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Dicyanopyrazine studies. Part VI: Absorption spectra and aggregation behaviour of tetrapyrazinoporphyrazines with long alkyl groups

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Abstract

Tetrapyrazinoporphyrazities with long alkyl groups drastically changed their absorption spectra by molecul aggregation depending on the polarity of solvent and temperature. Tetrapyrazinoporphyrazinato aluminium hydroxi showed red fluorescence with a small Stokes shift indicating less structure changes in the excited state and high ef ciency of energy transformation of the absorbed light energy to the fluorescence. These porphyrazines have satisfacto solubility in chlorohydrocarbons, tetrahydrofuran and toluene. The syntheses and characterization of tetr pyrazinoporphyrazines derived from diaminomaleonitrile (DAMN) and phenylglyoxal or 1,2-dicarbonyl compoun with long alkyl groups are described. © 1998 Elsevier Science Ltd. All rights reserved.

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1. Introduction

Whilst many dye chromophores for use as functional materials have been developed and evaluated, the phthalocyanine is the best chromophore for partical use from the point of stability and durability for use in organic photoconductors (OPC), nonlinear optical materials (NLO) and information recording media [1]. The energy distributions of sunlight consists of 50% of visible light (300–700 nm) and 50% of infrared light (700–1800 nm). Near infrared (NIR) dyes absorb IR light efficiently and can thus be used as shielding materials from heat. Some phthalocyanine met complexes absorb light in the NIR region, a have been evaluated as optical recording medi But, in general, they have poor solubility in no polar organic solvents and their sensitivity nee to be improved [2]. Introduction of the phenylth groups into the phthalocyanine nucleus produc a bathochromic shift of λmax into the NIR regio and also enhances their solubility in organic s vents. Intermolecular $\pi - \pi$ interactions are ste cally restricted to form aggregates, and solubili is then improved [3]. In the case of phthalocyani macrocycles substituted with long alkyl chai segregation between the rigid aromatic moieties a the flexible alkyl chains generally occurs a columnar mesophases are observed [4].

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We have studied the syntheses of functional dye materials based on dicyanopyrazine chromophores, and correlated their physical properties with their structures [5,6].

In this paper, new tetrapyrazinoporphyrazines with long alkyl groups, were synthesized from diaminomaleonitrile and phenylglyoxal or 1,2-dicarbonyl compounds and their aggregation behaviour, depending on the polarity of solvents, and temperature, were correlated with their structures.

2. Results and discussion

Diaminomaleonitrile (DAMN) is now an established intermediate in the synthesis of 2,3-disubstituted-5,6-dicyanopyrazines and related dyes [7]. 4-Alkylacetophenone, obtained from alkylbenzene **1** and acetyl chloride, was reacted with selenium dioxide in dioxane to give the 4-alkylphenylglyoxal **2**. Condensation of **2** and **3** gave 2-(4-alkylphenyl)-5,6-dicyanopyrazine **4** in moderate yield. 2-*tert*-Butyl-5,6-dicyanopyrazine **5a** and 2,3-diethyl-5,6-dicyanopyrazine **5b**, respectively, were also obtained from **3** and *tert*-butylglyoxal or 3,4-hexanedione by a similar method.

