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Self-Assembling of Aminopyrazine Fluorescent Dyes and Their Solid State Spectra

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ABSTRACT

2,5-Diamino-3,6-dicyanopyrazine has strong yellowish-green fluorescence in spite of its small chromophoric system. Substitution at the amino groups, and hydrolysis followed by esterification of the cyano groups gave many types of fluorescent dyes. Their absorption and fluorescent spectra both in solution and solid state were correlated with their molecular stacking on vapor deposited thin film. Steric hindrances of the substitutents largely affected their solid state absorption and fluorescent spectra. Structural optimization by means of MOPAC PM3 method was conducted, and these results well indicated their molecular stacking behaviors. © 1998 Elsevier Science Ltd. All rights reserved

Keywords: aminopyrazine fluorescent dye, self-assembling, molecular stacking, solid state spectra, vapor deposited thin film, MOPAC PM3.

INTRODUCTION

Fluorescent dyes are currently of interest in various application fields, such as emitters for electroluminescence devices [1], copy-preventing ink, solar

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energy collecting materials, fluorescent film for greenhouse and color filter, fluorescent markers and colorants for various application fields.

We have reported previously the syntheses and fluorescent properties of new fluorescent chromophores derived from diaminomalonitrile [2–4] and 2,3-dichloro-5,6-dicyanopyrazine [5–7]. Recently we also reported the syntheses and fluorescent properties of 2,5-diamino-3,6-dicyanopyrazine dyes [8]. In this paper, the parent chromophoric system of 2,5-diamino-3,6-dicyanopyrazine **1** was evaluated by the PPP MO method, and the basic chemical modifications of **1**, such as alkylation and acylation of the amino group, hydrolysis and esterification of the cyano group are reported, together with their spectral properties. Except for our recent publications few pyrazine derivatives have been described as dye chromophores, but their biological applications had been comprehensively reported by Du Pont [9]. 2,5-Diamino-3,6-dicyanopyrazine **1** has a small molecular size, but has strong fluorescence. (fluoresent quantum yield was 0.3) and shows a large Stokes' shift of 80 nm. Derivatives show wide variation of absorption and fluorescent spectra both in solution and powder state, depending on their substitutents [8].

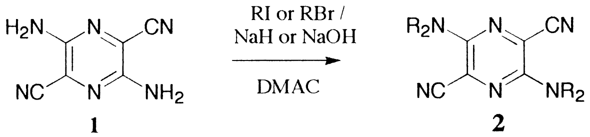
We have investigated the spectral changes of dye chromophores from solution to solid state and which are affected by molecular stacking, depending on the intermolecular $\pi-\pi$ interactions [10, 11].

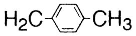
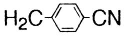
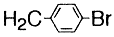
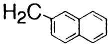
In this paper, we report the self-assembling of aminopyrazine fluorescent dyes derived from **1**, and substituent effects on their solid state spectra as evaluated on vapor deposited thin film. The optimization of the molecular structure was conducted by the MOPAC PM3 [12] method, and these results were correlated to their molecular stacking behavior.

RESULTS AND DISCUSSION

2,5-Bis(N,N-dialkylamino)-3,6-dicyanopyrazine 2

Syntheses of **2** having various N,N-dialkyl substituents were carried out by the reaction of **1** with appropriate alkyl halides in dimethylacetamide as reported in a previous paper [8] (Scheme 1). Their absorption characteristics, such as λ max in chloroform and on vapor deposited thin film, fluorescent maximum (Fmax) in solution and powder state, were evaluated to correlate to their substituent effects. The differences in λ max and Fmax from solid state to solution are indicated by $\Delta\lambda$ and , respectively. The Stokes' shift is denoted by the SS value. These results are summarized in Table 1. Dye **2a**, having N,N-dimethylamino groups, absorbed at 498 nm in chloroform but at 592 nm on the solid state. A large $\Delta\lambda$ of 94 nm was observed, which may be



No.	R	No.	R	No.	R
2a	Me	**2e**	$(CH_2)_4CH_3$	**2i**	
2b	Et	**2f**	$(CH_2)_9CH_3$	**2j**	
2c	n-Pr	**2g**	CH_2-CH=CH_2	**2k**	
2d	n-Bu	**2h**	CH_2Ph	**2l**	

Scheme 1

TABLE 1
Visible and Fluorescence Spectra of **2** in Chloroform and Solid States

No.	*λ max(nm)*		*Δλ*[b] *(nm)*	*Fmax (nm)*		*ΔF*[e] *(nm)*	*SS*[f] *(nm)*
	Solution	*Film*[a]		*Solution*[c]	*solid*[d]		
2a	498	592 (broad)	94	601	623	22	103
2b	516	553 (broad)	37	602	608	6	86
2c	520	586 (broad)	66	607	625	18	87
2d	523	562 (broad)	39	614	637	23	91
2e	512	558 (broad)	46	624	652	28	112
2f	524	523 (sharp)	−1	612	644	32	88
2g	496	531 (broad)	35	581	614	33	85
2h	491	495 (sharp)	4	588	583	−5	97
2i	492	502 (sharp)	10	590	561	−29	98
2j	464	482 (sharp)	18	569	568	−1	105
2k	485	492 (sharp)	7	576	581	5	91
2l	490	496 (sharp)	6	585	587	2	95

[a] Vapor deposited thin film.
[b] $\Delta\lambda = \lambda$ max(film)$-\lambda$ max(solution).
[c] Fmax(solution) excited at λ max(solution) value.
[d] Solid state Fmax excited at λ max(film) value.
[e] ΔF = Fmax(solid)$-$Fmax(solution).
[f] Stokes' shift.

caused by the strong intermolecular $\pi-\pi$ interactions of the pyrazine chromophore. A similar value of 89 nm in also indicates the special molecular stacking in the solid state. It is generally observed that increase of the alkyl chain length in dye **2** causes a decrease both in the $\Delta\lambda$ and values indicating the increase of steric hindrance between the N-alkyl groups, thus resulting in a consequent decrease in the intermolecular $\pi-\pi$ interactions of the pyrazine chromophore. Comparing the λ max of **2a** and **2f** in solution, an increase of 26 nm was observed from **2a**(C_1) to **2f**(C_{10}) due to the electron donating properties of the alkyl groups at the amino substituent. However, a much larger difference of 95 nm in $\Delta\lambda$ was observed between **2a** to **2f**. No difference in the $\Delta\lambda$ of **2f** indicated that none of the intermolecular $\pi-\pi$ interactions were considered in the solid state, and that the π-electron energy level of **2f** is the same as monomer state in solution.

