecules, such as *s*-*cis*/*E* form in the case of **1**. **1** (*s*-*cis*/*E*) is a rod-shape molecule at a geometrical glance. Compared to **1**, both **2** (*s*-*trans*/*E*) and **3** (*s*-*cis*/*E*) are extremely banana shape and deviate from rod shape, which cause a decreasing of the clearing point.[11,12]

The liquid crystallinity of 2-[*p*-(alkoxy)benzylideneamino]fluorenes depends on the carbon number of the alkyl group.[9] In the case of the carbon number being 2 or 4, the Schiff base shows only a nematic phase. A base having carbons of 6 (**7**), 8 (**1**), 10 (**8**), or 12, has two mesophases (smectic and nematic). A base having 14 (**9**) or more carbons indicates only a smectic phase. The thermal stability of the mesophase, or the width between melting point and clearing point, of **7**, **1**, **8**, and **9** is 54—73 °C. The introduction of an acetyl group to the 7-position of fluorene moiety of **7**, **1**, **8**, and **9** afforded **10**, **4**, **11**, and **12**, respectively. As shown in Table 1, acetyl group results in increasing (121—133 °C) the thermal stability of the mesophase, and shows only a smectic phase with a disappearance of the nematic phase.

In order to estimate the effect of the acyl group, propionyl (**13**, **14**, **15**), dodecanoyl (**16**, **17**, **18**), or octadecanoyl group (**19**, **20**, **21**) was replaced instead of the acetyl group of 2-acetyl-7-[*p*-(hexyloxy)- (**10**), -(octyloxy)- (**4**), and -(decyloxy)-benzylideneamino]fluorenes (**11**), respectively. The smectic phase was observed between 148, 144, and 153 °C, for **13**, **14**, and **15**, respectively. Also, the ranges of the smectic phase of **16**, **17**, and **18** are between 106—134 °C, and those of **19**, **20**, and **21** are between 90—113 °C, respectively. This indicates that the propionyl group contributes best to the thermal stability of the mesophase among the series examined here. The range of the mesophase of the propionyl series is wider than that of the acetyl series in spite of the general consideration that an increase of carbon number of side chain(s) leads to a lowering of the clearing point.[13,14] The introduction of an octadecanoyl group as a long side chain does not result in decreasing of the melting temperature, based on the findings that the melting point (120—129 °C) is nearly similar to the case of mother 2-[*p*-(alkoxy)benzylideneamino]fluorenes (115—125 °C).

The Schiff bases derived from fluorene, namely, **7**, **1**, and **8**, show liquid crystallinity at a lower temperature and a wider range of temperatures than the bases derived from biphenyl, or **22**, **23**, and **24**.[9] This tendency is adopted in the case of propionyl derivatives by a comparison of the fluorene series (**13**, **14**, and **15**) with a biphenyl series (**25**, **26**, and **27**). However, the Schiff base derived from biphenyl shows a mesophase from lower temperature and over a wider temperature range than a base derived from fluorene in the cases of dodecanoyl and octadecanoyl derivatives, by a comparison of dodecanoylfluorenes (**16**, **17**, and **18**) with dodecanoylbiphenyls (**28**, **29**, and **30**), and of octadecanoylfluorenes (**19**,



5

6

7 ($R{=}C_6H_{13}$), **8** ($R{=}C_{10}H_{21}$), **9** ($R{=}C_{14}H_{29}$)

4 ($R{=}C_8H_{17}$), **10** ($R{=}C_6H_{13}$), **11** ($R{=}C_{10}H_{21}$), **12** ($R{=}C_{14}H_{29}$),

13 ($R{=}C_6H_{13}$), **14** ($R{=}C_8H_{17}$), **15** ($R{=}C_{10}H_{21}$)

16 ($R{=}C_6H_{13}$), **17** ($R{=}C_8H_{17}$), **18** ($R{=}C_{10}H_{21}$)

19 ($R{=}C_6H_{13}$), **20** ($R{=}C_8H_{17}$), **21** ($R{=}C_{10}H_{21}$)