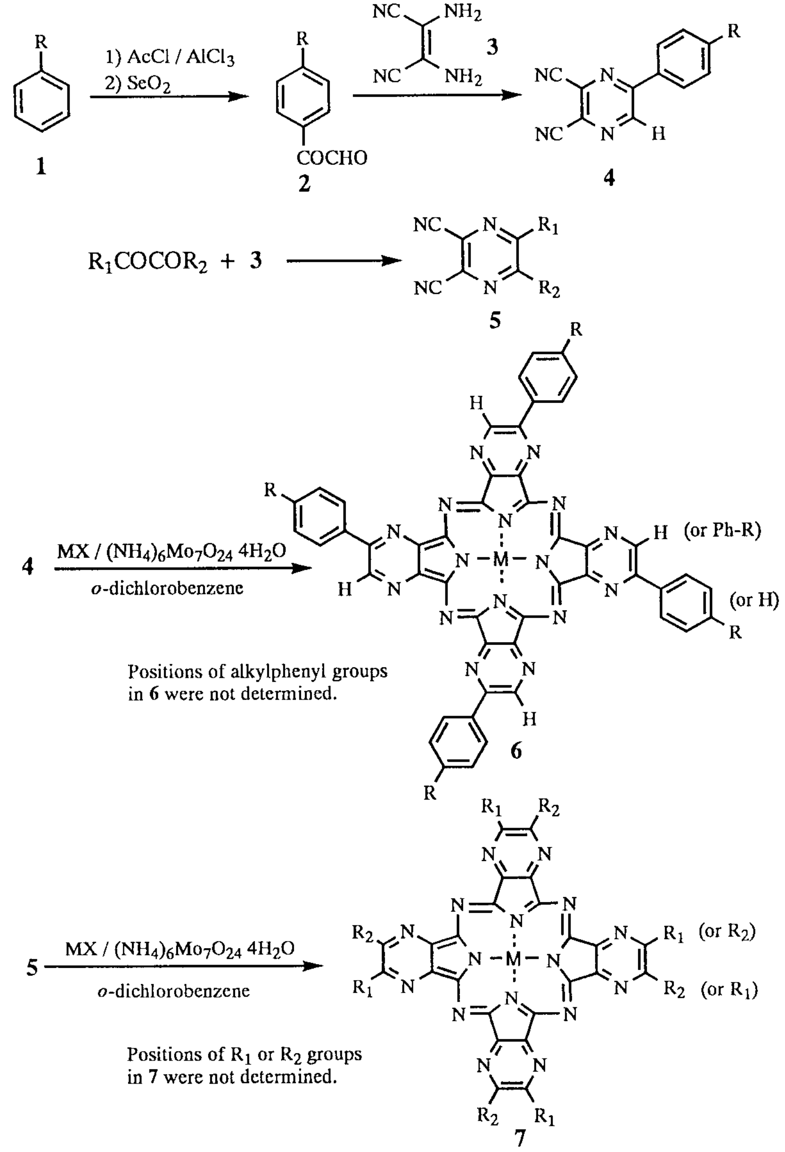
The synthesis of the tetrapyrazinoporphyrazinato metal complexes **6** or **7** were accomplished by reaction of **4** or **5** with the appropriate metal salt (CuCl, VCl_3, $AlCl_3$)in 1,2-dichlorobenzene in the presence of hexaammonium heptamolybdate tetrahydrate as catalyst. The results are summarized in Scheme 1 and Table 1.

The formation of tetrapyrazinoporphyrazines was confirmed by ^{1}H NMR, IR, and microanalyses. The IR spectra of **6** and **7** showed a broad band around 3400 cm^{-1} indicating hydrated structure. The bands at 2920 and 2851 cm^{-1} are assigned to the C–H stretching of the alkyl group. The strongest band at 1310 cm^{-1} is characteristic of the isoindole ring, with a large contribution of C–N stretching in the 16-membered inner ring. Five typical bands were detected in the following ranges; 1640–1608, 1560–1530, 1250–1215, 960–920, 710–690 cm^{-1}. The positions of the substituents in **6** and **7** were not determined. The NMR spectra of **6** and **7** showed broad peaks for each of the protons, and the products are pr posed to be isomeric mixtures (cf. Experiment section).

Phthalocyanines are well known to show cryst morphologies, and their crystal structures ha been correlated to intermolecular $\pi - \pi$ intera tions [8]. Some tetrapyrazinoporphyrazines ha interesting properties, such as fluorescence, aggr gation and high solubility in cyclohexane. T absorption maxima of the tetrapyrazino porphy azines **6** and **7** were observed at around 63 651 nm and fluorescence at 635–662 nm. Dyes and **6f** did not show any detectable fluorescen (Table 2). The Stokes shift (SS) indicates t energy loss in the excited state, and the less stru tural changes in the excited state in comparis with the ground state gave small SS value. Tetr pyrazinoporphyrazinato aluminium complex showed red fluorescence with a small SS valu which indicates a high efficiency of energy tran formation of the absorbed light energy to t fluorescence. The fluorescence of the tetr pyrazinoporphyrazinato aluminium complex w greatly influenced by molecular aggregation. T Q band spectra due to the first $\pi - \pi^*$ transition the tetrapyrazinoporphyrazinato aluminium com plex in *N*,*N*-dimethylacetamide showed a cha acteristic pattern for the monomer species, a fluorescence maxima were observed at arou 635–662 nm. Those in chloroform and benzene d not show any fluorescence, and a characterist spectral pattern for aggregates was observ (Fig. 1).