On the other hand, the N,N-dibenzylamino derivatives(**2h**–**2k**) have serious steric hindrances between the substituents and consequently no intermolecular $\pi-\pi$ interactions were observed. They absorbed at shorter wavelength than **2a** and showed small or negative $\Delta\lambda$ and values, respectively. The additional 4-substituent at the phenyl group had not much affect on the λ max in solution, but negative values of $\Delta\lambda$ and were observed in some cases which may be due to additional electronic and steric influences on their molecular stacking in the solid state.

The absorption curves of the vapor deposited thin film were characteristic of intermolecular $\pi-\pi$ interactions; the sharp mono peak, as well as that in solution is the case of no interactions (**2f** and **2h**–**2l**), and the broad curves, indicate the contributions of interactions (**2a**–**2e** and **2g**). Dye **2g** absorbed at much shorter wavelength compared with **2c** because of the lower electron donating ability of the allyl group, but smaller $\Delta\lambda$ and values of **2g** may be due to the steric hindrance of the rigid olefinic moiety of the allyl substituent.

In the molecular level, dye **2** has the same π-system, and the observed λ max, Fmax and the SS values are generally in accord with electronic effects of the substituents, but their solid state spectra were largely affected by intermolecular $\pi-\pi$ interactions caused by the steric requirements of the substituents. Comparison of steric requirements affecting the intermolecular $\pi-\pi$ interactions of the pyrazine moiety is shown in Fig. 1 One of the optimized structures for **2a** and **2h** calculated by means of the MOPAC PM3 method, is shown, and steric requirements of the substituents can be compared between **2a** and **2h**. It is clear that **2a** has smaller methyl substituents with less steric requirements in comparison with the benzyl group of **2h**. The pyrazine moiety of **2h** cannot interact because of the steric hindrance of the tetrabenzyl moieties.

Dialkyl 2,5-diaminopyrazine-3,6-dicarboxylate 4

The synthesis of dialkyl 2,5-diaminopyrazine-3,6-dicarboxylate **4** was carried out by esterification of the carbonyl group of 2,5-diaminopyrazine-3,6-dicarboxylic acid **3** with alkylhalide in the presence of diazabicycloundecene (DBU) in dimethylacetamide [8] (Scheme 2). Visible and fluorescence spectra of dye **4** in chloroform and solid state are summarized in Table 2.

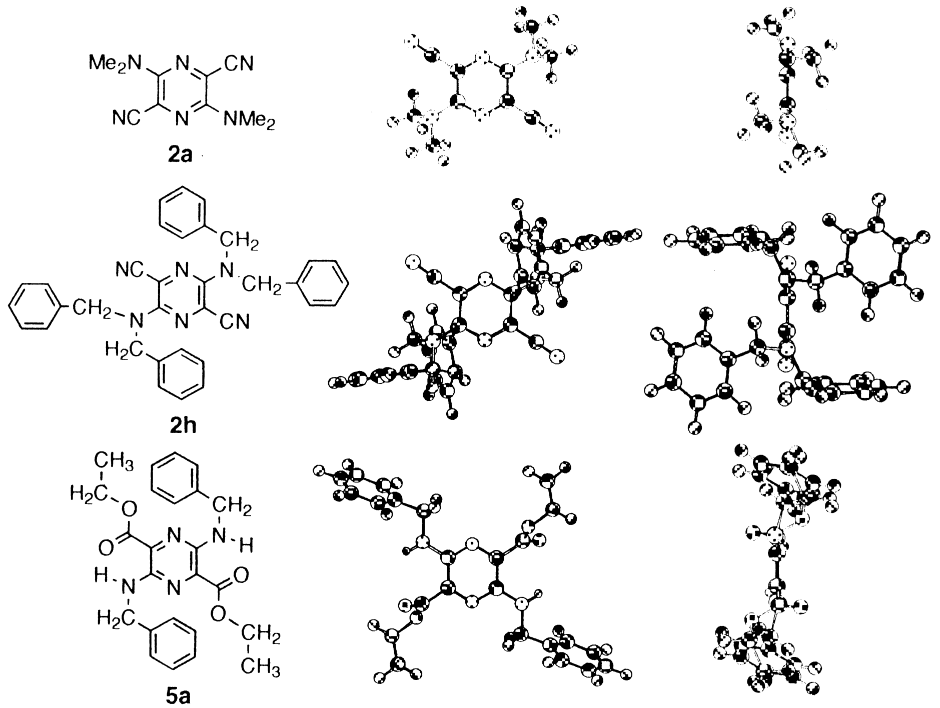
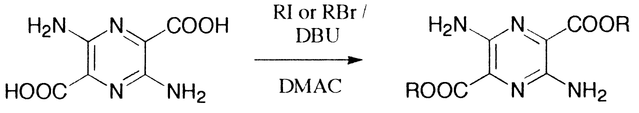
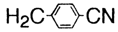
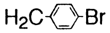
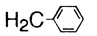
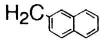
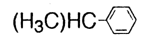
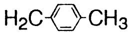


Fig. 1. One optimized structure calculated by the MOPAC PM3 method for **2a**, **2h** and **5a**.



3 **4**

NO.	R	NO.	R	NO.	R	NO.	R
4a	Me	**4f**	sec-Bu	**4k**	CH_2- $CH{=}CH_2$	**4p**	
4b	Et	**4g**	$(CH_2)_4CH_3$	**4l**	CH_2CN	**4q**	
4c	n-Pr	**4h**	$(CH_2)_9CH_3$	**4m**		**4r**	
4d	i-Pr	**4i**	$(CH_2)_4Br$	**4n**			
4e	n-Bu	**4j**	CH_2COOCH_3	**4o**			

Scheme 2

Substituent effects of the alkyl group on their λ max and Fmax were very small in solution, because these substituents did not conjugate with the parent chromophore and, as a result, did not have much affect on the electron withdrawing ability of the carboxyl groups. Small bathochromic shifts of the

TABLE 2
Visible and Fluorescence Spectra of Compound **4** in Chloroform and Solid States

