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Synthesis and Solid State Absorption Spectra of some Aminonaphthoquinone Dyes

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ABSTRACT

The 2,6- and 4,8-bisarylamino-1,5-naphthoquinone derivatives **3b–d** *and* **6a–e** *were synthesized by the amination of naphthazarin (***1***) and naphthazarin intermediate (***4***), respectively. Their chromophoric systems were evaluated by the PPP MO method, and their absorption spectra in solution and the solid state were investigated to evaluate the intermolecular* π–π *interactions of the dye molecules in the solid state. In the case of dyes* **3a–d**, *large* $\Delta\lambda$ *values of over 100 nm were obtained, but in* **3b–d** *another absorption maximum at shorter wavelength was also observed. On the other hand, dyes* **6c–e** *showed large* $\Delta\lambda$ *values of over 90 nm, but dyes* **6a** *and* **6b** *showed relatively small* $\Delta\lambda$ *values of less than 45 nm. The chain length of the alkyl and alkoxy substituents influenced the molecular stacking of the dye in the solid state. Copyright © 1996 Elsevier Science Ltd*

INTRODUCTION

A number of investigations have been carried out on the syntheses of aminonaphthoquinone derivatives, which are of interest in the dyeing industry[1,2] and in biological[3] and pharmaceutical areas.[4]

There is current interest in the development of 3rd order nonlinear optical (NLO) materials with respect to dye chromophores. Quinoid dyes have large

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π-conjugated systems and a strong intramolecular charge-transfer chromophoric system, and are thus of interest as candidates for 3rd order NLO materials.

Aminonaphthoquinones have a large dipole moment in the ground state and a larger dipole moment in the excited state, factors which are favorable for a large photoinduced polarization. The amino and hydroxy groups in the quinone nucleus act as a donor moiety and the para-quinone group acts as an acceptor moiety, thus constructing a strong intramolecular charge-transfer chromophoric system. In addition, the amino and hydroxy groups act as hydrogen donors and the quinone carbonyl groups act as hydrogen acceptors for intra- and intermolecular hydrogen bonding.[5] Intermolecular interactions induced by strong hydrogen bonding and the interlayer π–π interactions with charge-transfer characters make possible the formation of three-dimensional molecular stacking in crystals or vapor deposited thin films.[5] In previous papers, metal promoted amination of anthraquinones[6] and naphthoquinones[7] catalyzed by copper ions have been studied.

In the present paper, 2,6- and 4,8-bisarylamino-1,5-naphthoquinone derivatives were synthesized by the amination of naphthazarin (**1**) and of naphthazarin intermediate (**4**), respectively. Their chromophoric systems were evaluated by the PPP MO method, and their absorption spectra in solution and the solid state were investigated, to ascertain the intermolecular π–π interactions of the dye molecules in the solid state.

RESULTS AND DISCUSSION

Syntheses of bisarylamino-1,5-naphthoquinones

It has been found that the formation of a copper complex between the carbonyl groups and the hydroxy groups of naphthazarin (**1**) plays an important role in selective β-aminations of the naphthazarin nucleus, and that atmospheric oxygen acts as an effective oxidant in the reaction.[7] The 2,6-bis(alkyl or aryl)amino-4,8-dihydroxy-1,5-naphthoquinones **3a–d** were obtained in moderate yields by the copper catalyzed amination of **1** with alkylamines or arylamines in the presence of cuprous chloride (Fig. 1). Absorption spectra data are given in Table 1.

In the solid state absorption spectra of dyes **3b–d**, two absorption maxima around 430 and 640 nm were observed. For dye **3a**, only one absorption maximum was observed and the band splitting could thus be considered to be due to the arylamino substituents in dyes **3b–d**; this factor is discussed in a later section.

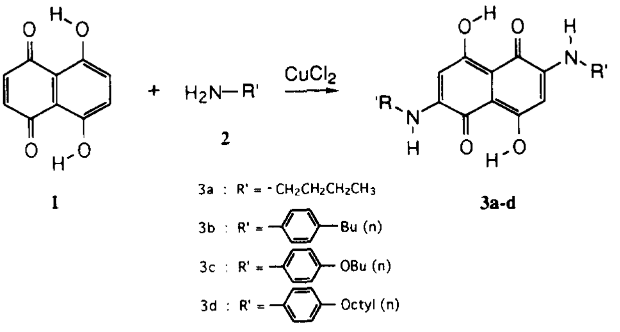


Fig. 1. Syntheses of 2,6-bis(alkyl or arylamino)-4,8-dihydroxy-1,5-naphthoquinones.

