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Tuning of phthalocyanine absorption ranges by additional substituents

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Abstract

A new phthalonitrile derivative with two different substituents on 4- and 5-positions has been synthesized and its cyclotetramerization in the presence of anhydrous metal salts without any solvent resulted with phthalocyanines (**4–6**) containing a hexylthio group and malonylester on each benzo unit. When phthalocyanine formation was carried out in high-boiling alcohols in the presence of a base transesterification of malonyl esters gave products with enhanced solubility in apolar solvents. These new compounds have been characterized by ^{1}H NMR, FT-IR, UV–vis and mass spectroscopies.

Keywords: Phthalocyanine; Phthalonitrile; Transesterification; Zinc; Cobalt; Copper

1. Introduction

For many years phthalocyanines (pcs) have attracted attention as a consequence of their diverse electronic, optical, structural and coordination properties, which offer applications in the fields of non-linear optics, liquid crystals, Langmuir–Blodgett films, electrochromic devices, molecular metals, gas sensors, photosensitisers and diagnostic and therapeutic agents in pharmacology [1–4]. However, their insolubility in common organic solvents causes difficulties for many applications, rendering the syntheses of soluble derivatives an important task. Whereas, peripheral substitution with bulky groups [5–10] or long alkyl, alkoxy or alkylthio chains [11–17] leads to phthalocyanine products soluble in apolar solvents, on the contrary, sulfo or quaternary ammonium groups enhance solubility in a wide pH range of aqueous solutions [18–22]. The size and the nature of the substituents are not the only criteria for the solubility of the substituted phthalocyanines; the change in symmetry caused by these moieties on periphery is also important. Generally, tetra substituted phthalocyanines are more soluble than symmetrically octasubstituted ones due to the formation of four positional isomers in the case of tetra substituted analogues [1,23]. Thus, a mixture of similar positional isomers may practically be preferred than a single less soluble isomer [24]. In this sense, phthalocyanines derived from disubstituted phthalonitrile derivatives with two different substituents in the 4- and 5-positions have been expected to show similar behaviour.

Because of the difficulty in obtaining phthalonitrile precursors with two different substituents, relatively few examples of phthalocyanines substituted with two different groups on each benzo unit have been reported [25–28]. In a sense, these types of derivatives might be considered as alternatives to unsymmetrically substituted phthalocyanines which are getting more and more important for their non-linear optical properties, LB film formation and mesogenic tendencies [29–31].

Recently, we have shown for the first time that the acidic nature of the CH_2 group among two ester moieties in the diethylmalonate can be used to displace one of the chloro-groups in 4,5-dichlorophthalonitrile to obtain 1-chloro-3,4-dicyano-6-(1,1-dicarbethoxy-methyl)benzene probably as a consequence of steric hinderance of the bulky diethylmalonate group [27,28]. Our aim in the present work is to show the possibility of tuning the optical properties of phthalocyanines by making use of the reactivity of the remaining chloro-group with

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aliphatic mercaptans. The inclusion of long aliphatic chains on pcs is expected to increase the solubility in organic solvents and also promote columnar liquid crystal behaviour [32]. Besides, phthalocyanines with sulfanyl substituents tend to shift the intense Q absorption bands to longer wavelengths in the electronic spectra [33].

This paper describes the synthesis of substituted phthalonitrile with a diethylmalonate in the 4-position and alkylthio group in the 5-position and the preparation of metal-free and metallo-phthalocyanines (M = Zn, Co and Cu) from this phthalonitrile derivative.

2. Experimental

Infrared (IR) spectra were recorded on a Perkin–Elmer Spectrum One FT-IR (ATR sampling accessory) spectrophotometer, electronic spectra on a Unicam UV2 spectrophotometer. Elemental analyses were performed by the instrumental analysis laboratory of the TÜBİTAK Marmara Research Centre. ^{1}H NMR spectra were recorded on a Bruker 250 MHz spectrometer using TMS as an internal standard. Mass spectra were measured on an Ultima Fourier Transform and Varian 711 mass spectrometers. 1,2-Dichloro-4,5-dicyanobenzene (**1**) [33] and 1-chloro-3,4-dicyano-6-(1,1-dicarbethoxy-methyl)benzene (**2**) [28] were prepared according to reported procedures.