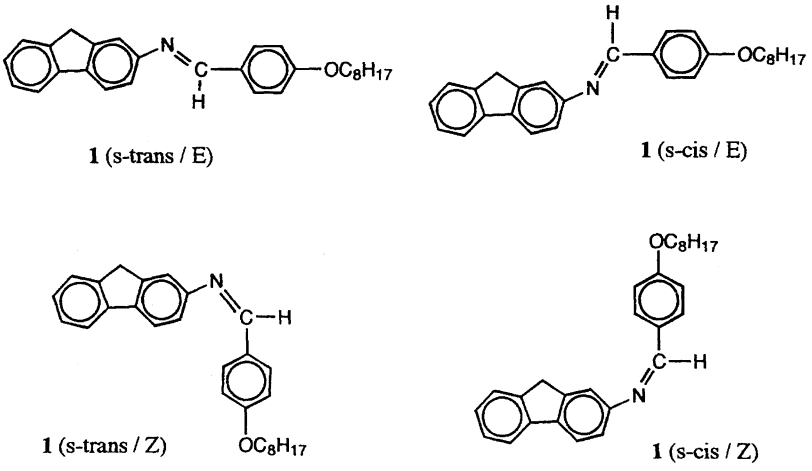
22 ($R{=}C_6H_{13}$), **23** ($R{=}C_8H_{17}$), **24** ($R{=}C_{10}H_{21}$)

25 ($R{=}C_6H_{13}$), **26** ($R{=}C_8H_{17}$), **27** ($R{=}C_{10}H_{21}$)

28 ($R{=}C_6H_{13}$), **29** ($R{=}C_8H_{17}$), **30** ($R{=}C_{10}H_{21}$)

31 ($R{=}C_6H_{13}$), **32** ($R{=}C_8H_{17}$), **33** ($R{=}C_{10}H_{21}$)

Scheme 1.



1 (s-trans / E)

1 (s-cis / E)

1 (s-trans / Z)

1 (s-cis / Z)

Fig. 1. Possible structures of **1**.

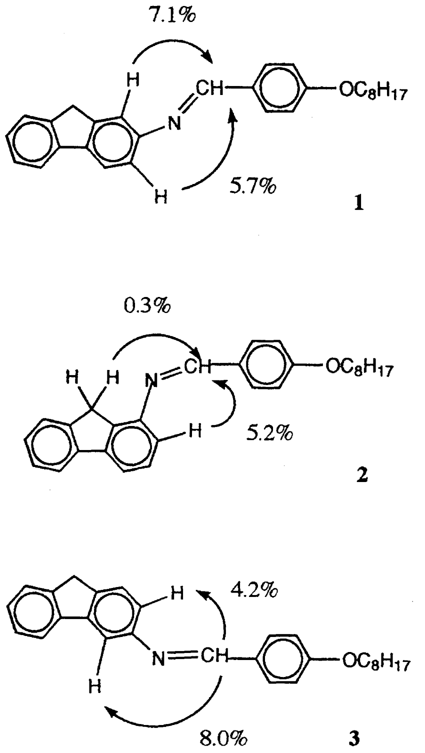


Fig. 2. NOE of **1**, **2**, and **3**.

20, and **21**) with octadecanoylbiphenyls (**31**, **32**, and **33**), respectively.

These findings are related to the length of the molecule and the deviation of the 2- and 7-substituents from the axis of the 4a–4b bond in the fluorene moiety.[13,15] The deviation does not affect to the aggregation of molecules in the case of a molecule having a relatively short side chain, such as acetyl and propionyl groups: The combination of deviation and planarity of fluorene moiety contributes effectively to the thermal stability of the mesophase compared to that of the biphenyl derivative. In the molecule attached by a relatively long side chain (doecanoyl and octadecanoyl groups), the deviation causes the banana shape, and significantly affects the aggregation of molecules.