TABLE 1
Absorption Spectra of Dyes **3a–d** in Solution and Solid State

Compound	*λmax* [a] *in soln (nm)*	*log ε*	*λmax* [b] *in film (nm)*	Δλ[c] *(nm)*
3a	459	(4.10)	568 ^{sh}	
	504	(4.14)	604	100
	543	(4.20)		61
3b	412 ^{sh}	(4.28)	436	
	492	(4.55)		
	520	(4.54)	584 ^{sh}	64
	560 ^{sh}	(4.48)	682	122
3c	415 ^{sh}	(4.60)	432	
			480 ^{sh}	
	510	(4.88)	628	118
	550 ^{sh}	(4.83)		78
3d	400 ^{sh}	(3.97)	429	
	494	(4.28)	590 ^{sh}	
	520	(4.26)	644	124
	557 ^{sh}	(4.20)		87

[a] In benzene.
[b] On vapor deposited thin film.
[c] Δλ = λsolid − λsoln.

The 4,8-bis(arylamino)-1,5-naphthoquinones were prepared by the known reaction of naphthazarin intermediate (**4**) with arylamines in acetic acid (Fig. 2); absorption spectra are shown in Table 2.

Absorption spectra on vapor deposited thin film

It is known that the λmax value of dyes is shifted to longer wavelength (by 30–80 nm) in the solid state compared with those in solution, and some experimental data pertinent to this have been reported.[10] The difference

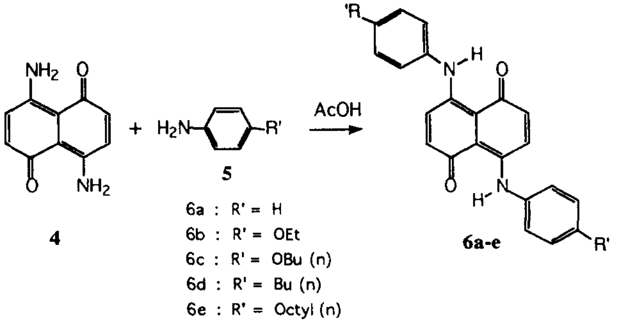


Fig. 2. Syntheses of 4,8-bis(arylamino)-1,5-naphthoquinones.

TABLE 2
Absorption Spectra of Dyes **6a–e** in Solution and Solid State

Compound	*λmax*[a] *in soln (nm)*	*log ε*	λmax[b] *in film (nm)*	Δλ[c] *(nm)*
6a	660	(4.28)	685	25
6b	672	(4.36)	716	44
6c	668	(4.42)	770	102
6d	670	(4.26)	760	90
6e	664	(4.36)	753	89

[a] In benzene.
[b] On vapor deposited thin film.
[c] Δλ = λsolid − λsoln.

(Δλ value) is the result of stronger intermolecular interactions of the dye molecules in the solid state.

Recently, we found that dye **3a** showed a large Δλ value (100 nm) and gave a high quality vapor deposited thin film which showed a large $\chi^{(3)}$ value for 3rd order NLO materials. X-ray crystal analysis of **3a** showed that strong intermolecular hydrogen bondings and interlayer π–π interactions made possible the formation of rigid molecular stacking in crystals.[5]

With dyes **3b–d**, large Δλ values (over 100 nm) were obtained, but another absorption maximum at shorter wavelength was also observed for each of these dyes. The absorption spectra of dye **3b** in solution and thin film are shown in Fig. 3. Dyes **3b–d** showed visible absorption with vibrationally split bands around 500–550 nm and an additional weak absorption at 400 nm (as a shoulder) in solution, but showed two distinct absorption maxima in the shorter wavelength region around 430 nm and in the longer wavelength around 630–680 nm in vapour deposited thin film.