*2.1. Synthesis of 1-hexylthio-3,4-dicyano-6-(1,1-dicarbethoxy-methyl)benzene (**3**)*

Compound **2** (2 g, 6.2 mmol) was dissolved in 13 cm^3 of dry DMF at 45 °C under N_2 atmosphere and hexanethiol (0.87 ml, 6.2 mmol) was added. After stirring for 15 min, 1.5 g finely ground anhydrous K_2CO_3 (10.6 mmol) was added portion wise during 2 h with efficient stirring. The reaction mixture was stirred under nitrogen at 45 °C for further 48 h. Then the mixture was poured into 400 cm^3 of ice-water. The resulting creamy solid was collected by filtration and washed with water until the washings were neutral. After drying in vacuo at 50 °C, the crude product was recrystallised from hexane. The compound was soluble in $CHCl_3$, CH_2Cl_2, THF, methanol, ethanol, and acetone. Yield: 1.9 g (76.13%); m.p.: 58 °C; ^{1}H NMR ($CDCl_3$, δ, 250 MHz): 7.83 (s, H, Ar–H), 7.57 (s, H, Ar–H), 5.17 (s, H, CH), 4.33–4.15 (q, 4H, O–CH$_2$), 3.02–2.97 (t, 2H, S–CH$_2$), 1.75–1.42 (m, 2H, S–C–CH$_2$), 1.40–1.38 (m, 2H, S–C–C–CH$_2$), 1.31–1.24 (m, 10H, COO–C–CH$_3$ and S–C–C–C–CH$_2$–CH$_2$), 1.04–0.85 (m, 3H, S–C–C–C–C–C–CH$_3$); IR (KBr): γ (cm^{-1}): 3080 (CH, aromatic), 2978–2876 (CH, aliphatic), 2238 (C≡N), 1727 (C=O), 1295 (C–O ester), 1190–1115 (C–O–C). $C_{21}H_{26}N_2O_4S$. Found (%): C 62.15, H 6.43, N 6.23, calculated (%): C 62.66, H 6.51, N 6.96.

*2.2. Synthesis of metallo-phthalocyanines (**4–6**)*

A mixture of compound **3** (120 mg, 0.298 mmol) and 0.085 mmol anhydrous metal salts ($CoCl_2$, 11.5 mg; $CuCl_2$, 11.4 mg or $Zn(CH_3COO)_2$, 15.4 mg) was fused in a glass tube (10 × 75 mm). The mixture was heated to 110 °C under N_2 on an oil bath and kept at the indicated temperature and period for each complex: **4**, 165 °C, 10 h; **5**, 190 °C, 8 h; **6**, 170 °C, 24 h. The resulting dark green solid was chromatographed and eluted with a mixture of $CHCl_3$/THF (100:2) to give the desired product.

*2.2.1. 2,9,16,23-Tetra(diethoxymalonyl)-3,10,17,24-tetrahexylthio phthalocyaninatocobalt(II) (**4**)*

Yield 40 mg, 28%. IR (KBr): γ (cm^{-1}): 2974–2870 (CH aliphatic), 1728 (C=O), 1295 (C–O, ester), 1165–1114 (C–O–C); UV–vis ($CHCl_3$): λ/nm ($10^{-4}\varepsilon$/l mol^{-1} cm^{-1}): 686 (7.03), 319 (4.35). MALDI calc. (found) *m/e* (%): 1523.84 (1523.5) (100) $[M+H-2(CO_2C_2H_5)]$. $C_{84}H_{104}N_8O_{16}S_4Co$. Found (%): C 60.25, H 6.42, N 6.53, calculated (%): C 60.45, H 6.28, N 6.71.

*2.2.2. 2,9,16,23-Tetra(diethoxymalonyl)-3,10,17,24-tetra-hexylthiophthalocyaninatocopper(II) (**5**)*

Yield 24 mg, 16.8%. IR (KBr): γ (cm^{-1}): 2980–2873 (CH aliphatic), 1730 (C=O), 1292 (C–O, ester), 1167–1115 (C–O–C); UV–vis ($CHCl_3$): λ/nm ($10^{-4}\varepsilon$/l mol^{-1} cm^{-1}): 698 (8.15), 344 (2.70). MALDI calc. (found) *m/e* (%): 1529.45 (1529.5) (100) $[M+H-2(CO_2C_2H_5)]$. $C_{84}H_{104}N_8O_{16}S_4Cu$. Found (%): C 60.45, H 6.11, N 6.87, calculated (%): C 60.28, H 6.26, N 6.69.