Experimental

The melting points (Table 1) are uncorrected. The NMR spectra (0.7 ml $CDCl_3$) were recorded with a Varian VXR-300. The DSC curves and electronic spectra (EtOH) were obtained with a Rigaku DSC-8230 and a Shimadzu UV-180. The elemental analyses were measured with an EA 1108 CHNS-O (Fison Instruments).

Materials. *p*-Alkoxybenzaldehydes were prepared in the usual way. Fluorene-1-amine,[16] -2-amine,[17] and -3-amine,[18] 7-acetylfluorene-2-amine,[19] and biphenyl-4-amine[20] were obtained in a manner similar to that described elsewhere.

7-Acetylfluorene-1-amine. Typical Procedure. To a mixture of 1-nitrofluorene (211 mg, 1.0 mmol, obtained by the oxidation of fluorene-1-amine with *m*-chloroperoxybenzoic acid) in nitrobenzene (5 ml) was added anhydrous $AlCl_3$ (400 mg, 3 mmol) and the whole was stirred. AcCl (0.10 ml, 1.4 mmol) was dropped to the mixture for 10 min at 55 °C, and the resulting mixture was stirred at 60—65 °C for 8 h. After the usual treatment, the crude product was recrystallized from EtOH to give 7-acetyl-1-nitrofluorene (207 mg, 82%): Mp 166—168 °C; IR 1520, 1345 cm^{-1}; ^{1}H NMR $\delta = 2.69$ (3H, s, Me), 4.47 (2H, s, H_9), 7.63 (1H, t, $J = 8.1$ Hz, H_3), 7.90 (1H, d, $J = 8.1$ Hz, H_5), 8.07 (1H, dd, $J = 8.1$, 0.9 Hz, H_6), 8.15 (1H, d, $J = 8.1$ Hz, H_4), 8.22 (1H, d, $J = 0.9$ Hz, H_8), 8.25 (1H, d, $J = 8.1$ Hz, H_2). Found: C, 70.86; H, 4.25; N, 5.49%. Calcd for $C_{15}H_{11}NO_3$: C, 71.14; H, 4.38; N, 5.53%.

To a suspension of 7-acetyl-1-nitrofluorene (152 mg, 0.6 mmol) in EtOH (10 ml) were added powdered zinc (1.0 g) and aqueous $CaCl_2$ (350 mg/1 ml); the mixture was stirred for 4 h under refluxing. Upon the usual treatment, the crude product was recrystallized from EtOH to yield 7-acetylfluorene-1-amine (105 mg, 78%): Mp 178—180 °C; IR 3450, 3350, 3250, 1670 cm^{-1}; ^{1}H NMR $\delta = 2.66$ (3H, s, Me), 3.72 (2H, s, H_9), 3.82 (2H, s, NH_2), 6.74 (1H, dd, $J = 7.5$, 1.2 Hz, H_2), 7.27 (1H, t, $J = 7.5$ Hz, H_3), 7.32 (1H, dd, $J = 7.5$, 1.2 Hz, H_4), 7.80 (1H, d, $J = 8.1$ Hz, H_5), 7.99 (1H, dd, $J = 8.1$, 1.5 Hz, H_6), 8.15 (1H, d, $J = 0.6$ Hz, H_8).

In a manner similar to that described above, the following compounds were synthesized: 2-Nitro-7-propionylfluorene (mp 209—211 °C, recrystallized from AcOH); 7-propionylfluorene-2-amine (mp 202—204 °C, EtOH); 2-dodecanoyl-7-nitrofluorene (mp 118—120 °C, EtOH); 7-dodecanoylfluorene-2-amine (mp 113—116 °C, EtOH); 2-nitro-7-octadecanoylfluorene (mp 120—122 °C, AcOH); 7-octadecanoylfluorene-2-amine (mp 117—119 °C, EtOH); 2-acetyl-6-nitrofluorene (mp 181—183 °C, EtOAc); 2-acetylfluorene-6-amine (mp 199—201 °C, EtOAc); 4-nitro-4′-propionylbiphenyl (mp 130—132 °C, EtOH); 4′-propionylbiphenyl-4-amine (mp 182—184 °C, EtOH); 4-dodecanoyl-4′-nitrobiphenyl (mp 52—65 °C, EtOH); 4′-dodecanoylbiphenyl-4-amine (mp 134—136 °C, EtOH); 4-nitro-4′-octadecanoylbiphenyl (mp 66—82 °C, EtOH); 4′-octadecanoylbiphenyl-4-amine (mp 117—119 °C, EtOH).