The λ_{max} value of 2,3,9,10,16,17,23,24-octaeth tetrapyrazinoporphyrazinato aluminium hydr oxide **7b** showed a hypsochromic shift of abo 17 nm compared with that of the metal free d reported by Tokita et al. [9]. The bathochrom shift of 33 nm in the Q band of **6** compared with is attributed to enlargement of the π conjugatio The Soret band was observed as a broad peak around 365 nm.

Fig. 2 indicates the temperature dependence the absorption spectrum of **6e**. The aggregate speci were much more predominant at lower temperatur but monomeric species became predominant wi increase of temperature. The absorption spectra the aggregate species showed split Q band arou



Positions of alkylphenyl groups in 6 were not determined.

Positions of R1 or R2 groups in 7 were not determined.

Scheme 1.

630 and 740 nm due to coupling of the transition moment between a pair (or more) of the chromophore. Mizuguchi et al., have recently reported that the molecular distortion of titanylphthalocyanine in the solid state produces a doubly degenerate excited level, giving split absorption bands. Reduction in molecular symmetry ongoing from the monomeric state to the dimeric state resolves the doubly degenerate level of the LUMO, and gives two $\pi - \pi^*$ transitions whose transiti moments are on the molecular plane and orth gonal [8,10].

Similar changes in molecular aggregation we also observed depending on the polarity of solve (Fig. 3). The intensity of the Q band at arou 640 nm decreased, but bands at around 610 a 770 nm increased on adding carbon tetrachlori to the chloroform solution of **6f**. Temperatu

Table 1
Syntheses of tetrapyrazinoporphyrazines

Compound	*R*	M	Yield (%)
6a	iso-Bu	Al(OH)	68
6b	n-C_8H_{17}	Al(OH)	74
6c	n-$C_{12}H_{25}$	Al(OH)	71
6d	n-$C_{16}H_{33}$	Al(OH)	64
6e	n-$C_{16}H_{33}$	V(O)	76
6f	n-$C_{16}H_{33}$	Cu	84
7a	$R_1 =$ *tert*-Bu, $R_2 = H$	Al(OH)	64
7b	$R_1 = R_2 = C_2H_5$	Al(OH)	79

Table 2
Absorption and fluorescent spectra of tetrapyrazinoporphyrazines

Compound	λ_{max} (nm)[a]	F_{max} (nm)[b]	SS (nm)[c]
6a	651	656	5
6b	651	655	4
6c	650	656	6
6d	650	656	6
6e	647	–[d]	–
6f	640	–[d]	–
7a	632	635	3
7b	636	638	2

[a] In chloroform.
[b] In *N*,*N*-dimethylacetamide.
[c] Stokes shift.
[d] Not detectable.

dependences of the absorption spectra can be applied as dye optical shutter, in which **6e** or **6f**, for example, were embedded in window glasses. Applications of these new tetrapyrazino porphyrazine derivatives for functional dye materials are under further investigation.

The thermal properties of tetrapyrazinoporphyrazine were evaluated by means of DSC (differential scanning calorimetry), TG (thermal gravimetric) and DT (differential thermal) analyses. The DSC curve of **6d** showed a broad endothermic peak at 326°C. The TG curve indicated weight loss starting at around 230°C and simultaneously, the DT curve showed exthothermic curves at the same temperature range (Fig. 4). The weight loss of **6d** started at 230°C and 13% loss was observed at 388°C and another 44% loss at 597°C, accompanying two steps of exthothermic decompositions by DTA, respectively. The copper complex **6f** showed similar DSC, TGA and DTA data of **6d**, but heat of fusion was observ at 117°C and weight loss proceeded rapidly around 510°C (48% loss), and **6f** was mo unstable than **6d**.

3. Experimental

Melting points were determined on a Yanagimo micro melting point apparatus without correctio The NMR spectra were taken on a FT-NMR Q 300 MHz GEC spectrometer. The ms spectra we recorded on a M-80 B Hitachi mass spectromete The visible and fluorescence spectra were me sured on a U-3410 Hitachi spectrophotometer ar a Shimadzu RF-5000 fluorescence spectr photometer. Microanalysis was conducted with Yanaco CHN MT-3 recorder. Thermal analys were determined on a DuPont 2001 Model 9 differential scanning calorimeter and a DuPo 9900 Model 951 thermal gravimetric analyzer. A chemicals were reagent grade and used witho further purification unless otherwise specified. Substituted acetophenone [11], 2-*tert*-butyl-5, dicyanopyrazine **5a** [12] and 2,3-diethyl-5,6-dicy nopyrazine **5b** [9] were prepared by known met ods.