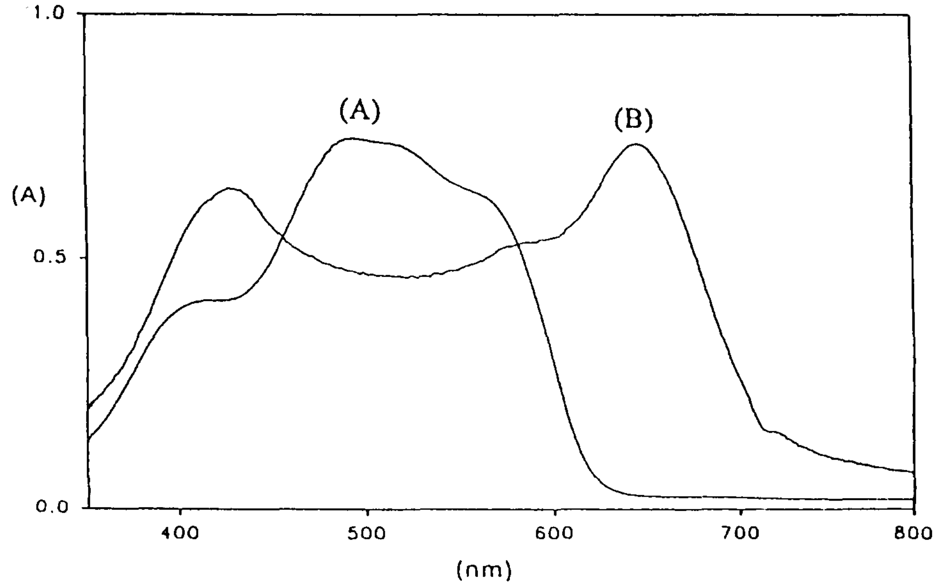


Fig. 3. Absorption spectra of dye **3b** in solution (A) and vapor deposited thin film (B).

The PPP MO calculations for dyes **3a**, **3b** and 1,5-naphthazarin are summarized in Table 3. The π-electron density changes accompanying the first excitation of these dyes are shown in Fig. 4.

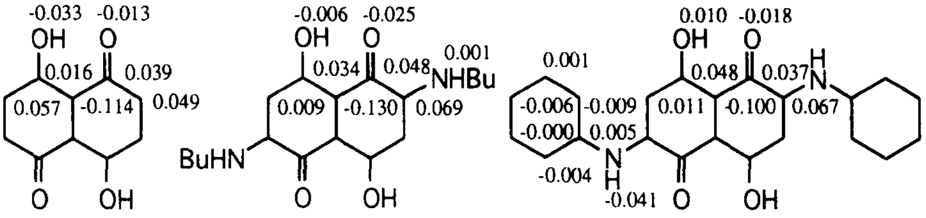
It was generally observed that the first excitation energy (ΔE_1) of these dyes corresponded to the transition from the HOMO to LUMO, and that the ΔE_1

TABLE 3

PPP MO Calculation Results of Dyes **3a**, **3b**, and 1,5-Naphthazarin

	1[a]	*3a*	*3b*
ΔE_1 (ev) before CI	2.56227	2.55954	2.28840
ΔE_1 (ev) after CI	2.50191	2.45704	2.20776
λ1max (nm)	495.6	504.7	561.7
f1 Oscillator strength	0.5123	0.8011	1.3511
Transition[a]	H → L	H → L	H → L
Transition moment	1.5294	1.9299	2.6442
Direction (degree)	$\alpha = 9.72$	$\alpha = 19.67$	$\alpha = 13.47$
ΔE_2 (ev) before CI	3.49304	3.06251	2.90713
ΔE_2 (ev) after CI	4.58071	3.92906	3.53405
λ2max (nm)	270.7	315.6	350.9
f2 Oscillator strength	0.2331	0.2878	0.1369
Transition[a]	next H → L	next H → L	next H → L
Transition moment	0.7625	0.9149	0.6652
Direction (degree)	$\alpha = 92.42$	$\alpha = 65.77$	$\alpha = 34.92$

[a] H = HOMO, L = LUMO, next H = next HOMO.



1 **3a** **3b**

Fig. 4. π-Electron density changes accompanying the first excitation.

values before configuration interaction (CI) were much larger than those after CI, whilst the ΔE_2 values after CI were much larger than those before CI. The ΔE_2 values corresponded to the transition from the next HOMO to LUMO, respectively. The strength of the transition moment for **3b** was much larger than that for **3a**, and the direction of the transition moment evaluated by the angle α was slightly larger in dye **3a** compared with that for **3b**. The π-electron density changes accompanying the first excitation indicated that **3b** has an intramolecular charge-transfer chromophoric system in which the arylamino groups act as strong donors and the naphthazarin moiety acts as an acceptor. On the other hand, **3a** has a very similar chromophoric system to naphthazarin (**1**), and the butylamino groups at the 2,6-positions have little affect on the first excitation but contribute largely to the second excitation. The anomalous π-electron density decreases at the hydroxy and carbonyl groups in these dyes are attributed to the intramolecular hydrogen bonding between the two groups and the existence of tautomers. The hydroxy group, in general, acts as an electron donor and the carbonyl group acts as an acceptor, but with tautomerism, the electronic character is changed and the reverse electronic effects are attained. As a result, the calculated π-electron density decreases at both of the oxygen atoms. The tautomerism in these dyes has been evaluated by the *ab initio* method and the results published.[11]

