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ScienceDirect
Dyes and Pigments 77 (2008) 351–356
DYES and PIGMENTS
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The synthesis and characterization of novel porphyrazines containing 5*H*-dibenz[*b*,*f*]azepine units

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Received 27 March 2007; received in revised form 28 May 2007; accepted 12 June 2007

Abstract

The synthesis of novel metal-free (**H_2Pz**) and metalloporphyrazines (**MgPz**), peripherally substituted with eight 5*H*-dibenz[*b*,*f*]azepine was performed by the cyclotetramerization of 1,5-bis(dibenz[*b*,*f*]azepinepropylthio)maleonitrile which was synthesized from 5*H*-dibenz[*b*,*f*]azepine and 1,10-diiodo-5,6-dicyano-4,7-dithia-5-decene. The new compounds were characterized by elemental analysis, ^{1}H NMR, ^{13}C NMR, IR, UV–vis and mass spectral data.

Keywords: Porphyrazinatomagnesium; Metal-free porphyrazine; Dibenzazepine; Template effect; Magnesium

1. Introduction

The two cornerstone tetrapyrrolic macrocyclic systems are porphyrins and tetraazaporphyrins, which include phthalocyanines and porphyrines and their aza-analogues [1]. These tetrapyrrolic compounds have been investigated intensively in many directions, as biomedical agents for diagnosis, chemical sensors, Langmuir–Blodgett films, liquid crystals, non-linear optical materials, including their applications in material science [2]. Phthalocyanines and related macrocycles are the most widely investigated fields such as mentioned above [3]. In contrast, the structural similarities, porphyrazines and their derivatives have been less studied since their first synthesis almost 60 years ago. Recently, a variety of porphyrazines have been obtained showing interesting electronic and novel physico-chemical properties, including fluorescence and inter-system crossing properties [4]. In addition to the magnetic, optical and electronic properties, the presence of S donor atoms in peripheral functionalised porphyrazines play an important function in affecting the solid state interactions [5]. The physical and chemical properties of the porphyrazines can be enhanced by addition of macrocycles with two, four or six peripheral thiols, amines or alcohols [6].

Fluorescent chemosensors have drawn increasing attention for their use in fields as diverse as chemistry, biology, medicine, environmental monitoring and material science [7]. On the other hand, a considerable amount of researches have been carried out for synthesising receptors of binding and sensing ions selectively due to anions and cations playing the major role in many chemical and biological processes [8]. Especially, fluorescent anion chemosensors are of great importance because of their high sensitivity and low dedection limit [9]. In addition to that, iminostilbene structure which connected to porphyrazine skeleton in this study, a tricyclic tertiary amine, is related to a class of anticonvulsants which are employed in the prevention or treatment of epileptic seizures. Iminostilbene is used as an intermediate for the synthesis of specific analgesic and antipsychotic agents. It also shows protective activity of aromatic amines and imines against oxidative nerve cell death and bifunctional dipolar electroluminescent material properties [10].