*3.1. Preparation of 2-(4-alkylphenyl)-5,6-dicyanopyrazine **4***

General procedure:-

A mixture of dioxane (25 ml), water (1 ml), sel nium dioxide (5.5 g, 50 mmol) and a 4-substitut acetophenone (50 mmol) was refluxed for 6 h. T separated selenium was filtered and the resid washed with dioxane (5 ml). To the resulting w added diaminomaleonitrile (5.4 g, 50 mmol), ar mixture was then refluxed for 2 h and the solve then evaporated under reduced pressure. The re due was extracted with chloroform (100 ml) ar concentrated under reduced pressure.

3.1.1. 2-(4-iso-Butylphenyl)-5,6-dicyanopyrazine

The crude product was recrystallized fro ethanol to give **4a** as a white solid, m.p. 82\–83° ms: *m/z* 262 (M^+); ^1H NMR ($CDCl_3$): 0.95 (d, 6.6, 6H, CH_3), 1.94 (m, 1 H, CH), 2.57 (d, *J* 6.

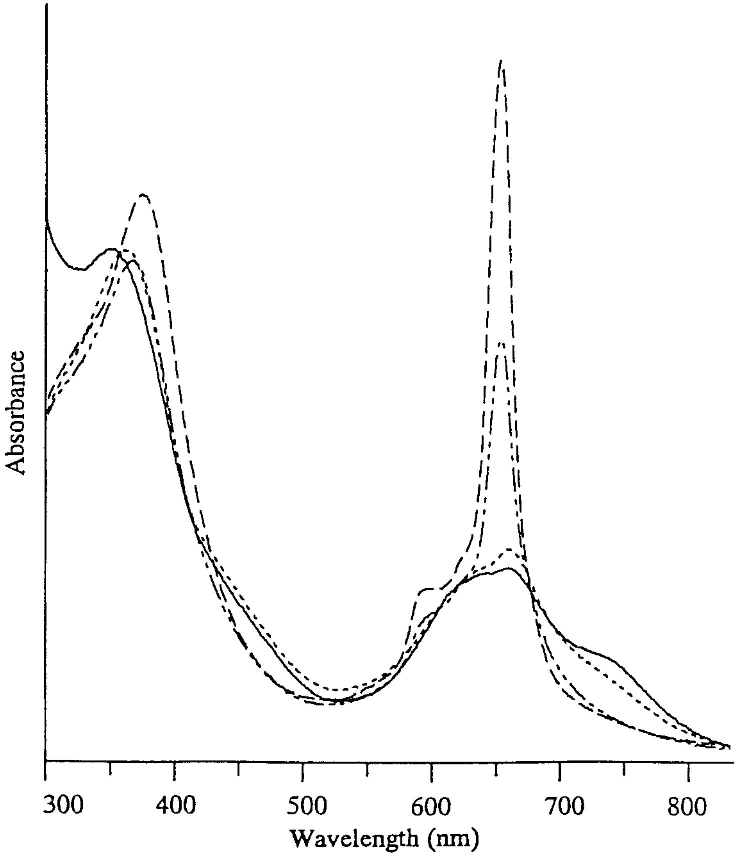


Fig. 1. Absorption spectra of 2,9,16,23-tetra(4-*n*-octylphenyl)tetrapyrazinoporphyrazinato aluminium hydroxide **6b**; in benzene (- chloroform (· · · ·), tetrahydrofuran (– · · –), *N*,*N*-dimethylacetamide (– – – –).

2 H, CH_2), 7.39 (d, *J* 7.5, 2 H, phenyl protons), 8.04 (d, *J* 7.5, 2 H, phenyl protons), 9.27 (s, 1 H, pyrazine proton). Anal. Calcd. for $C_{16}H_{14}N_4$: C, 73.26; H, 5.38; N, 21.36. Found: C,73.31; H, 5.35; N, 21.38.