*2.2.3. 2,9,16,23-Tetra(diethoxymalonyl)-3,10,17,24-tetra-hexylthio phthalocyaninatozinc(II) (**6**)*

Yield 6 mg, 4.2%. ^{1}H NMR ($CDCl_3$, δ, 250 MHz): 8.05–7.52 (br, 8H, Ar–H), 5.28 (s, 4H, CH), 4.41–4.06 (q, 16H, O–CH$_2$), 3.05–2.91 (t, 8H, S–CH$_2$), 1.80–0.87 (m, 68H, S–C–CH$_2$–CH$_2$–CH$_2$–CH$_2$–CH$_3$ and O–C–CH$_3$); IR(KBr): γ (cm^{-1}): 2982–2871 (CH aliphatic), 1729 (C=O), 1294 (C–O, ester), 1165–1112 (C–O–C); UV–vis ($CHCl_3$): λ/nm ($10^{-4}\varepsilon$/l mol^{-1} cm^{-1}) 699 (9.11), 363 (6.40). $C_{84}H_{104}N_8O_{16}S_4Zn$. Found (%): C 60.46, H 6.41, N 6.50, calculated (%): C 60.22, H 6.26, N 6.69.

*2.3. Transesterification reactions (**7–10**)*

A mixture of dinitrile **3** (100 mg, 0.25 mmol), anhydrous metal salt ($Zn(CH_3COO)_2$, 11.4 mg, 0.0625 mmol; $CoCl_2$, 8.1 mg, 0.0625 mmol or $CuCl_2$, 8.35 mg, 0.0625 mmol) and 10 µl DBU for metallo(pcs) in *n*-hexanol (1 ml) was heated at 150 °C, under N_2 atmosphere with stirring for 24 h. After evaporation of the solvent, the residue was purified by column chromatography with a mixture of $CHCl_3$/THF or $CHCl_3$ to obtain the desired product.

2.3.1. 2,9,16,23-Tetra(dihexoxymalonyl)-3,10,17,24-tetrahexylthio phthalocyaninatozinc(II) (7)

SiO_2, eluent $CHCl_3$/THF (100:2), yield 19 mg, 14.5%. ^{1}H NMR ($CDCl_3$, δ, 250 MHz): 8.89–7.30 (br, 8H, Ar–H), 4.26–4.01 (m, 20H, CH, O–CH$_2$), 3.84–3.39 (m, 8H, S–CH$_2$), 2.91–0.87 (m, 132H, O–C–CH$_2$–CH$_2$–CH$_2$–CH$_2$–CH$_3$

and S−C−CH_2−CH_2−CH_2−CH_2−CH_3); IR (KBr): γ (cm^{-1}): 2960−2857 (CH aliphatic), 1733 (C═O), 1328 (C−O, ester) 1156−1018 (C−O−C); UV−vis ($CHCl_3$): λ/nm ($10^{-4}\varepsilon$/l mol^{-1} cm^{-1}): 695 (8.76), 358 (2.38). $C_{116}H_{168}N_8O_{16}S_4Zn$. Found (%): C 65.76, H 8.11, N 5.07, calculated (%): C 65.59, H 7.97, N 5.27.

2.3.2. *2,9,16,23-Tetra(dihexoxymalonyl)-3,10,17, 24-tetrahexylthio phthalocyaninatocobalt(II) (**8**)*

SiO_2, eluent $CHCl_3$/THF (100:2), yield 18 mg, 13.7%. IR (KBr): γ (cm^{-1}): 2963−2860 (CH aliphatic), 1732 (C═O), 1322 (C−O, ester) 1162−1021 (C−O−C); UV−vis ($CHCl_3$): λ/nm ($10^{-4}\varepsilon$/l mol^{-1} cm^{-1}) 687 (7.42), 317 (4.97). FAB-MS calc. (found) *m/e* (%): 1604.15 (1604.7) (100) [$M + 3H - 4(CO_2C_6H_{13})$]. $C_{116}H_{168}N_8O_{16}S_4Co$. Found (%): C 66.03, H 8.12, N 5.09, calculated (%): C 65.78, H 7.99, N 5.29.