1-[*p*-(Octyloxy)benzylideneamino]fluorene (2). Typical Procedure. *p*-(Octyloxy)benzaldehyde (129 mg, 0.55 mmol) was added to a suspension of fluorene-1-amine (91 mg, 0.5 mmol) and a trace amount of AcOH in EtOH (3 ml); the mixture was refluxed for 10 min. Upon evaporation of the solvent, the residue was recrystallized from hexane to afford **2** (145 mg, 73%); UV λ_{max} (log ε) 273 (4.50), 279 nm (4.50); ^{1}H NMR $\delta = 0.90$ (3H, t, $J = 6.6$ Hz, Me), 1.20—1.56 (10H, m, CH_2), 1.82 (2H, qui, $J = 6.6$ Hz, CH_2), 3.97 (2H, s, H_9), 4.04 (2H, t, $J = 6.6$ Hz, CH_2), 6.99 (1H, dd, $J = 7.8$, 1.2 Hz, H_2), 7.00 (2H, d, $J = 8.7$ Hz, A_2B_2 system of *p*-phenylene, $H_{3',5'}$), 7.31 (1H, td, $J = 7.5$, 1.2 Hz, H_7), 7.38 (1H, td, $J = 7.8$, 1.2 Hz, H_3), 7.41 (1H, t, $J = 7.5$ Hz, H_6), 7.56 (1H, dd, $J = 7.5$, 0.9 Hz, H_8), 7.64 (1H, dd, $J = 7.5$, 0.6 Hz, H_5), 7.81 (1H, d, $J = 7.8$ Hz, H_4), 7.90 (2H, d, $J = 8.7$ Hz, A_2B_2 system of *p*-phenylene, $H_{2',6'}$), 8.48 (1H, s, N=CH). Found: C, 84.37; H, 7.92; N, 3.43%. Calcd for $C_{28}H_{31}NO$: C, 84.59; H, 7.86; N, 3.52%.

3-[*p*-(Octyloxy)benzylideneamino]fluorene (3). Yield, 76%; UV λ_{max} (log ε) 281 nm (4.50); ^{1}H NMR $\delta = 0.90$ (3H, t, $J = 6.6$ Hz, Me), 1.22—1.54 (10H, m, CH_2), 1.82 (2H, qui, $J = 6.6$ Hz, CH_2), 3.91 (2H, s, H_9), 4.03 (2H, t, $J = 6.6$ Hz, CH_2), 6.99 (2H, d, $J = 8.7$ Hz, A_2B_2 system of *p*-phenylene, $H_{3',5'}$), 7.16 (1H, dd, $J = 8.1$, 2.1 Hz, H_2), 7.31 (1H, td, $J = 7.5$, 1.2 Hz, H_7), 7.39 (1H, td, $J = 7.5$, 1.2 Hz, H_6), 7.50—7.58 (2H, m, $H_{1,8}$), 7.62 (1H, d, $J = 1.8$ Hz, H_4), 7.80 (1H, d, $J = 7.5$ Hz, H_5), 7.87 (2H, d, $J = 8.7$ Hz, A_2B_2 system of *p*-phenylene, $H_{2',6'}$), 8.49 (1H, s, N=CH). Found: C, 84.58; H, 7.74; N, 3.45%. Calcd for $C_{28}H_{31}NO$: C, 84.59; H, 7.86; N, 3.52%.