3.1.2. 2-(4-n-Octylphenyl)-5,6-dicyanopyrazine **4b**

The crude product was recrystallized from ethanol to give **4b** as a white solid, m.p. 57–58'C; ms: *m*/*z* 318 (M^+); ^1H NMR ($CDCl_3$): 0.88 (t, *J* 6.9, 3 H, CH_3), 1.27–1.36 (br. s, 10 H, CH_2), 1.67 (m, 2 H, CH_2), 2.71 (t, *J* 6.9, 2 H, CH_2), 7.42 (d, *J* 7.5, 2 H, phenyl protons), 8.06 (d, *J* 7.5, 2 H, phenyl protons), 9.26 (s, 1 H, pyrazine proton). Anal. Calcd. for $C_{20}H_{22}N_4$: C, 75.43; H, 6.97; N, 17.61. Found: C,75.47; H, 6.88; N, 17.49.

3.1.3. 2-(4-n-Dodecylphenyl)-5,6-dicyanopyrazin
4c

The crude product was recrystallized fro
ethanol to give **4c** as a white solid,m.p. 76–78°
ms: *m*/*z* 374 (M^+); ^1H NMR ($CDCl_3$): 0.88 (t,
6.9, 3 H, CH_3), 1.27–1.36 (br. s, 18 H, CH_2), 1.
(m, 2 H, CH_2), 2.68 (t, *j* 6.9, 2 H, CH_2) , 7.41 (d,
7.5, 2 H, phenyl protons), 8.03 (d, *J* 7.5, 2 H, ph
nyl protons), 9.26 (s, 1 H, pyrazine proton). An
Calcd. for $C_{24}H_{30}N_4$: C, 76.97; H, 8.07; N, 14.9
Found: C, 76.96; H, 8.04; N, 14.97.

3.1.4. 2-(4-n-Hexadecylphenyl)-5,6-dicyanopyrazine **4d**

The crude product was recrystallized fro
ethanol to give **4d** as a white solid, m.p. 78–82°

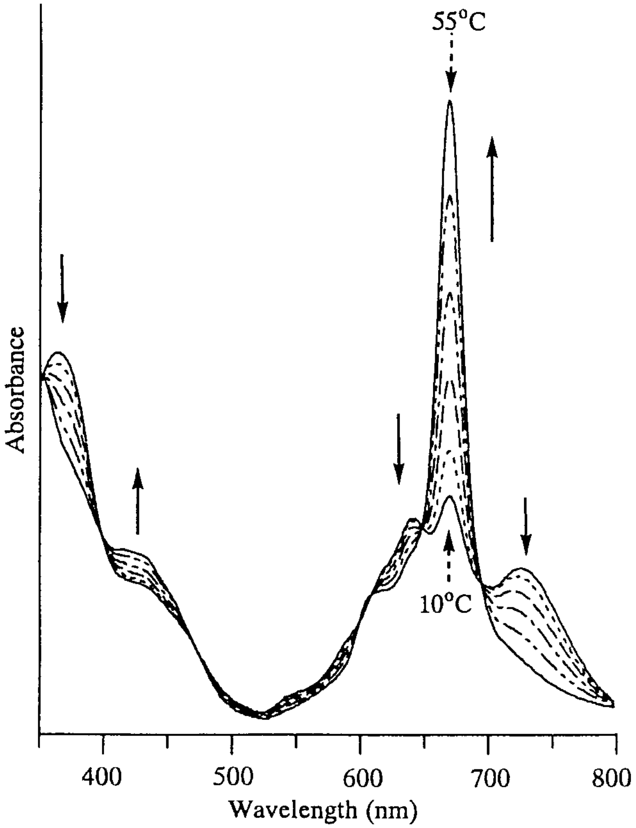


Fig. 2. Temperature dependence of the absorption spectra of 2,9,16,23-tetra(4-*n*-hexadectylphenyl)tetrapyrazinoporphyrazina vanadium oxide **6e** in benzene; 15°C (· · · ·), 25°C (– – – –), 35°C (– · – ·), 45°C (– · · –).

ms: *m*/*z* 430 ($M^{+\cdot}$); ^{1}H NMR ($CDCl_3$): 0.88 (t, *J* 6.9, 3 H, CH_3), 1.27–1.36 (br. s, 26 H, CH_2), 1.66 (rn, 2 H, CH_2), 2.68 (t, *J* 6.9, 2 H, CH_2), 7.41 (d, *J* 7.5, 2 H, phenyl protons), 8.03 (d, *J* 7.5, 2 H, phenyl protons), 9.26 (s, 1 H, pyrazine proton). Anal. Calcd. for $C_{28}H_{38}N_4$: C, 78.10; H, 8.89; N, 13.01. Found: C, 78.17; H, 8.79; N, 12.92.