2.3.3. *2,9,16,23-Tetra(dihexoxymalonyl)-3,10,17, 24-tetrahexylthio phthalocyaninatocopper(II) (**9**)*

SiO_2, eluent $CHCl_3$, yield 17 mg, 12.9%. IR(KBr): γ (cm^{-1}): 2965−2858 (CH aliphatic), 1730 (C═O), 1327 (C−O, ester) 1160−1016 (C−O−C); UV−vis ($CHCl_3$): λ/nm (10^{-4} ε/l mol^{-1} cm^{-1}) 698 (9.12), 345 (3.07). FAB-MS calc. (found) *m/e* (%): 1608.76 (1608.7) (49) [$M + 3H - 4(CO_2C_6H_{13})$]. $C_{116}H_{168}N_8O_{16}S_4Cu$. Found (%): C 65.83, H 7.82, N 5.47, calculated (%): C 65.64, H 7.98, N 5.28.

2.4. *2,9,16,23-Tetra(dihexoxymalonyl)-3,10,17, 24-tetrahexylthio phthalocyanine (**10**)*

A mixture of dinitrile **3** (100 mg, 0.25 mmol) and 25 µl DBU in *n*-hexanol (1 ml) was heated at 150 °C under N_2 atmosphere with stirring for 24 h. After evaporation of the solvent, the residue was purified by column chromatography to obtain the desired product.

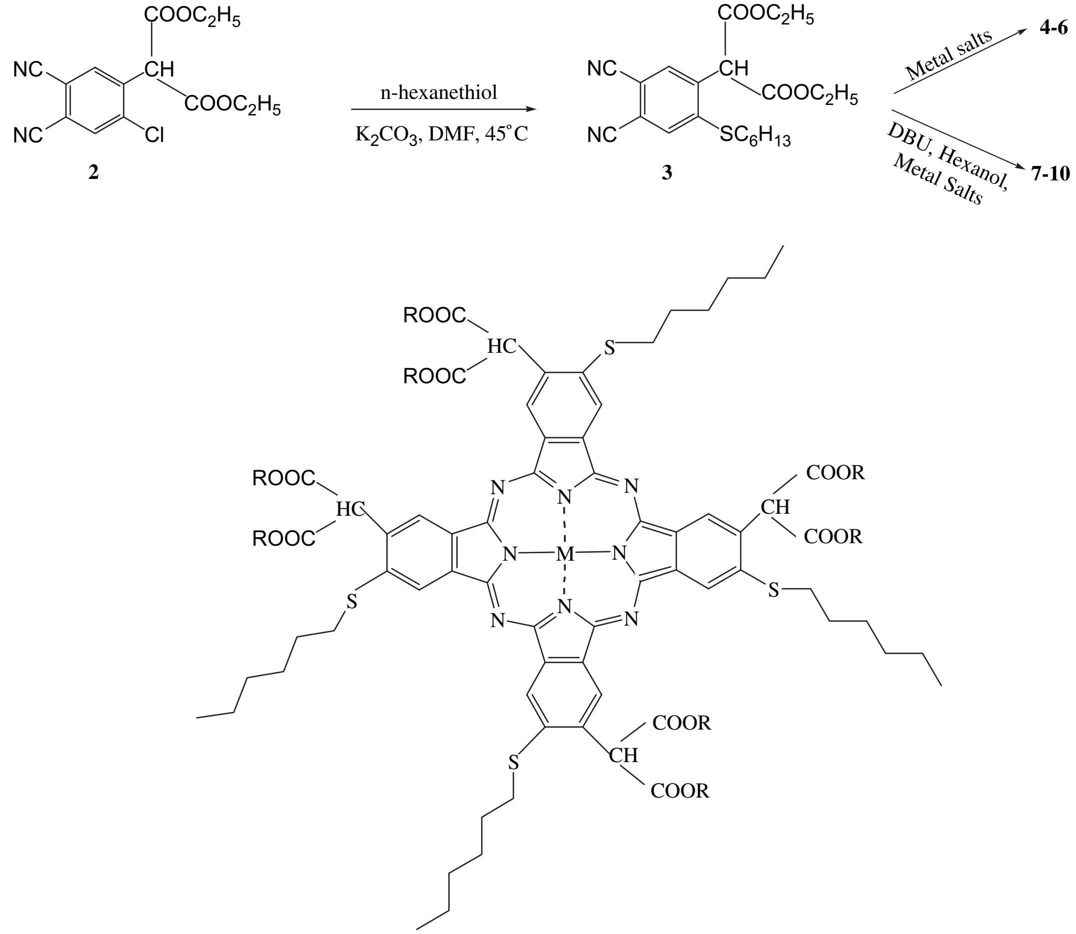
SiO_2, eluent $CHCl_3$/MeOH (200:1), yield 36 mg, 28%. ^1H NMR ($CDCl_3$, δ, 250 MHz): 9.37−8.45 (br, 8H, Ar−H), 4.41−4.25 (m, 20H, CH, O−CH_2), 3.76−3.48 (m, 8H, S−CH_2), 2.16−0.78 (m, 132H, O−C−CH_2−CH_2−CH_2−CH_2−CH_3 and S−C−CH_2−CH_2−CH_2−CH_2−CH_3), −3.35 (br, 2H, NH); IR(KBr): γ (cm^{-1}): 3280 (N−H), 2954−2850 (CH aliphatic), 1733 (C═O), 1328 (C−O, ester) 1156−1017 (C−O−C); UV−vis ($CHCl_3$): λ/nm ($10^{-4}\varepsilon$/l mol^{-1} cm^{-1}) 718 (9.88), 684 (8.54), 348 (4.01). $C_{116}H_{170}N_8O_{16}S_4$. Found (%): C 67.37, H 8.16, N 5.62, calculated (%): C 67.60, H 8.31, N 5.44.