2-Acetyl-7-[*p*-(octyloxy)benzylideneamino]fluorene (4). Yield, 74%; IR 1670 cm^{-1}; UV λ_{max} (log ε) 352 nm (4.58); ^{1}H NMR $\delta = 0.89$ (3H, t, $J = 6.6$ Hz, Me), 1.19—1.55 (10H, m, CH_2), 1.81 (2H, qui, $J = 6.6$ Hz, CH_2), 2.66 (3H, s, $COCH_3$), 3.98 (2H, s, H_9), 4.03 (2H, t, $J = 6.6$ Hz, CH_2), 6.99 (2H, d, $J = 6.9$

Hz, A_2B_2 system of *p*-phenylene, $H_{3',5'}$), 7.28 (1H, dd, J = 8.1, 2.1 Hz, H_6), 7.42 (1H, t, J = 1.5 Hz, H_8), 7.78—7.91 (4H, m, $H_{4,5}$, $H_{2',6'}$), 8.01 (1H, dd, J = 8.1, 1.5 Hz, H_3), 8.14 (1H, d, J = 0.9 Hz, H_1), 8.46 (1H, s, N=CH). Found: C, 81.86; H, 7.82; N, 3.51%. Calcd for $C_{30}H_{33}NO_2$: C, 81.79; H, 7.57; N, 3.19%.

7-Acetyl-1-[*p*-(octyloxy)benzylideneamino]fluorene (5). Yield, 67%; IR 1665 cm^{-1}; UV $\lambda_{\max}$ (log ε) 304 nm (4.61); ^{1}H NMR δ = 0.90 (3H, t, J = 6.6 Hz, Me), 1.20—1.57 (10H, m, CH_2), 1.85 (2H, qui, J = 6.6 Hz, CH_2), 2.66 (3H, s, $COCH_3$), 4.02 (2H, s, H_9), 4.04 (2H, t, J = 6.6 Hz, CH_2), 7.01 (2H, d, J = 8.7 Hz, A_2B_2 system of *p*-phenylene, $H_{3',5'}$), 7.06 (1H, dd, J = 7.8, 0.9 Hz, H_2), 7.45 (1H, t, J = 7.8 Hz, H_3), 7.70 (1H, dd, J = 7.8, 0.9 Hz, H_4), 7.85 (1H, d, J = 8.1 Hz, H_5), 7.90 (2H, d, J = 8.7 Hz, A_2B_2 system of *p*-phenylene, $H_{2',6'}$), 8.02 (1H, dd, J = 8.1, 1.5 Hz, H_6), 8.12 (1H, d, J = 0.6 Hz, H_8), 8.48 (1H, s, N=CH). Found: C, 81.82; H, 7.72; N, 3.30%. Calcd for $C_{30}H_{33}NO_2$: C, 81.79; H, 7.57; N, 3.19%.

2-Acetyl-6-[*p*-(octyloxy)benzylideneamino]fluorene (6). Yield, 33%; IR 1670 cm^{-1}; UV $\lambda_{\max}$ (log ε) 301 nm (4.63); ^{1}H NMR δ = 0.90 (3H, t, J = 6.6 Hz, Me), 1.18—1.56 (10H, m, CH_2), 1.82 (2H, qui, J = 6.6 Hz, CH_2), 2.67 (3H, s, $COCH_3$), 3.97 (2H, s, H_9), 4.04 (2H, t, J = 6.6 Hz, CH_2), 7.00 (2H, d, J = 8.7 Hz, A_2B_2 system of *p*-phenylene, $H_{3',5'}$), 7.24 (1H, dd, J = 8.1, 1.8 Hz, H_7), 7.58 (1H, t, J = 8.1 Hz, H_8), 7.67 (1H, d, J = 1.8 Hz, H_5), 7.85 (1H, d, J = 8.1 Hz, H_4), 7.88 (2H, d, J = 8.7 Hz, A_2B_2 system of *p*-phenylene, $H_{2',6'}$), 8.02 (1H, dd, J = 8.1, 1.8 Hz, H_3), 8.16 (1H, d, J = 1.8 Hz, H_1), 8.49 (1H, s, N=CH). Found: C, 81.71; H, 7.69; N, 3.24%. Calcd for $C_{30}H_{33}NO_2$: C, 81.79; H, 7.57; N, 3.19%.