As indicated in Table 3, **3b** has the calculated second excitation at 350 nm as a weak absorption but **3a** has it at 315 nm. It is proposed that the absorption of **3b** at around 400 nm might correspond to the second excitation which is shifted to 430 nm in the solid state, the first excitation around 500–550 nm being shifted to 600–680 nm, as shown in Fig. 3. This previously unreported band splitting could be caused by molecular aggregation and orientation against the substrate during the vapor deposition. The correlation between the orientation of molecules and their absorption spectra on vapor deposited thin film was investigated and it was observed that the absorption spectra in the solid state was affected primarily by the deposition conditions, i.e. temperature, deposition rate and distance to the substrate. The $\Delta\lambda$ values were also influenced by the chain length of the alkyl groups at

TABLE 4
Syntheses of Aminonaphthoquinones **3** and **6**

Compound	*Amine*	*Time (h)*	*Temp (°C)*	*Yield (%)*	*Recrystallization solvent* [a]
3a	*n*-butylamine	24	60	32	benzene
3b	4-*n*-butylaniline	24	reflux	26	b/c (v/v = 2/1)
3c	4-*n*-butoxyaniline	36	80	27	b/c (v/v = 2/1)
3d	4-*n*-octylaniline	36	80	34	b/c (v/v = 1/2)
6a	aniline	10	reflux	59	b/c (v/v = 2/1)
6b	4-ethoxyaniline	10	reflux	25	b/c (v/v = 1/1)
6c	4-*n*-butoxyaniline	10	reflux	36	cyclohexane
6d	4-*n*-butylaniline	10	reflux	17	b/c (v/v = 1/1)
6e	4-*n*-octylaniline	10	reflux	35	c/n (v/v = 2/1)

[a] b/c = benzene/cyclohexane; c/n = cyclohexane/*n*-hexane.

the 4-positions, as well as by the phenyl groups in **3b–d**. The large $\Delta\lambda$ values of dyes **3b–d** indicate that these dyes have strong three-dimensional interlayer π–π interactions in the solid state, as in the case of **3a**, and that they are thus of interest as possible 3rd order NLO materials.

On the other hand, dyes **6a–e** also have a strong intramolecular charge-transfer chromophoric system which has been evaluated by the PPP MO method.[8] They do not show any tautomerism and exist in the 4,8-bis-arylamino-1,5-naphthoquinone form. Dyes **6c–e** showed large $\Delta\lambda$ values of over 90 nm, but dyes **6a** and **6b** showed smaller $\Delta\lambda$ values of less than 45 nm. The dyes differ in the chain length of the alkyl group. It is proposed that the length of the alkyl group does not greatly affect their electronic character (as confirmed by their λmax values in solution), but does affect their molecular stacking in the solid state. From the results shown in Table 4, whilst the phenyl and 4-ethoxyphenyl groups are not optimal for effective molecular stacking, longer alkyl or alkoxy groups result in effective molecular stacking, giving a large $\Delta\lambda$ value. Band splitting was not observed for dyes **6a–e**, and parallel shift of each peak to longer wavelength was observed, as indicated in Fig. 5. The molecular stacking in the solid state using X-ray crystal analysis and correlation with $\chi^{(3)}$ values for 3rd NLO materials will be the subject of future investigations.