3. Results and discussion

The precursor material chosen for the synthesis of substituted phthalocyanines with four hexylthio and four diethylmalonyl groups on the periphery is 1-chloro-3,4-dicyano-6-(1,1-dicarbethoxy-methyl)benzene (**2**). This compound was first reacted with *n*-hexanethiol to give 1-hexylthio-3, 4-dicyano-6-(1,1-dicarbethoxy-methyl)phthalonitrile (**3**) in presence of a base (K_2CO_3) in anhydrous DMF at 45 °C for two days. Cyclotetramerization of this new asymmetrically disubstituted phthalonitrile derivative **3** into phthalocyanines (**4**−**6**) was accomplished by reaction with anhydrous salts ($CoCl_2$, $CuCl_2$, $Zn(CH_3COO)_2$) in fused state. Here only metallophthalocyanines could be obtained. When the reaction was carried out in high-boiling alcohols, metal-free phthalocyanine was also obtained together with metallo-derivatives. Another important outcome of these reactions in solution at relatively high temperature was the transesterification of the malonyl group while some organic bases such as DBU was also present in the reaction medium [16,28]. The series of reactions are outlined in Scheme 1.

All phthalocyanine compounds were purified by column chromatography on silicagel by using $CHCl_3$, $CHCl_3$/THF and $CHCl_3$/MeOH mixtures as the eluent. The green products are extremely soluble in various solvents such as chloroform, THF, acetone, ethanol, methanol, diethylether, DMF and DMSO. Due to the presence of two different substituents on 4- and 5-positions of phthalonitrile (**3**), phthalocyanines obtained from this compound are naturally a mixture of positional isomers [23]. When the whole molecule is taken into account, it is not possible to define D_{4h} for all the isomers of metallo-phthalocyanines. Similar argument is true also for the metal-free derivative and describing it with D_{2h} symmetry is ambiguous. Therefore, it should be clear that the products are a mixture of isomers and D_{4h} and D_{2h} symmetries could be pronounced only when the inner phthalocyanine core is taken into account.