No.	*λ max(nm)*		*Δλ*[b] *(nm)*	*Fmax (nm)*		*ΔF*[e] *(nm)*	*SS*[f] *(nm)*
	Solution	*Film*[a]		*Solution*[c]	*solid*[d]		
4a	461	499, 550[s]	38, 89	546	576	30	85
4b	460	522	62	546	610	64	86
4c	458	500, 523	42, 65	549	576	27	91
4d	456	483, 510[s]	27, 54	555	568	13	99
4e	457	503, 522	46, 65	546	571	25	89
4f	455	488	33	545	575	30	90
4g	459	494, 525[s]	35, 66	553	572	19	94
4h	461	487, 535[s]	26, 74	546	571	25	85
4i	458	494, 520[s]	36, 62	546	576	30	88
4j	470	527	57	574	613	39	104
4k	463	508, 530[s]	45, 67	553	603	50	90
4l	475	497, 540[s]	22, 65	594	605	11	119
4m	462	507, 550[s]	45, 88	548	609	61	86
4n	460	484	24	554	570	16	94
4o	464	490, 545[s]	26, 81	574	616	42	110
4p	470	450[s], 500	−20, 30	581	615	34	105
4q	466	519, 550[s]	53, 84	561	630	69	95
4r	467	430[d], 508, 550[s]	−37, 41, 83	578	598	20	111

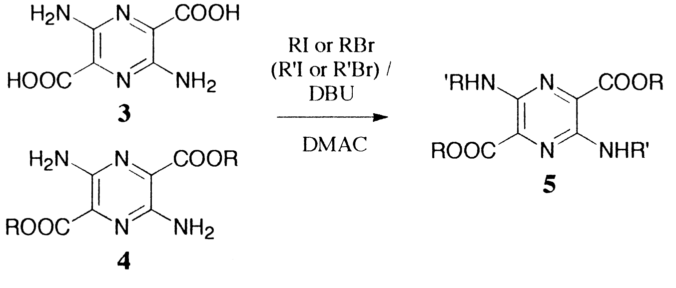
[a] Vapor deposited thin film.
[b] $\Delta\lambda = \lambda$ max(film)$-\lambda$ max(solution).
[c] Fmax(solution) excited at λ max(solution) value.
[d] Solid state Fmax excited at λ max(film) value.
[e] ΔF = Fmax(solid)$-$Fmax(solution).
[f] Stokes' shift.
[s] Shoulder.

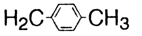
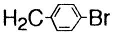
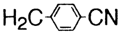
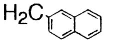
λ max of **4j**, **4l** and **4p** in comparison with that of **4a** may be due to the additional negative inductive effect of the cyano (**4l** and **4p**) and of the methoxycarbonyl group (**4j**), respectively. The Fmax and SS values of these dyes in solution were also not much affected much by the substituents, because the pyrazine chromophore was isolated from the electronic and steric effects of the substituents. These results are reasonable from their chemical structure.

On the other hand, the solid state spectra were very much affected by the substituents, as indicated by the $\Delta\lambda$ and values. Dyes **4a**–**4r** showed a single absorption peak at around 460–470 nm in solution, but either split peaks or a single peak with a shoulder were generally observed on the vapor deposited thin film. These results indicate that there are some aggregates or crystal morphologies in the solid state. Almost all dyes **4**, except **4b**, **4f**, **4j** and **4n**, have two $\Delta\lambda$ values of 20–50 nm and 60–90 nm depending on the substituents, but in general, these values did not vary much with the nature of the substituents. The molecular structure of dye **4** showed that substituent R did not have much on the coplanarity of the parent chromophore. From these results of solid state absorption spectra, the longer wavelength absorption (larger $\Delta\lambda$) is due to stronger molecular stacking, and shorter absorption (smaller $\Delta\lambda$) due to weaker interactions. Exceptionally, dyes **4p** and **4r** showed very short wavelength absorption spectra at around 430–450 nm as a shoulder peak, which may due to the large steric hindrances between the substituents; Coplanarity of the parent chromophore is partially lost in the molecular stacking. In contrast, Fmax showed a single peak both in solution and solid state, and values are generally smaller than $\Delta\lambda$ values. The fluorescence is emitted from the lowest excited energy level and only a single peak is thus observed. The Stokes' shift of dyes **4a**–**4r** are also quite large, of 85–120 nm, which was related to the intermolecular charge-transfer chromophoric system as well as the case of **2**.

Dialkyl 2,5-bis(N-ethylamino)pyrazine-3,6-dicarboxylate 5

Two synthetic routes were applied for the preparation of **5**; viz., direct N-alkylation, accompanying esterification of the carbonyl group of **3**, and N-alkylation of the ester **4** (Scheme 3). Visible and fluorescence spectra of **5** are summarized in Table 3. The λ max value of **5** in solution showed a bathochromic shift of around 50–60 nm, and Fmax shifts to longer wavelength of



No.	R	R'	No.	R = R'	No.	R = R'
5a	Et	CH_2Ph	**5e**	Et	**5j**	
5b	n-Pr	CH_2Ph	**5f**	n-Bu	**5k**	
5c	i-Pr	CH_2Ph	**5g**	$(CH_2)_4CH_3$	**5l**	
5d	CH_2COOCH_3	CH_2Ph	**5h**	CH_2- $CH=CH_2$	**5m**	
			5i	CH_2Ph		

Scheme 3

TABLE 3
Visible and Fluorescence Spectra of **5** in Chloroform and Solid States

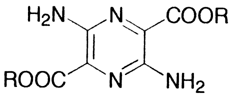
No.	*λ max(nm)*		*Δλ[b] (nm)*	*Fmax (nm)*		*ΔF[e] (nm)*	*SS[f] (nm)*
	Solution	*Film[a]*		*Solution[c]*	*solid[d]*		
5a	505	530, 555	25, 50	604	620	16	99
5b	505	515[s], 550	10, 45	600	592	−8	95
5c	500	529	29	598	586	−12	98
5d	522	525[s], 583	3, 61	613	626	13	91
5e	512	504, 550[s]	−8, 38	614	629	15	102
5f	517	495, 555[s]	−22, 38	624	643	19	107
5g	518	514, 550[s]	−4, 32	627	671	44	109
5h	508	516, 555[s]	8, 47	607	615	8	99
5i	511	505, 531	−6, 20	607	591	−16	96
5j	513	500, 528	−13, 15	609	571	−38	96
5k	508	458, 540[s], 570	−50, 32, 62	601	614	13	93
5l	502	435[d], 500	−67, −2	596	595	−1	94
5m	509	455[d], 501, 525[s]	−54, −8, 16	607	585	−22	98

[a] Vapor deposited thin film.
[b] $\Delta\lambda = \lambda$ max(film)$-\lambda$ max(solution).
[c] Fmax(solution) excited at λ max(solution) value.
[d] Solid state Fmax excited at λ max(film) value.
[e] ΔF = Fmax(solid)−Fmax(solution).
[f] Stokes' shift.
[s] Shoulder

60–80 nm relative to the corresponding ester **4** due to increase of the donor properties of the alkylamino groups. There were only very small differences in the λ max in solution depending on the substituents, but quite large differences of λ max were observed in the solid state. Band splitting was generally observed except for **4b**, **4f**, **4j** and **4n**. In the case of **4p** and **4r**, another peak was observed at around 450 nm (**4p**) and 430 nm (**4r**). These results indicated that there are some crystal morphologies or aggregates on the vapor deposited thin film.