3.2. Preparation of tetrapyrazinoporphyrazinato metal 6 and 7

3.2.1. General procedure:

A mixture of dicyanopyrazine (5 mmol) and the appropriate metal salt ($AlCl_3$, CuCl, VCl_3, 1.25 mmol) was refluxed in 1,2-dichlorobenzene (20 ml) in the presence of hexaammonium heptamolybdate tetrahydrate as catalyst. After refluxing for 8 h, the solvent was removed *in vacuo*. The residual mixture was poured into 5% aqueo hydrochloric acid (200 ml) and then stirred for 2 The solid was filtered and washed with 10% aqueo ammonia (2×80 ml) and methanol (3×50 ml).

3.2.2. 2,9,16,23-Tetra(4-isobutylphenyl) tetrapyr zinoporphyrazinato aluminium hydroxide 6a

The crude product was recrystallized fro ethylacetate and *n*-hexane to give **6a** in 68% yie as a green solid, ν (KBr)/cm^{-1}: 3448, 2953, 286 1635, 1539, 1314, 1232, 935, 699; ^{1}H NM ($CDCl_3$): 0.93 (br. d, *J* 6.0, 24 H, CH_3), 1.85 (4 H, CH), 2.59 (br. d, *J* 6.0, 8 H, CH_2), 7.42 (br. 8 H, phenyl protons), 8.24(br. s, 8 H, phenyl pr tons), 9.41 (br. s, 4 H, pyrazine proton). An Calcd. for $C_{64}H_{56}N_{16}Al(OH)(4H_2O)$: C, 65.97; 5.19; N, 19.23. Found: C, 65.38; H, 5.07; 18.87.

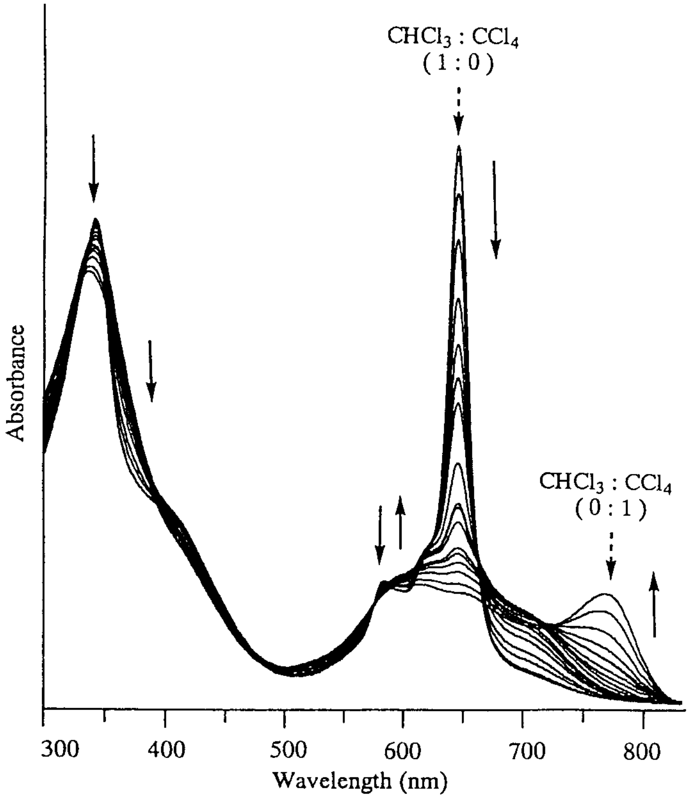


Fig. 3. The effects of carbon tetrachloride on the absorption spectra of 2,9,16,23-tetra(4-*n*-hexadectylphenyl)tetrapyrazinoporph azinato copper **6f** in chloroform.

*3.2.3. 2,9,16,23-Tetra(4-n-octylphenyl) tetra pyrazinoporphyrazinato aluminium hydroxide **6b***

The crude product was recrystallized from DMF and ethanol to give **6b** in 74% yield as a green solid, ν (KBr)/cm^{-1}: 3448, 2925, 2853, 1635, 1539, 1313, 1233, 936, 697; ^{1}H NMR ($CDCl_3$): 0.96 (br. s, 12 H, CH_3), 1.20–1.60 (br. m, 48 H, CH_2), 2.94 (br. m, 8 H, CH_2), 7.43 (br. s, 8 H, phenyl protons), 8.02 (br. s, 8 H, phenyl protons), 9.60 (br. s, 4 H, pyrazine proton). Anal. Calcd. for $C_{80}H_{88}N_{16}Al(OH)(4H_2O)$: C, 69.14; U, 6.46; N, 16.13. Found: C, 69.33; H, 6.26; N, 16.21.