Spectral data on the newly synthesized compounds are consistent with the proposed structures. Comparison of the IR spectra of dinitriles **2** and **3** showed some signs as the structure of the compounds. The IR spectra of **3** clearly prove the presence of the long alkyl chain by the intense absorption peak for aliphatic group at around 2900 cm^{-1}. After conversion of the dinitrile derivative (**3**) into the phthalocyanines (**4**−**10**), the sharp peak for the C≡N vibration around 2238 cm^{-1} disappeared. The NH group of the metal-free phthalocyanine (**10**) in the inner core gave a weak absorption peak at 3280 cm^{-1}. The NH proton of metal-free phthalocyanine was also identified in the ^1H NMR spectrum with a broad peak at $\delta = -3.35$ ppm and the signal disappears on deuterium exchange. ^1H NMR spectra of the phthalonitrile (**3**) and the phthalocyanines with diamagnetic metal ions in the core (**6**, **7** and **10**) are consistent with proposed structures. In the ^1H NMR spectrum of **3** in $CDCl_3$, the aromatic protons appear as two singlets at 7.83 and 7.57 ppm and the CH proton of malonyl unit as a singlet at 5.17 ppm. The other aliphatic CH_2 and CH_3 protons appear in the range at 4.33−0.85 ppm. The ^1H NMR spectra of **6**, **7** and **10** are somewhat broader than the corresponding signals in the dinitrile derivative **3**. It is likely that the broadening is due to chemical exchange caused by aggregation−disaggregation equilibria and the fact that the product obtained in these reactions is a mixture of positional isomers which are expected to show chemical shifts that differ slightly from each other. Even using a high field instrument and multiple scans on dilute solutions afforded spectra showing broad absorptions. This would suggest that the presence of isomeric mixture is the more plausible explanation for peak broadening. In addition,



M = Co R = C_2H_5 (4)
M = Cu R = C_2H_5 (5)
M = Zn R = C_2H_5 (6)
M = Zn R = C_6H_{13} (7)
M = Co R = C_6H_{13} (8)
M = Cu R = C_6H_{13} (9)
M = 2H R = C_6H_{13} (10)

Scheme 1. 4-Alkylthio-5-alkyl-phthalonitrile and phthalocyanines derived from it.

the ^{1}H NMR spectrum of **6** indicates aliphatic –CH protons at 5.28 ppm. In the case of transesterification products, these aliphatic protons of –CH shifted to higher field. Compound **7** exhibited the protons of –CH and –CH_2 together around 4.26–4.01 ppm and also compound **10** showed these protons together around 4.41–4.25 ppm as a multiplet.

FAB-MS and MALDI gave spectra consistent with the proposed structures of compounds **4**, **5**, **8** and **9**. The spectra of **4** and **5** were obtained by MALDI technique. In the case of **4**, in addition to the [M^+] peak at 1669.6, fragment ions corresponding to the loss of ([$M - CO_2C_2H_5]^+$) at 1595.6, ([$M - 2(CO_2C_2H_5) + H]^+$) at 1523.5, ([$M - 3(CO_2C_2H_5) + 2H]^+$ at 1451.5) were easily identified.

The molecular ion peak [M^+] and the other fragment ions of compound **5** are shown in Fig. 1, together with the corresponding leaving groups.

Also, FAB-MS technique was used to identify compounds **8** and **9**. It has been obtained that [M^+] peak at 2117 and the other ions such as ([$M - (CO_2C_6H_{13}) + 3H]^+$) at 1991.1, ([$M - 4(CO_2C_6H_{13}) + 3H]^+$) at 1604.7, ([$M - 4(CO_2C_6H_{13}) - C_6H_{13} + 4H]^+$) at 1520.6, ([$M - 3(CO_2C_6H_{13}) - 3C_6H_{13} + 2H]^+$) at 1476.6 for the compound **8**. Besides, the fragment ions of **9** can be observed that correspond to peaks ([$M - (CO_2C_6H_{13}) + 2H]^+$) at 1995.1, ([$M - 4(C_6H_{13}) + 3H]^+$) at 1784.80, ([$M - (CHCO_2C_6H_{13}) - C_6H_{13} + 6H]^+$) at 1758.8, ([$M - 4(CO_2C_6H_{13}) + 3H]^+$) at 1608.7.