Typical examples of the additional substituent effect (Δ) of R′ on their λ max and Fmax are summarized in Table 4. Large differences of Δ values from solution to solid state were observed. As indicated before, the Δ values in solution were reasonably in accord with the electronic effects of the substituent, but those in solid state were changed one by one, affected by the steric requirements of the substituents. These results indicate that some special molecular stacking affected the λ max and Fmax values. Negative, and rather small Δ values in λ max in the solid state compared with those in solution are due to steric hindrance between neighboring substituents. The MOPAC PM3 calculation results also indicated some steric hindrance between R and R′ which prevented intermolecular $\pi-\pi$ interactions of the pyrazine chromophore (Fig. 1).

TABLE 4
Additional Substituent Effects (Δ) of R′ on their λ max and Fmax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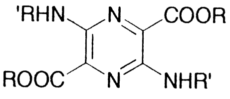
5

No.	*R*	*R′*	*λmax*	*Fmax*	*SSsolution*	*λ max*	*Fmax*	*SSsolid*
4b	Et	H	460	546	86	522	610	88
5e	Et	Et	512	614	102	504	629	125
Δ			52	68	16	−18	19	37
4e	n-Bu	H	457	546	89	522	571	49
5f	n-Bu	n-Bu	517	624	107	495	643	148
Δ			60	78	18	−27	72	99
4m	Bz	H	462	548	86	507	609	102
5i	Bz	Bz	511	607	96	505	591	86
Δ			49	59	10	−2	−18	−16

Bz: benzyl.

EXPERIMENTAL

Materials and equipment

Melting points were determined with a Yanagimoto micro melting point apparatus and are uncorrected. Preparative thin layer chromatography(TLC) was performed on Merck silica get 60 F_{254} plate(1 mm layer thickness). IR spectra were recorded on a Nicolet FT/IR Impact 400D spectrophotometer. ^{1}H NMR spectra were obtained with a FT-NMR QE 300 MHz Shimadzu spectromer. UV-Vis spectra were measured with a Hitachi U-3410 spectrophotometer. Solid state fluorescence spectra were obtained with a Hamamatsu photonic multi-channel analyzer PMA-11 using a Jasco SM-3 type monochrometer as a light source. Preparation of vapor deposited thin film of dyes was performed with a Nippon Shinku Kikou VSP-060 apparatus. Microanalyses were performed with a Yanaco CHN MT-3 elemental analyzer. The mass spectra were obtained with M-80 B Hitachi and Shimadzu GCMS-5000 mass spectrometers. N,N-Dimethylacetamide(DMAC) was stored over 4 Å molecular sieves. All reagents were used without further purification. 2,5-Diamino-3,6-dicyanopyrazine was supplied from Nippon Soda Co. Ltd.

General procedure for 2,5-bis(N,N-dialkylamino)-3,6-dicyanopyrazines 2

To a mixture of 2,5-diamino-3,6-dicyanopyrazine **1**(1.88 mmol) an alkyl iodide(**2a**–**2g**) or alkyl bromide(**2h**–**2l**) (**2a**, **2b**: 30 mmol; **2e**: 25 mmol; **2d**–**e**:

20 mmol; **2g**–**2l**: 12 mmol) in dimethylacetamide was slowly added with a base(powered sodium hydroxide 12 mmol for **2a**–**2c** or sodium hydride 7.5 mmol for **2d**–**2l**) at 5°C and the reaction was carried out at 5–20°C for 1–3 h. After completion of the reaction (TLC), water (60 ml) was added to the reaction mixture and the liquor was extracted with ethyl acetate. The extract was evaporated to give a residue which was purified by prep. TLC using benzene or benzene–hexane mixture as eluent. Compounds **2a**, **2d**, **2g** and **2**h have been previously described [8].

2,5-Bis(N,N-diethylamino)-3,6-dicyanopyrazine 2b
Red solid; 22%; mp: 50–51°C; δ_H(CDCl$_3$) 3.54(8H, q, *J*7.1), 1.23 (12H, t, *J* 7.1); ν cm^{-1} (KBr)2978, 2216, 1515, 1444, 1221, 791; EA, Calcd.: $C_{14}H_{20}N_6$(C, 61.76; H, 7.35; N, 30.88) Found: (C, 61.94; H, 7.40; N, 30.27); Mass, m/z(M$^+$): 272.

2,5-Bis(N,N-di-n-propylamino)-3,6-dicyanopyrazine 2c
Red solid; 13%; mp: 81–82°C; δ_H(CDCl$_3$) 3.43(8H, t, *J* 7.8), 1.64(8H, sixt, *J* 7.4), 0.92(12H, t, *J* 7.4); ν cm^{-1}(KBr)2967, 2211, 1515, 1444, 1216, 993; EA, Calcd.: $C_{18}H_{28}N_6$(C, 65.85; H, 8.54; N, 25.61) Found: (C, 66.08; H, 8.57 N, 25.37); Mass, m/z(M$^+$): 328.

2,5-Bis(N,N-di-n-pentylamino)-3,6-dicyanopyrazine 2e
Red liquid; 9%; δ_H(CDCl$_3$) 3.45(8H, t, *J* 7.7), 1.60(8H, quint, *J* 7.4), 1.39–1.26(16H, m), 0.90(12H, t, *J* 6.9); ν cm^{-1} (Neat)2956, 2216, 1515, 1466, 1216, 966; Mass, m/z(M$^+$): 440.

2,5-Bis(N,N-di-n-dodecylamino)-3,6-dicyanopyrazine 2f
Red liquid; 6%; δ_H(CDCl$_3$) 3.45(8H, t, *J* 7.7), 1.59–1.26(64H, m), 0.87(12H, t, *J* 6.6); ν cm^{-1} (Neat)2923, 2227, 1509, 1471, 1216, 97t; Mass, m/z(M$^+$): 720.