3.2.4. 2,9,16,23-Tetra(4-n-dodecylphenyl) tetrapyrazinoporphyrazinato aluminium hydroxide 6c

The crude product was recrystallized from DMF and ethanol to give **6c** in 71% yield as a green solid, ν (KBr)/cm^{-1}: 3447, 2924, 2852, 1636, 1541, 1313, 1234, 936, 697; ^{1}H NMR (CDCl
0.97 (br. s, 12 H, CH_3), 1.20–1.60 (br. m, 80
CH_2), 2.90 (br. s, 8 H, CH_2), 7.45 (br. s, 8 H, ph
nyl protons), 8.06 (br. s, 8 H, phenyl protons), 9.
(br. s, 4 H, pyrazine proton). Anal. Calcd. f
$C_{96}H_{120}N_{16}Al(OH)(6H_2O)$: C, 69.87; H, 7.39;
13.58. Found: C, 70.05; H, 7.14; N, 13.40.

3.2.5. 2,9,16,23-Tetra(4-n-hexadecylphenyl) tetrapyrazinoporphyrazinato aluminium hydroxid 6d

The crude product was recrystallized fro
DMF and ethanol to give **6d** in 64% yield as
green solid, ν (KBr)/cm^{-1}: 3494, 2922, 2852, 163
1542, 1313, 1234, 937, 698; ^{1}H NMR (CDCl
0.94 (br. s, 12 H, CH_3), 1.20–1.60 (br. m, 112
CH_2), 2.87 (br. s, 8 H, CH_2), 7.47 (br. s, 8 H, ph
nyl protons), 8.02 (br. s, 8 H, phenyl protons), 9.
(br. s, 4 H, pyrazine proton). Anal. Calcd. f