The new metallo-phthalocyanines show typical electronic spectra with two strong absorptions in the region 300–700 nm. The UV–vis spectra of the phthalocyanines **4–10** provide additional data on the diminishing inclination of these compounds to form aggregates. All metallo-phthalocyanines (**4–9**) show intense Q bands around 686–698 nm with

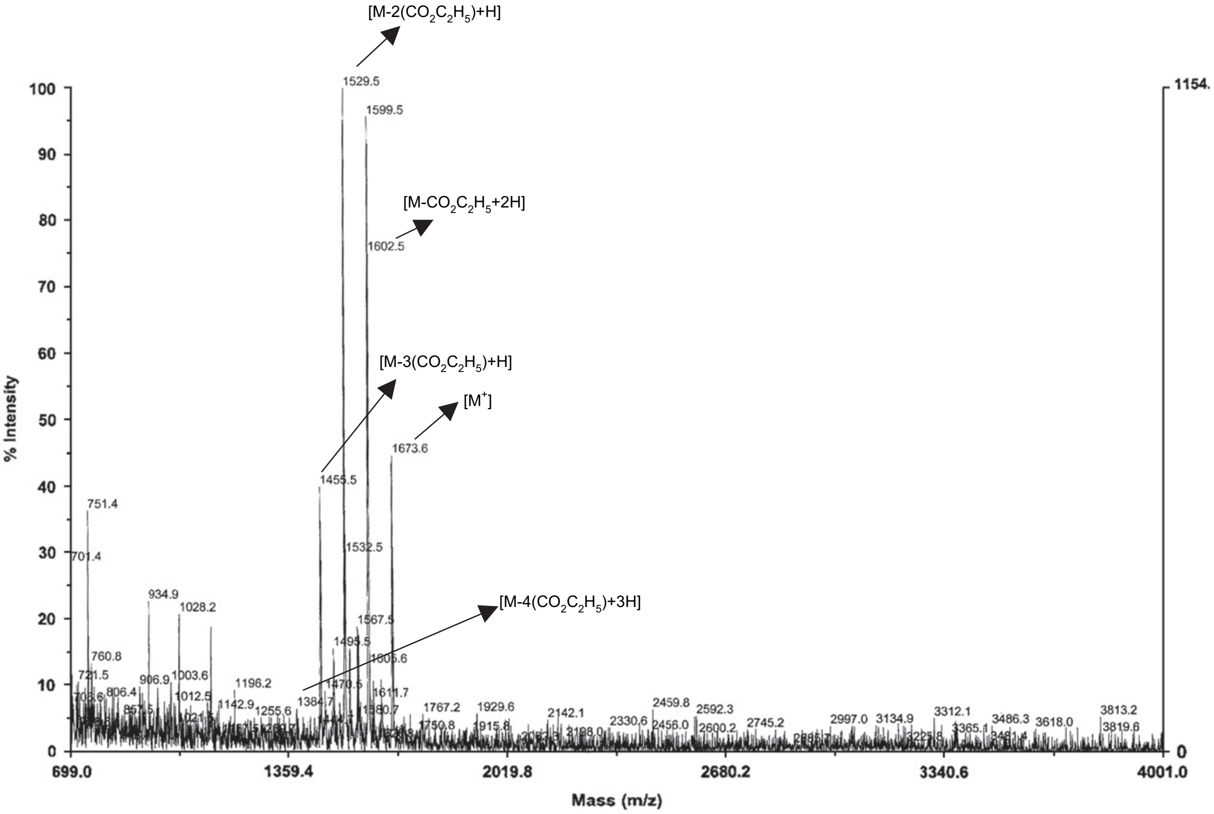


Fig. 1. Mass spectrum of **5**.

relatively sharp absorption peaks and almost no shoulder on the higher energy side, which would correspond to aggregated species [5,16,34,35]. There is almost no appreciable change in the molar absorptivities of the Q bands in the concentration range of 10^{-3}–10^{-5} M. The metal-free phthalocyanine (**10**) gives doublet Q band in the visible region (684 and 718 nm) as a result of the D_{2h} symmetry [5,35]. When compared with diethylmalonate and chlorine substituted derivatives reported earlier, substitution of chloro-group with alkylsulfanyl moiety leads to a shift of 17–19 nm to longer wavelength and it might be important to bring a new approximation for tuning the optical properties of phthalocyanines.

In conclusion, the reactive chloro functionality in 1-chloro-3,4-dicyano-6-(1,1-dicarbethoxy-methyl)benzene (**2**) can be used for tuning optical property and electron density of phthalocyanines as efficiently as in the case of unsymmetrical phthalocyanines.

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