2,5-Bis[N,N-di-(4-methylphenyl)methylamino]-3,6-dicyanopyrazine 2i
Orange solid; 11%; mp: 154–155°C; δ_H (CDCl$_3$)7.13(8H, d, *J* 8.7), 7.10(8H, d, *J* 8.4), 4.67(SH, s), 2.34(12H, s); ν cm^{-1}(KBr)2855, 2227, 1477, 1422, 1112, 808; EA, Calcd.: $C_{38}H_{36}N_6$, (C, 79.17; H, 6.25; N, 14.58) Found: (C, 79.22; H, 6.36; N, 14.61); Mass, m/z(M$^+$): 576

2,5-Bis[N,N-di-(4-cyanophenyl)methylamino]-3,6-dicyanopyrazine 2j
Scarlet solid; 17%; mp: 293–296°C; δ_H (DMSO-d_6)7.87(8H, d, *J* 8.1), 7.45(8H, d, *J* 8.1), 4.81(8H, s); ν cm^{-1}(KBr)2923, 2222, 1509, 1232, 949, 824; EA, Calcd.: $C_{38}H_{24}N_{10}$ (C, 73.55; H, 3.87; N, 22.58) Found: (C, 73.43; H, 4.14; N, 21.14); Mass, m/z(M$^+$): 620.

2,5-Bis[N,N-di-(4-bromophenyl)methylamino]-3,6-dicyanopyrazine 2k.
Yellow solid; 10%; mp: 207–208°C; δ_H ($CDCl_3$)7.46(8H, d, *J* 8.4), 7.09(8H, d, *J* 8.4), 4.65(8H, s); ν cm^{-1}(KBr)2890, 2233, 1482, 1352, 1123, 819; EA, Calcd.: $C_{34}H_{24}N_6Br_4$ (C, 48.80; H, 2.87; N, 10.05) Found: (C, 48.88; H, 3.04; N, 9.76); Mass, m/z(M^+): 836.

2,5-Bis[N,N-di-(2-naphthyl)methylamino]-3,6-dicyanopyrazine 2l.
Orange solid; 28%; mp: 203–206°C; δ_H($CDCl_3$)7.85–7.33(28H, m), 4.95(8H,s); ν cm^{-1} (KBr)3054, 2858, 2227, 1477, 1368, 819; EA, Calcd.: $C_{50}H_{36}N_6$ (C, 83.33; H, 5.00; N, 11.67) Found: (C, 82.27; H, 5.06; N, 11.64); Mass, m/z(M^+): 720.

Preparation of 2,5-diaminopyrazine-3,6-dicarboxylic acid 3

To a mixture of the 2,5-diamino-3,6-dicyanopyrazine **1** (3.2 g, 0.02mole) and NaOH(3.2 g, 0.08 mole) in 40% aq. EtOH (250 ml), 30% $H_2O_2$40 ml was added dropwise at r.t. The resultant mixture was refluxed for 2.5 h, after which it was filtered hot and the residue washed with water to give an orange solid, 2,5-diaminopyrazine-3,6-dicarboxamide (2.5 g, 63.8%). mp: >300°C; δ_H(DMSO-*d*,): 7.73(2H, s, br), 7.67(2H, s, br), 6.48(4H, s, br); Mass, m/z(M^+): 196; EA, Calcd.: $C_6H_8N_6O_2$ (C, 36.73; H, 4.08; N, 42.86) Found: (C,36.96; H,4.11; N,42.57); ν cm^{-1} (KBr) 3440, 3380, 3320, 1689, 1580, 1227, 710.

The 2,5-diaminopyrazine-3,6-dicarboxamide (2.05 g, 0.01 mole) thus obtained was heated at reflux in 8% aq. NaOH (50 ml) for 6 h. Then 100 ml water was then added to the reaction mixture which was then refluxed for 1 h. The solution was filtered and acidified with conc. HCl 12 ml. The precipitated solid was filtered, washed with water and dried to give a red solid **3**(2.0 g, 97%). mp: >300°C; Mass, m/z(M^+):198; EA, Calcd.: $C_6H_6N_4O_4$(C, 36.36;H, 3.03; N, 28.28) Found: (C, 36.58; H, 3.22; N, 28.10); ν cm^{-1} (KBr) 3429, 3331, 3021, 1618, 1227, 759.

General procedure for dialkyl 2,5-diaminopyrazine-3,6-dicarboxylates 4

To a stirred solution of 2,5-diaminopyrazine-3,6-dicarboxylic acid **3** (0.51 mmol) and diazabicycloundecene(DBU) (1.32 mmol) in dimethylacetamide(DMAC) 7 ml was added the appropriate alkyl halide(2.50 mmol). The reaction was then continued at room temperature for 0.5–2.5 h for **4a**, **4c**, **4e**, **4g**, **4k**–**4m** and **4p**–**4r**, and 40–70°C for 0.5–2 h for **4b**, **4d**, **4f**, **4h**–**4j** and **4o**. The reaction mixture was poured into saturated aq. $NaHCO_3$ (60 ml) and the precipitate which separated was collected, washed with water and small amounts of methanol, and the dried to give **4**. Compounds **4b**, **4d** have been previously reported [8].

Dimethyl 2,5-diaminopyrazine-3,6-dicarboxylate 4a
Red solid; 18%; mp: 247–250°C; δ_H(CDCl$_3$) 5.94(4H, s, br), 3.99(6H, s); ν cm^{-1}(KBr)3473, 3298, 1694, 1596, 1194, 802; EA, Calcd.: $C_8H_{10}N_4O_4$(C, 42.48; H, 4.42; N,24.78) Found: (C, 42.63; H, 4.45; N, 23.80); Mass, m/z(M$^+$): 226.

Di-n-propyl 2,5-diaminopyrazine-3,6-dicarboxylate 4c
Scarlet solid; 21%; mp: 184–185°C; δ_H(CDCl$_3$)5.89(4H,s,br), 4.35(4H,t,*J* 7.1),1.83(4H, sixt, *J*7.2), 1.01(6H,t,*J* 7.4); ν cm^{-1}(KBr)3462, 3304, 1689, 1602, 1134, 802; EA, Calcd.: $C_{12}H_{18}N_4O_4$(C, 51.06; H, 6.38; N, 19.86) Found: (C, 50.84; H, 6.32; N, 19.62); Mass, m/z(M$^+$): 282.