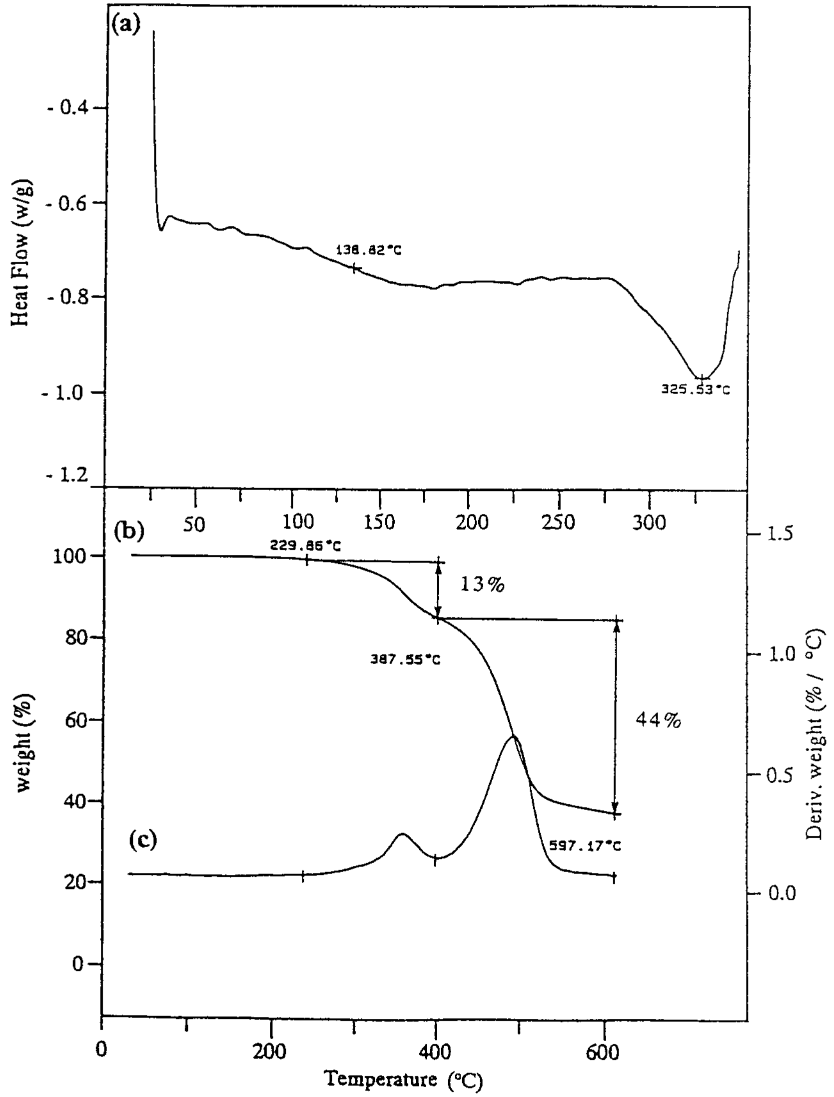


Fig. 4. (a) DSC, (b) TGA and (c) DTA curves of dye **6d**.

$C_{112}H_{152}N_{16}Al(OH)(7H_2O)$: C, 71.08; H, 8.15; N, 11.84. Found: C, 71.30; H, 8.28; N, 11.37.

3.2.6. 2,9,16,23 -Tetra (4-n-hexadecylphenyl) tetrapyrazinoporphyrazinato vanadium oxide ***6e***

The crude product was recrystallized from DMF and ethanol to give **6e** in 76% yield as a green solid, ν (KBr)/cm^{-1}: 3449, 2923, 2851, 1609, 1538, 1310, 1227, 988, 695; ^{1}H NMR ($CDCl_3$): 0.89 (br. s, 12 H, CH_3), 1.20–1.60 (br. m, 112 H, CH_2), 2.94 (br. s, 8 H, CH_2), 7.45 (br. s, 8 H, phen protons), 8.05 (br. s, 8 H, phenyl protons), 9. (br. s, 4 H, pyrazine proton). Anal. Calcd. f $C_{112}H_{152}N_{16}V(O)(4H_2O)$: C, 72.26; H, 8.23; 12.04. Found: C, 72.63; H, 8.31; N, 12.04.

3.2.7. 2,9,16,23-Tetra(4-n-hexadecylphenyl)-tetrapyrazinoporphyrazinato copper ***6f***

The crude product was recrystallized fro DMF and ethanol to give **6f** in 84% yield as green solid, ν (KBr)/cm^{-1}: 3468, 2922, 2851, 1635, 1558, 1310, 1219, 935, 694; ^{1}H NMR (CDCl$_3$): 0.91 (br. s, 12 H, CH$_3$), 1.20–1.60 (br. m, 112 H, CH$_2$), 2.84 (br. s, 8 H, CH$_2$), 7.44 (br. s, 8 H, phenyl protons), 8.03 (br. s, 8 H, phenyl protons), 9.49 (br. s, 4 H, pyrazine proton). Anal. Calcd. for $C_{112}H_{152}N_{16}Cu(4H_2O)$: C, 73.10; H, 8.33; N, 12.18. Found: C, 73.49; H, 8.17; N, 12.39.

*3.2.8. 2,3,9,10,16,17,23,24-Octaethyltetrapyrazinoporphyrazinato aluminium hydroxide **7a***

The crude product was recrystallized from DMF to give **7a** in 64% yield as a green solid, ν (KBr)/cm^{-1}: 3445, 2966, 2864, 1637, 1542, 1330, 1246, 921, 707; ^{1}H NMR (DMSO-d_6): 1.25 (br. t, *J* 7.2, 12 H, CH$_3$), 1.76 (br. q, *J* 7.2, 8 H, CH$_2$). Anal. Calcd. for $C_{40}H_{40}N_{16}Al(OH)(5H_2O)$: C, 54.61; H, 4.70; N, 25.50. Found: C, 54.75; H, 4.92; N, 24.94.

*3.2.9. 2,9,16,23-Tetra(*tert*-butyl)tetrapyrazinoporphyrazinato aluminium hydroxide **7b***

The crude product was recrystallized from ethylacetate and *n*-hexane to give **7b** in 79% yield as a blue solid, ν (KBr)/cm^{-1}: 3445, 2965, 2930, 1630, 1532, 1366, 1250, 956, 697; ^{1}H NMR (CDCl$_3$): 1.49 (br. s, 36 H, CH$_3$), 8.77 (br. s, 4 H, pyrazine proton). Anal. Calcd. for $C_{40}H_{40}N_{16}$-$Al(OH)(5H_2O)$: C, 54.61; H, 4.70; N, 25.5
Found: C, 53.99; H, 4.95; N, 25.96.

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