EXPERIMENTAL

Materials and equipment

Characterization of all compounds was carried out by general procedures using the following equipment; m.p.: Yanagimoto micro melting point

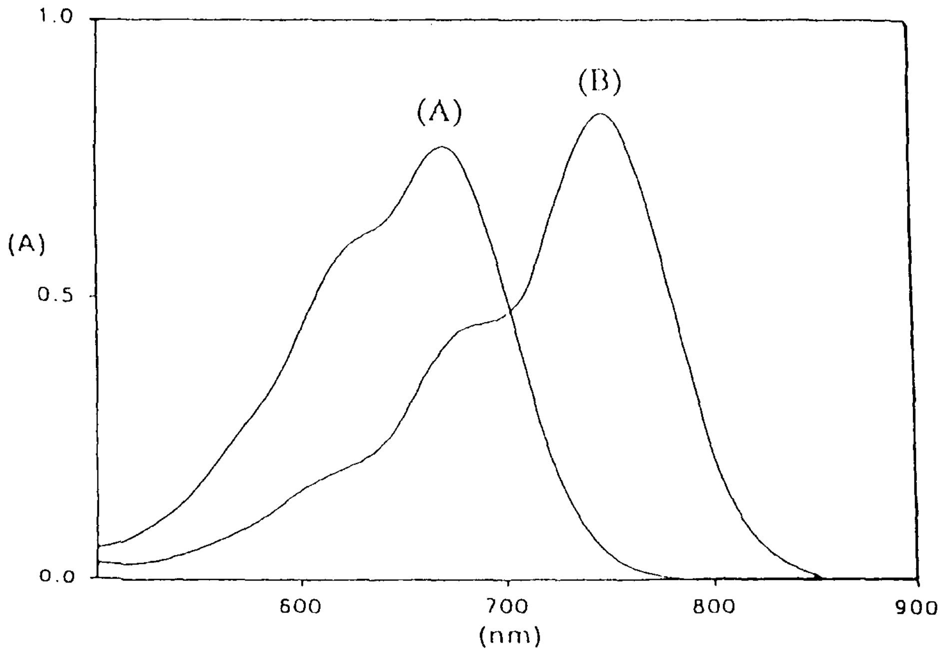


Fig. 5. Differences in absorption spectra of dye **6e** in solution (A) and vapor deposited thin film

apparatus, uncorrected. NMR Spectra: FT-NMR QE 300 MHz Shimadzu spectrometer; chemical shifts in ppm with reference to TMS. Mass spectra: M-80 B Hitachi mass spectrometer. UV-Vis spectra: U-3410 Hitachi spectrophotometer.

All chemicals were reagent grade and used without further purification unless otherwise specified. Naphthazarin (**1**)[9] and naphthazarin intermediate (**4**)[10] were synthesized by known methods. Preparations of vapor deposited thin film of dye were performed using the Nippon Shinku Kikou VSP-060 apparatus.

Reaction of naphthazarin (1) with amines (2a–d)

A mixture of **1** (1 mmol) and cuprous chloride (2.3 mmol) in pyridine (5 ml) was heated at 80°C for 1 h to prepare the copper complex and then cooled to room temperature. To the mixture was added the appropriate amine **2a–d** (50 mmol) (Fig. 1) in pyridine (2 ml) and the mixture was heated under the conditions shown in Table 1. The reaction mixture was poured into aqueous 10% hydrochloric acid and the product was extracted with chloroform, evaporated and dried. The crude products were purified by chromatography on silica-gel using benzene as eluent and recrystallized prior to analysis.

Reaction of naphthazarin intermediate (4) with amines

The appropriate amine **5a–e** (1 mmol) (Fig. 2) was added dropwise to a solution of **4** (2.3 mmol) in glacial acetic acid (5 ml) and the mixture refluxed for 10 h. The reaction mixture was poured into aqueous 10% hydrochloric acid and the separated product was extracted with chloroform, purified by column chromatography on silica-gel using benzene as eluent, and recrystallized for analysis.

Identification of products (3a–d, 6a–e)

3a: m.p. 189–190°C; ^{1}H-NMR (300 MHz, $CDCl_3$): δ 14.40 (2H, S), 6.19 (2H, broad), 5.77 (2H, S), 3.24 (4H, q), 1.69 (4H, m), 1.45 (4H, m), 0.98 (6H, m); MS *m/z* (M^+): 332. Calcd for $C_{18}H_{24}N_2O_4$: C, 65.04; H, 7.28; N, 8.43. Found: C, 64.95; H, 7.27; N, 8.10.

3b: m.p. 214–216°C; ^{1}H-NMR (300 MHz, $CDCl_3$): δ 14.18 (2H, s), 7.76 (2H, s), 7.21 (8h, d), 6.39 (2H, s), 2.63 (4H, t), 1.60 (4H, m), 1.37 (4H, m), 0.94 (6H, t); MS *m/z* (M^+): 484. Calcd for $C_{30}H_{32}N_2O_4$: C, 74.38; H, 6.61; N, 5.79. Found: C, 74.02; H, 6.68; N, 5.61.