Di-n-butyl 2,5-diaminopyrazine-3,6-dicarboxylate 4e
Scarlet solid; 45%; mp: 186–187°C; δ_H(CDCl$_3$) 5.91(4H, s, br), 4.37(4H, t, *J* 6.9), 1.78(4H, sixt, *J* 7.2), 1.44(4H, quint, *J* 7.5), 0.95(6H, t, *J* 7.4); ν cm^{-1} (KBr)3462, 3304, 1689, 1591, 1129, 792; EA, Calcd.: $C_{14}H_{22}N_4O_4$(C, 54.19; H, 7.10; N, 18.06) Found: (C, 53.91; H, 6.44; N, 18.11); Mass, m/z(M$^+$): 310.

Di-sec-butyl 2,5-diaminopyrazine-3,6-dicarboxylate 4f
Scarlet solid; 77%; mp: 136–137°C; δ_H(CDCl$_3$) 5.86(4H, s, br), 5.09(2H, sixt, *J* 6.4), 1.79(4H, m), 1.37(6H, d, *J* 6.3), 0.97(6H, t, *J* 7.4); ν cm^{-1} (KBr)3467, 3309, 1689, 1596, 1140, 802; EA, Calcd.: $C_{14}H_{22}N_4O_4$(C, 54.19; H, 7.10; N, 18.06) Found: (C, 53.84; H, 6.99; N, 17.74); Mass, m/z(M$^+$): 310.

Di-n-pentyl 2,5-diaminopyrazine-3,6-dicarboxylate 4g
Scarlet solid; 41%; mp: 185–188°C; δ_H(CDCl$_3$) 5.91(4H, s, br), 4.37(4H, t, *J* 7.1), 1.80(4H, m), 1.40–1.36(8H, m), 0.91(6H,t,*J*7.1); ν cm^{-1} (KBr)3462, 3304, 1694, 1596, 1140, 802;EA, Calcd.:$C_{16}H_{26}N_4O_4$(C, 56.80; H, 7.69; N, 16.57) Found: (C, 56.84; H, 7.63 ; N, 16.44); Mass, m/z(M$^+$): 338.

Di-n-dodecyl 2,5-diaminopyrazine-3,6-dicarboxylate 4h
Scarlet solid; 84%; mp: 174–175°C; δ_H(CDCl$_3$) 5.90(4H, s, br), 4.38(4H, t, *J* 6.9), 1.80(4H, quint, *J* 7.1), 1.26(28H, m), 0.88(6H, t, *J* 6.6); ν cm^{-1} (KBr)3473, 3326, 2918, 1694, 1596, 1129; EA, Calcd.: $C_{26}H_{46}N_4O_4$(C, 65.27; H, 9.62; N, 11.72) Found: (C, 65.18; H, 9.80; N, 11.50); Mass, m/z(M$^+$): 478.

Bis(4-bromobutyl) 2,5-diaminopyrazine-3,6-dicarboxylate 4i
Scarlet solid; 47%; mp: 204–206°C; δ_H(CDCl$_3$) 5.89(4H, s, br), 4.42(4H, t, *J* 6.3), 3.49(4H, t, *J* 6.3), 2.00(8H, m); ν cm^{-1} (KBr)3456, 3298, 1689, 1590, 1140, 645; EA, Calcd.: $C_{14}H_{20}N_4O_4Br_2$(C, 35.90; H, 4.27; N, 11.96) Found: (C, 36.50; H, 4.31; N, 11.82); Mass, m/z(M$^+$): 468.

Bis(methoxycarbonylmethyl) 2,5-diaminopyrazine-3,6-dicarboxylate 4j
Red solid; 59%; mp: 241–242°C; δ_H(CDCl$_3$) 5.94(4H, s, br), 4.91(4H, s), 3.80(6H, s); ν cm^{-1} (KBr)3467, 3309, 1754, 1705, 1601, 1129; EA, Calcd.: $C_{12}H_{14}N_4O_4$(C,42.10; H, 4.09; N, 16.37) Found:(C, 42.86; H, 4.34; N, 15.64); Mass, m/z(M$^+$): 342.

Diallyl 2,5-diaminopyrazine-3,6-dicarboxylate 4k
Red solid; 21%; mp: 160–163°C; δ_H(CDCl$_3$) 6.05(2H, ddt, *J* 17.4, 10.4, 5.7), 5.91(4H, s, br), 5.43(2H, ddt, *J* 10.5, 2.7, 1.2), 5.32(2H, ddt, *J* 17.1, 2.4, 1.2), 4.89(4H, ddd, *J* 5.7, 1.2, 1.2); ν cm^{-1}(KBr)3473, 3309, 1700, 1596, 1134, 802; EA, Calcd.: $C_{12}H_{14}N_4O_4$(C, 51.80; H, 5.04; N, 20.14) Found: (C, 52.19 H,5.02; N, 19.60); Mass, m/z(M$^+$): 278.

Dicyanomethyl 2,5-diaminopyrazine-3,6-dicarboxylate 4l
Red solid; 58%; mp: 250–251°C; δ_H(DMSO-*d*$_6$) 6.66(4H, s, br), 5.18(4H, s); ν cm^{-1}(KBr)3470, 3358, 2265, 1726, 1614, 1130; EA, Calcd.: $C_{10}H_8N_6O_4$(C, 43.48; H, 2.90; N, 30.43) Found: (C, 43.89; H, 3.01; N, 30.04); Mass, m/z(M$^+$): 276.

Dibenzyl 2,5-diaminopyrazine-3,6-dicarboxylate 4m
Red solid; 58%; mp: 229–230°C; δ_H(CDCl$_3$) 7.46–7.35(10H, m), 5.88(4H, s, br), 5.41(4H, s); ν cm^{-1}(KBr)3473, 3288, 1694, 1602, 1134, 699; EA, Calcd.: $C_{20}H_{18}N_4O_4$(C,63.49; H,4.76; N, 14.8 1) Found: (C, 62.81; H, 4.78; N, 14.75); Mass, m/z(M$^+$): 378.

Bis(1-phenylethyl) 2,5-diaminopyrazine-3,6-dicarboxylate 4n
Scarlet solid; 39%; mp: 198–200°C; δ_H(CDCl$_3$) 7.46–7.25(10H, m), 6.10(2H, q, *J* 6.6), 5.83(4H, s, br), 1.70(6H, d, *J* 6.6); ν cm^{-1} (KBr)3451, 3320, 1694, 1602, 1129, 699; EA, Calcd.: $C_{22}H_{22}N_4O_4$(C,65.02; H, 5.42; N, 13.79) Found: (C, 64.89; H, 5.46; N, 13.68); Mass, m/z(M$^+$): 406.