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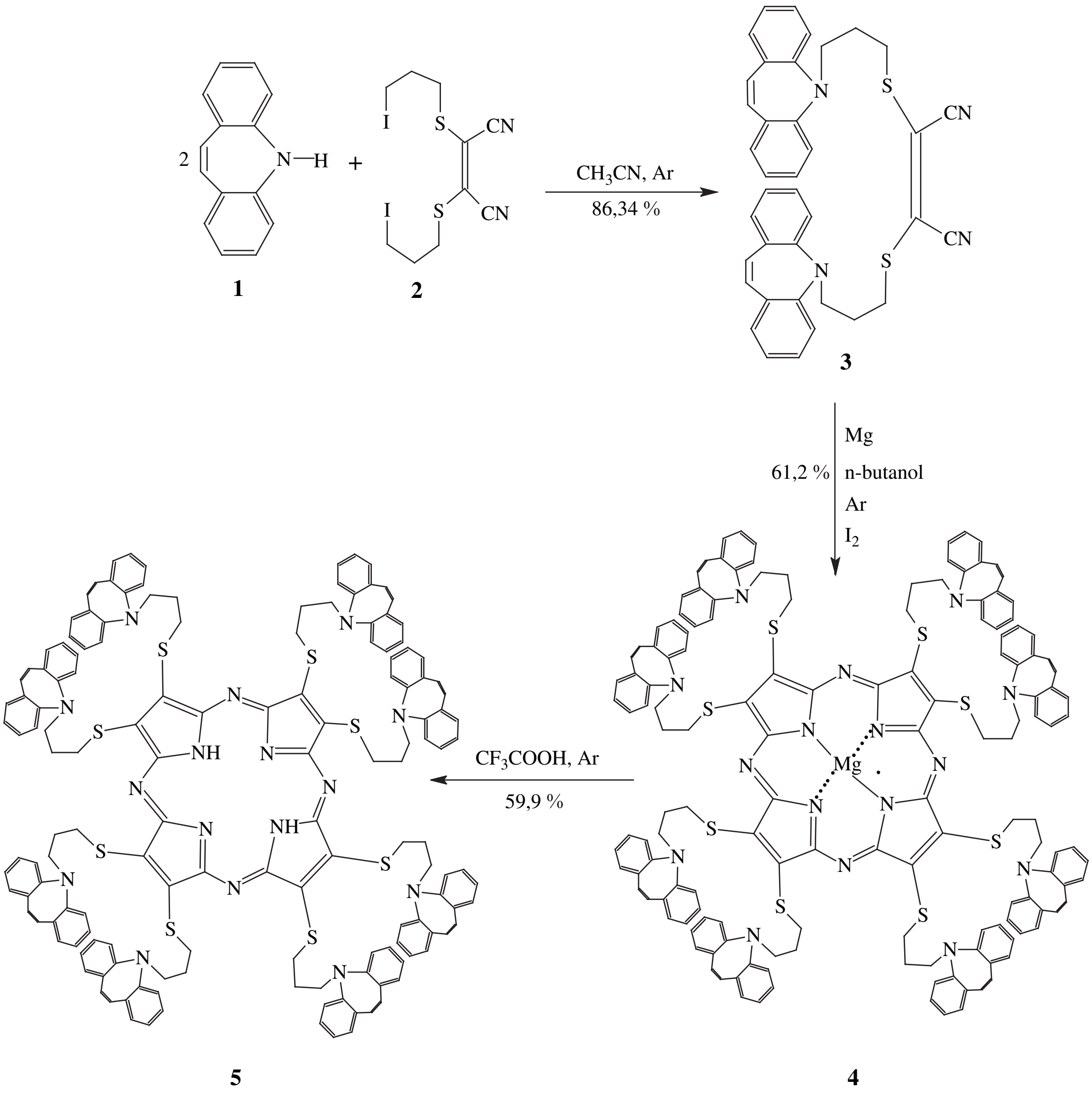
0143-7208/$ - see front matter © 2007 Published by Elsevier Ltd.
doi:10.1016/j.dyepig.2007.06.002

In the present study, we report the synthesis and characterization of substituted porphyrazino magnesium (**4**) and metal-free derivative (**5**), which are connected to the propylene spacer to iminostilbene as fluorophore.

2. Results and discussion

Our synthesis began with disodium salt of 1,2-dicyanoethylene-1,2-dithiolate. The intermediate 1,10-diiodo-5,6-dicyano-4,7-dithia-6-decene (**2**) was prepared according to the literature procedure [11]. The synthesis of **3** was carried out by condensing intermediate compound (**2**) with iminostilbene (**1**) in the presence of Na_2CO_3 in dry acetonitrile at reflux temperature (Scheme 1). This new compound was characterized by its spectroscopic and analytical data. The ^1H NMR spectrum of **3** showed expected signals such as $-CH_2$, $-SCH_2$, $-NCH_2$ protons at $\delta = 1.91$, 3.11 and 3.82 ppm, respectively. The chemical shift concerning NH protons in the starting material (**1**) disappeared after the condensation reaction. The doublets and triplet at $\delta = 7.28$, 6.77 and 7.02 ppm correspond to the aromatic moieties belonging to iminostilbene compound as expected. Proton-decoupled ^{13}C NMR spectrum of this compound clearly indicates the presence of nitrile and double bond signals at $\delta = 112.07$ and 120.18 ppm. This spectrum also reveals that the characteristic carbon atoms from iminostilbene (Fig. 1) are unequivalent at $\delta = 149.83$, 121.24, 123.59, 128.82, 129.22 and 132.04 ppm whereas the other carbon resonance concerning the C=C bond comes out at $\delta = 132.04$ ppm as expected. The rest of the carbon signals of this compounds are quite similar to those of the precursor compound (**2**). The IR spectrum of **3** was easily verified with disappearance of N–H stretching motion and the presence of C≡N vibrations at 2208 cm^{-1}. The remaining resonances due to iminostilbene moiety and aliphatic groups do not shift significantly on condensation reaction. This compound displayed the expected molecular ion peak at $m/z = 609$, indicating formation of $[M+1]^+$.



Scheme 1.

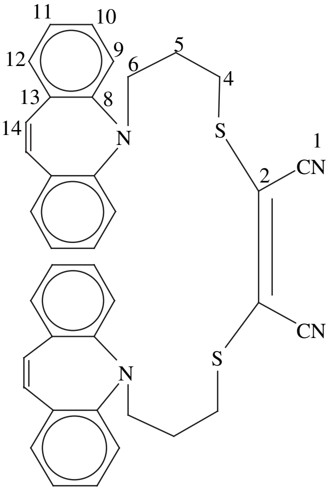


Fig. 1.