2-[*p*-(Hexyloxy)benzylideneamino]-7-propionylfluorene (13). Yield, 71%; IR 1670 cm^{-1}; ^{1}H NMR δ = 0.92 (3H, t, J = 6.9 Hz, Me), 1.26 (3H, t, J = 7.2 Hz, CH_3), 1.31—1.42 (4H, m, CH_2), 1.48 (2H, br, CH_2), 1.82 (2H, qui, J = 6.9 Hz, CH_2), 3.07 (2H, t, J = 7.2 Hz, CH_2), 3.98 (2H, s, H_9), 4.03 (2H, t, J = 6.9 Hz, CH_2), 6.99 (2H, d, J = 8.7 Hz, A_2B_2 system of *p*-phenylene, $H_{3',5'}$), 7.27 (1H, dd, J = 8.1, 1.8 Hz, H_3), 7.42 (1H, d, J = 1.5 Hz, H_1), 7.80 (1H, d, J = 8.1 Hz, H_4), 7.84 (1H, d, J = 7.8 Hz, H_5), 7.86 (2H, d, J = 8.7 Hz, A_2B_2 system of *p*-phenylene, $H_{2',6'}$), 8.02 (1H, dd, J = 7.8, 1.5 Hz, H_6), 8.14 (1H, d, J = 0.9 Hz, H_8), 8.46 (1H, s, N=CH). Found: C, 82.07; H, 7.41; N, 3.23%. Calcd for $C_{29}H_{31}NO_2$: C, 81.85; H, 7.34; N, 3.29%.

2-Dodecanoyl-7-[*p*-(hexyloxy)benzylideneamino]fluorene (16). Yield, 91%; IR 1670 cm^{-1}; ^{1}H NMR δ = 0.88 (3H, t, J = 7.2 Hz, Me), 0.92 (3H, t, J = 6.6 Hz, CH_3), 1.18—1.56 (22H, m, CH_2), 1.70—1.88 (4H, m, CH_2), 3.01 (2H, t, J = 7.2 Hz, CH_2), 3.98 (2H, s, H_9), 4.03 (2H, t, J = 6.6 Hz, CH_2), 6.99 (2H, d, J = 8.7 Hz, A_2B_2 system of *p*-phenylene, $H_{3',5'}$), 7.27 (1H, dd, J = 8.1, 1.8 Hz, H_6), 7.42 (1H, d, J = 1.2 Hz, H_8), 7.80 (1H, d, J = 8.1 Hz, H_5), 7.84 (1H, d, J = 7.8 Hz, H_4), 7.86 (2H, d, J = 8.7 Hz, A_2B_2 system of *p*-phenylene, $H_{2',6'}$), 8.01 (1H, dd, J = 7.8, 1.5 Hz, H_3), 8.14 (1H, d, J = 0.9 Hz, H_1), 8.46 (1H, s, N=CH). Found: C, 82.52; H, 8.96; N, 2.63%. Calcd for $C_{38}H_{49}NO_2$: C, 82.72; H, 8.94; N, 2.54%.

2-[*p*-(Decyloxy)benzylideneamino]-7-octadecanoylfluorene (21). Yield, 85%; IR 1670 cm^{-1}; ^{1}H NMR δ = 0.88 (3H, t, J = 6.9 Hz, Me), 0.89 (3H, t, J = 7.2 Hz, CH_3), 1.02—1.56 (44H, m, CH_2), 1.79 (2H, qui, J = 6.9 Hz, CH_2), 3.01 (2H, t, J = 7.5 Hz, CH_2), 3.98 (2H, s, H_9), 4.03 (2H, t, J = 6.9 Hz, CH_2), 6.99 (2H, d, J = 8.7 Hz, A_2B_2 system of *p*-phenylene, $H_{3',5'}$), 7.27 (1H, dd, J = 8.1, 2.1 Hz, H_3), 7.41 (1H, d, J = 2.4 Hz, H_1), 7.80 (1H, d, J = 8.1 Hz, H_4), 7.84 (1H, d, J = 8.1 Hz, H_5), 7.86 (2H, d, J = 8.7 Hz, A_2B_2 system of *p*-phenylene, $H_{2',6'}$), 8.01 (1H, dd, J = 8.1, 1.5 Hz, H_6), 8.14 (1H, s, H_8), 8.46 (1H, s, N=CH). Found: C, 83.47; H, 10.10; N, 1.94%. Calcd for $C_{48}H_{69}NO_2$: C, 83.30; H, 10.05; N, 2.02%.