Bis(4-methylphenylmethyl) 2,5-diaminopyrazine-3,6-dicarboxylate 4o
Red solid; 49%; mp: 232–233°C; δ_H(CDCl$_3$) 7.35(4H, d, *J*7.8),7.17(4H, d, *J*7.8), 5.85(4H, s, br), 5.38(4H, s), 2.34(6H, s); ν cm^{-1}(KBr)3467, 3288, 1694, 1601, 1134, 808; EA, Calcd.: $C_{22}H_{22}N_4O_4$(C, 65.02; H, 5.42; N, 13.79) Found: (C, 64.01; H, 5.39; N, 13.93); Mass, m/z(M$^+$): 406.

Bis(4-cyanophenylmethyl) 2,5-diaminopyrazine-3,6-dicarboxylate 4p
Red solid; 70%; mp: 286–287°C; δ_H(DMSO-*d*$_6$) 7.84(4H, d, *J* 8.4), 7.61(4H, d, *J* 8.1), 6.57(4H, s, br), 5.40(4H, s); ν cm^{-1}(KBr)3478, 3309, 2238, 1710, 1601, 1129; EA, Calcd.: $C_{22}H_{16}N_6O_4$(C, 61.68; H, 3.74; N, 19.63) Found: (C, 60.96; H, 4.03; N, 19.14); Mass, m/z(M$^+$): 428.

Bis(4-bromophenylmethyl) 2,5-diaminopyrazine-3,6-dicarboxylate 4q
Red solid; 37%; mp: 24.8–252°C; δ_H(CDCl$_3$) 7.50(4H, d, *J* 8.4), 7.33(4H, d, *J* 8.4), 5.87(4H, s, br), 5.36(4H, s); ν cm^{-1}(KBr)3462, 3320, 1705, 1602, 1129, 808; EA, Calcd.: $C_{20}H_{16}N_4O_4Br_2$(C, 44.78; H, 2.99; N, 10.45) Found: (C, 45.47; H, 3.38; N, 10.11); Mass, m/z(M$^+$): 536.

Bis(2-naphthylmethyl) 2,5-diaminopyrazine-3,6-dicarboxylate 4r
Red solid; 54%; mp: 259–260°C; δ_H(DMSO-d_6) 7.97–7.88(6H, m), 7.56–7.49(8H, m), 6.57(4H, s, br), 5.47(4H, s); ν cm^{-1}(KBr)3478, 3293, 1700, 1596, 1129, 759; EA, Calcd.: $C_{28}H_{22}N_4O_4$(C, 70.29; H, 4.60; N, 11.72) Found: (C, 70.67; H, 4.71; N, 11.28); Mass, m/z(M$^+$): 478.

General procedure for alkyl N-alkyl aminopyrazine carboxylates 5

A solution of the aminopyrazine carboxylic acid **3**(0.51 mmol: for **5e**–**m**) or alkylamino-pyrazine carboxylate **4**(0.51 mmol) in DMAC 7 ml was treated with DBU(2.64 mmol) and the appropriate alkyl halide(4–5 mmol). Reaction was then continued at 70–120°C for 2–3.5 r. The reaction mixture was poured into water(60 ml) and extracted with ethyl acetate. The resultant ethyl acetate extract was evaporated, and the residue purified by prep. TLC. using ethyl acetate or ethyl acetate–hexane mixture as eluent. Compound **5e** has been previously reported [8].

Diethyl 2,5-bis(N-benzylamino)pyrazine-3,6-dicarboxylate 5a
Red solid; 3%; mp: 114–115°C; δ_H(CDCl$_3$) 7.57(2H, t, br, *J* 5.7), 7.45–7.23(10H, m), 4.63(4H, d, *J* 6.0), 4.38(4H,q,*J*6.0),1.43(6H,t,*J*7.2); ν cm^{-1}(KBr) 3400, 2982, 1686, 1536, 1150, 727; EA, Calcd.: $C_{24}H_{26}N_4O_4$(C, 66.36; H, 5.99; N, 12.90) Found: (C, 66.38; H, 5.96; N, 12.68); Mass, m/z(M$^+$): 434.

Di-n-propyl 2,5-bis(benzylamino)pyrazine-3,6-dicarboxylate 5b
Red solid; 14%; mp: 123–124°C; δ_H(CDCl$_3$) 7.55(2H, t, br, *J* 5.9), 7.44–7.22(10H, m), 4.63(4H, d, *J* 6.0), 4.27(4H, t, *J* 6.6), 1.81(4H, sixt, *J* 7.1), 1.02(6H, t, *J* 7.5); ν cm^{-1}(KBr)3402, 2967, 1689, 1531, 1156, 694; EA, Calcd.: $C_{26}H_{30}N_4O_4$(C, 67.53; H, 6.49; N, 12.12) Found: (C, 67.37; H, 6.56; N, 11.98); Mass, m/z(M$^+$): 462.

Di-i-propyl 2,5-bis(benzylamino)pyrazine-3,6-dicarboxylate 5c
Scarlet solid; 7%; mp: 108–113°C; δ_H(CDCl$_3$)7.56(2H,t,*J*5.7), 7.47–7.18(10H, m),5.20(2H,sept,*J*6.2), 4.60(4H, d, *J* 6.0), 1.40(12H, d, *J* 6.3); δ cm^{-1}(KBr)3402, 2972, 1694, 1531, 1167, 699; EA, Calcd.:$C_{26}H_{30}N_4O_4$(C, 67.53; H, 6.49; N, 12.12) Found: (C, 67.58; H, 6.50; N, 11.98); Mass, m/z(M$^+$): 462.

Di(methoxycarbonylmethyl) 2,5-bis(benzylamino)pyrazine-3,6-dicarboxylate 5d
Red–violet solid; 7%; mp: 151–153°C; δ_H(CDCl$_3$)7.43–7.23(12H, m), 4.86(4H, s), 4.66(4H, d, *J* 5.7), 3.79(6H, s); ν cm^{-1}(KBr)3413, 1759, 1700, 1531, 1140, 726; EA, Calcd.: $C_{26}H_{26}N_4O_8$(C, 59.77; H, 4.98; N, 10.73) Found: (C, 59.93; H, 4.99; N, 10.27); Mass, m/z(M$^+$): 522.