3c: m.p. 210–212°C; ^{1}H-NMR (300 MHz, $CDCl_3$): δ 14.22 (2H, s), 7.68 (2H, s, broad), 7.20 (4H, d), 6.94 (4H, d), 6.23 (2H, s), 3.98 (4H, t), 1.79 (4H, m), 1.32 (4H, m), 0.99 (6H, t); MS *m/z* (M^+): 516. Calcd for $C_{30}H_{32}N_2O_6$: C, 69.77; H, 6.20; N, 5.43. Found: C, 69.08; H, 5.99; N, 5.60.

3d: m.p. 189°C; ^{1}H-NMR (300 MHz, $CDCl_3$): δ 14.18 (2H, s), 7.76 (2H, s, broad), 7.22 (8H, s), 6.39 (2H, s), 2.62 (4H, t), 1.57 (2H, m), 1.28 (20H, m), 0.82 (6H, t); MS *m/z* (M^+): 596. Calcd for $C_{38}H_{48}N_2O_4$: C, 76.51; H, 8.05; N, 4.70. Found: C, 77.18; H, 8.51; N, 4.65.

6a: m.p. 228–230°C; ^{1}H-NMR (300 MHz, $CDCl_3$): δ 14.30 (2H, s), 7.50 (2H, d), 7.47 (2H, d), 7.29 (6H, m), 7.05 (2H, d); MS *m/z* (M^+): 340. Calcd for $C_{22}H_{16}N_2O_2$: C, 77.65; H, 4.71; N, 8.24. Found: C, 77.79; H, 4.80; N, 8.11.

6b: m.p. 271–272°C; ^{1}H-NMR (300 MHz, $CDCl_3$): δ 14.31 (2H, s, broad), 7.39 (2H, d), 7.18 (4H, d), 7.00 (2H, d), 6.95 (4H, d), 4.07 (4H, q), 1.44 (6H, t); MS *m/z* (M^+): 428. Calcd for $C_{26}H_{24}N_2O_4$: C, 72.89; H, 5.61; N, 6.54. Found: C, 72.76; H, 5.70; N, 6.37.

6c: m.p. 160–161°C; ^{1}H-NMR (300 MHz, $CDCl_3$): δ 14.29 (2H, s, broad), 7.39 (2H, d), 7.18 (4H, d), 7.01 (2H, d), 6.96 (4H, d), 3.99 (4H, t), 1.80 (4H, m), 1.50 (4H, m), 0.99 (6H, t); MS *m/z* (M^+): 484. Calcd for $C_{30}H_{32}N_2O_4$: C, 74.38; H, 6.61; N, 5.79. Found: C, 73.97; H, 6.69; N, 5.63.

6d: m.p. 165–167°C; ^{1}H-NMR (300 MHz, $CDCl_3$): δ 14.35 (2H, s, broad), 7.47 (2H, d), 7.25 (4H, d), 7.17 (4H, d), 7.01 (2H, d), 2.65 (4H, t), 1.75 (4H, m), 1.51 (4H, m), 0.956 (6H, t); MS *m/z* (M^+): 452. Calcd for $C_{30}H_{32}N_2O_2$: C, 79.60; H, 7.13; N, 6.19. Found: C, 81.03; H, 7.33; N, 6.27.

6e: m.p. 120–121°C; ^{1}H-NMR (300 MHz, $CDCl_3$): δ 14.35 (2H, s, broad), 7.47 (2H, d), 7.01 (2H, d), 7.24 (4H, d), 7.17 (4H, d), 2.63 (4H, t), 1.59 (4H, m), 1.30 (20H, m), 0.88 (6H, t); MS *m/z* (M^+): 564. Calcd for $C_{38}H_{48}N_2O_4$: C, 80.85; H, 8.51; N, 4.96. Found: C, 79.46; H, 8.58; N, 4.80.

Preparation of vapor deposited thin film for solid state absorption spectra

Dyes were evaporated vertically from a heated plate onto the substrate (glass or quartz slide) under low pressure of about 5×10^{-6} Torr by using a vapor deposition apparatus. The distance between the sample and the substrate and the evaporating temperature were controlled depending on the properties of the dyes. The thicknesses of the films were around 1000 Å.

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