4-[*p*-(Octyloxy)benzylideneamino]-4′-propionylbiphenyl (27). Yield, 80%; IR 1680 cm^{-1}; ^{1}H NMR δ = 0.90 (3H, t, J = 6.6 Hz, Me), 1.14—1.57 (13H, m), 1.82 (2H, qui, J = 6.6 Hz, CH_2), 3.05 (2H, q, J = 7.2 Hz, CH_2), 4.03 (2H, t, J = 6.6 Hz, CH_2), 6.99 (2H, d, J = 9.0 Hz, A_2B_2 system of *p*-phenylene, $H_{3'',5''}$), 7.30 (2H, d, J = 8.7 Hz, A_2B_2 system of *p*-phenylene, $H_{3,5}$), 7.66 (2H, d, J = 8.7 Hz, A_2B_2 system of *p*-phenylene, $H_{2,6}$), 7.71 (2H, d, J = 8.4 Hz, A_2B_2 system of *p*-phenylene, $H_{2',6'}$), 7.86 (2H, d, J = 9.0 Hz, A_2B_2 system of *p*-phenylene, $H_{2'',6''}$), 8.04 (2H, d, J = 8.4 Hz, A_2B_2 system of *p*-phenylene, $H_{3',5'}$), 8.43 (1H, s, N=CH). Found: C, 81.79; H, 7.91; N, 3.20%. Calcd for $C_{30}H_{35}NO_2$: C, 81.60; H, 7.98; N, 3.17%.

4-Dodecanoyl-4′-[*p*-(hexyloxy)benzylideneamino]biphenyl (28). Yield, 79%; IR 1680 cm^{-1}; ^{1}H NMR δ = 0.88 (3H, t, J = 7.5 Hz, Me), 0.92 (3H, t, J = 6.9 Hz, Me), 1.18—1.55 (22H, m), 1.68—1.91 (4H, m, CH_2), 3.06 (2H, q, J = 7.5 Hz, CH_2), 4.04 (2H, t, J = 6.9 Hz, CH_2), 6.99 (2H, d, J = 8.7 Hz, A_2B_2 system of *p*-phenylene, $H_{3'',5''}$), 7.30 (2H, d, J = 8.7 Hz, A_2B_2 system of *p*-phenylene, $H_{3',5'}$), 7.66 (2H, d, J = 8.7 Hz, A_2B_2 system of *p*-phenylene, $H_{2',6'}$), 7.71 (2H, d, J = 8.7 Hz, A_2B_2 system of *p*-phenylene, $H_{2,6}$), 7.86 (2H, d, J = 8.7 Hz, A_2B_2 system of *p*-phenylene, $H_{2'',6''}$), 8.04 (2H, d, J = 8.7 Hz, A_2B_2 system of *p*-phenylene, $H_{3,5}$), 8.44 (1H, s, N=CH). Found: C, 82.51; H, 9.38; N, 2.56%. Calcd for $C_{37}H_{49}NO_2$: C, 82.33; H, 9.15; N, 2.59%.

4-[*p*-(Decyloxy)benzylideneamino]-4′-octadecanoylbiphenyl (33). Yield, 82%; IR 1680 cm^{-1}. Found: C, 83.21; H, 10.46; N, 2.06%. Calcd for $C_{47}H_{73}NO_2$: C, 83.01; H, 10.25; N, 2.06%.

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