Di-n-butyl 2,5-bis(n-butylamino)pyrazine-3,6-dicarboxylate 5f
Red solid; 28%; mp: 90–91°C; δ $_H$(CDCl$_3$) 7.08(2H, t, br), 4.31(4H, t, *J* 6.5), 3.44(4H, m), 1.77(4H, m), 1.68–1.37(12H, m), 0.98(6H, t, *J* 7.4), 0.94(6H, t, *J* 7.4); ν cm^{-1}(KBr)3366, 2958, 1684, 1534, 1152, 808; EA, Calcd.: $C_{22}H_{38}N_4O_4$(C, 62.56; H, 9.00; N, 13.27) Found: (C, 61.86; H, 8.88; N, 13.41); Mass, m/z(M$^+$): 422.

Di-n-pentyl 2,5-bis(n-pentylamino)pyrazine-3,6-dicarboxylate 5g
Red–Violet solid; 25%; mp: 80–81°C; δ_H(CDCl$_3$)7.07(2H,t,br,*J*5.6), 4.30(4H,t,J6.5), 3.43(4H,q,*J*6.8), 1.79(4H, quint, *J* 6.9), 1.62(4H, m) 1.49–1.34(16H, m), 0.94–0.87(12H, tt, *J* 6.8, 6.8); ν cm^{-1}(KBr)3364, 2929, 1683, 1531, 1150, 585; EA, Calcd.: $C_{26}H_{46}N_4O_4$,(C, 65.27; H, 9.62; N, 11.72) Found: (C, 65.14; H, 9.58; N, 11.72); Mass, m/z(M$^+$): 478.

Diallyl 2,5-bis(allylamino)pyrazine-3,6-dicarboxylate 5h
Red solid; 17%; mp: 118–119°C; δ_H(CDCl$_3$) 7.21(2H, t, br, *J* 5.6), 6.10–5.91(4H, m), 5.48(2H, ddt, *J* 17.1, 3.0, 1.5), 5.30(2H, ddt, *J* 17.0, 3.4, 1.5) 5.26(2H, ddt, *J* 10.2, 2.9, 1.5), 5.12(2H, ddt, *J* 10.2, 2.9, 1.5), 4.83(4H, ddd, *J* 5.4, 1.5, 1.5), 4.11(4H, ddd, *J* 5.7, 5.7, 1.5); ν cm^{-1}(KBr)3386, 2869, 1694, 1531, 1156, 917; EA, Calcd.: $C_{18}H_{22}N_4O_4$(C, 60.34; H, 6.15; N, 15.64) Found: (C,60.13; H, 6.15; N, 15.54); Mass, m/z(M$^+$): 358.

Dibenzyl 2,5-bis(benzylamino)pyrazine-3,6-dicarboxylate 5i
Scarlet solid; 7%; mp: 134–135°C; δ_H(CDCl$_3$) 7.5.5(2H, t, br, *J* 5.9), 7.44–7.18(20H, m), 5.36(4H, s), 4.61(4H, d, *J* 5.7); ν cm^{-1}(KBr)3404, 3022, 1684, 1523, 1158, 728; EA, Calcd.: $C_{34}H_{30}N_4O_4$(C, 73.12; H, 5.38; N, 10.04) Found: (C, 72.61; H, 5.45; N, 9.91); Mass, m/z(M$^+$): 558.

Bis(4-methylphenylmethyl) 2,5-bis(4-methylphenylmethylamino)pyrazine-3,6-dicarboxylate 5j
Red solid; 10%; mp: 154–155°C; δ_H(CDCl$_3$) 7.49(2H, t, br, *J* 5.9), 7.33 (4H, d, *J* 8.1), 7.24(4H, d, *J* 7.5), 7.17(4H, d, *J* 7.8), 7.00(4H, d, *J* 7.8), 5.32(4H, s), 4.54(4H,d,*J*6.0),2.36(6H,s),2.30(6R,s); ν cm^{-1}(KBr)3407, 2956, 1694, 1531, 1156, 802; EA, Calcd.: $C_{38}H_{38}N_4O_4$(C, 74.27; H, 6.19; N, 9.12) Found: (C, 73.98; H, 6.18; N, 9.06); Mass, m/z(M$^+$): 614.

Bis(4-bromophenylmethyl) 2,5-bis(4-bromophenylmethylamino)pyrazine-3,6-dicarboxylate 5k

Red solid; 6%; mp: 184–185°C; $\delta_{\mathrm{H}}(\mathrm{CDCl_3})$ 7.55(2H, t, br), 7.50(4H, d, J 8.4), 7.30(4H, d, J 8.4), 7.26(4H, d, J 8.4), 7.19(4H, d, J 8.7), 5.28(4H, s), 4.53(4H, d, J 6.0); ν cm^{-1}(KBr)3396, 2929, 1700, 1520, 1161, 802; EA, Calcd.: $\mathrm{C_{34}N_{26}N_4O_4Br_4}$(C, 46.68; H, 2.97; N, 6.41) Found: (C, 46.71; H, 3.01; N, 6.38); Mass, m/z(M$^+$): 874.

Bis(4-cyanophenylmethyl) 2,5-bis(4-cyanophenylmethylamino)pyrazine-3,6-dicarboxylate 5l

Scarlet solid; 18%; mp: 244–245°C; $\delta_{\mathrm{H}}(\mathrm{CDCl_3})$ 7.67(6H, d, J 8.1), 7.51(4H, d, J 8.1), 7.47(4H, d, J 8.1), 7.42(4H, d, J 8.1), 5.37(4H, s), 4.76(4H, d, J 6.0); ν cm^{-1}(KBr)3386, 2233, 1700, 1531, 1156, 824; EA, Calcd.: $\mathrm{C_{38}H_{26}N_8O_4}$(C, 69.30; H, 3.95; N, 17.02) Found: (C, 68.74; H, 4.03; N, 16.88); Mass, m/z(M$^+$): 658.

Bis(2-naphthylmethyl) 2,5-bis(2-naphthylmethylamino)pyrazine-3,6-dicarboxylate 5m

Red solid; 16%; mp: 214–217°C; $\delta_{\mathrm{H}}(\mathrm{CDCl_3})$7.90–7.27(30H, m), 5.53(4H, s), 4.81(4H, d, J 5.7); ν cm^{-1}(KBr)3418, 2940, 1683, 1526, 1161, 824; EA, Calcd.: $\mathrm{C_{50}OH_{38}N_4O_4}$(C, 79.16; H, 5.01; N, 7.39) Found: (C, 78.47; H, 5.05; N, 7.33); Mass, m/z(M$^+$): 758.

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