The cyclotetramerization of *S*,*S*′-substituted maleonitrile (**3**) to the corresponding porphyrazinatomagnesium (**4**) was achieved according to the standard Linstead and Whalley route [12]. Magnesium was used as the template in *n*-butanol at reflux for 24 h under argon atmosphere. In the IR spectrum of this compound, a diagnostic feature of the formation of **4** from **3** is the disappearance of the sharp C≡N resonances and the presence of C=N stretching vibrations at 1634 cm^{-1} confirms the formation of **MgPz**. In the ^{1}H NMR spectrum of **4**, the signals relating to $-CH_2$, $-SCH_2$, $-NCH_2$ and aromatic groups in the iminostilbene moieties and porphyrazine skeleton gave significant resonances characteristic of the proposed structure. In ^{13}C NMR spectrum of this compound, all signals are identical for the precursor substituted maleonitrile derivative (**3**) except for the C≡N carbons as expected (Fig. 2). The chemical shift appeared at $\delta = 155.53$ ppm of this compound should be related to inner core C=N signals [13]. The elemental analysis of **4** is in accord with its calculated results. This is also supported by the presence of the main peak in the mass spectrum of **4** at *m*/*z* = 2456.9 $[M]^+$.

Porphyrazinatomagnesium (**4**) was demetallated by the treatment with trifluoroacetic acid at room temperature for 4 h to give the metal-free porphyrazine [14]. The dark purple solid was purified by column chromatography to give metal-free porphyrazine. In the ^{1}H NMR spectrum of **5**, inner core NH protons appear as a deuterium exchangeable broad chemical shift at $\delta = -1.52$ ppm as a consequence of the 18π electron systems of the planar structure [15]. The other characteristic protons and carbon resonances in the NMR spectra of **5** showed significant absorbance for the target compound. This spectrum is closely similar to that of the precursor compound as expected. The presence of N–H stretching vibrations at 3276 cm^{-1}, in the IR spectrum of this compound, also confirms the formation of **5**. The convenience of elemental analysis results and the mass spectrum data of **5** contained a strong peak at *m*/*z* = 2435.17 $[M+1]^+$ for the parent ion, which can be attributed to the formation of the metal-free porphyrazine Fig. 3.

The best indications for porphyrazine systems are given by their UV–vis spectra in chloroform solution (10^{-5} M) at room temperature (Fig. 4). The absorption spectra of **4** and **5** show the same typical B and Q bands of symmetrical substituted **Pz**. The single band at 674 nm, in the UV–vis spectrum of **4**, is characteristic of tetrapyrrolic macrocycle with D_{4h} symmetry [16]. The presence of bulky electron-donating S-groups is expected to give porphyrazines absorbing electromagnetic radiation just in the same range as phthalocyanines [17]. The Q and Soret band absorptions could be attributed to $\pi \rightarrow \pi^*$ transition from a_{1u}, a_{2u} HOMOs to the double degenerate e_g LUMOs [18]. The broad absorption band around 491 nm is assigned to the $n \rightarrow \pi^*$ transitions of the nonbonding electrons of the peripheral sulfur atoms and the macrocyclic π system [19]. Both the metallated and metal-free compounds exhibit split Q-bands with the degree of splitting being greater for the metal-free derivative. The splitting reflects the change in symmetry $D_{4h} \rightarrow D_{2h}$ and could be rationalized by Gouterman's four-orbital model for the optical spectra of porphyrins [20]. A typical spectrum of **5** (Fig. 4) in chloroform showed

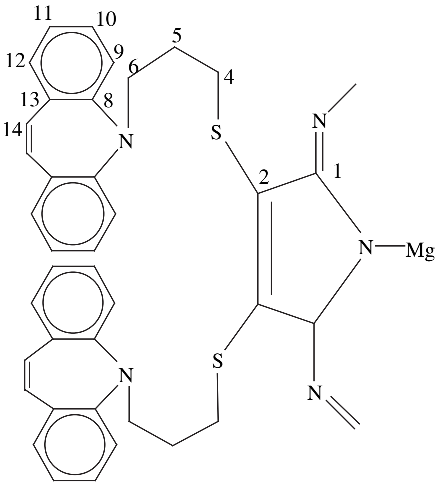


Fig. 2.

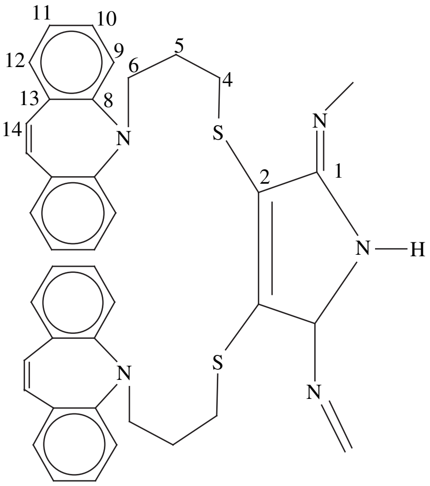


Fig. 3.

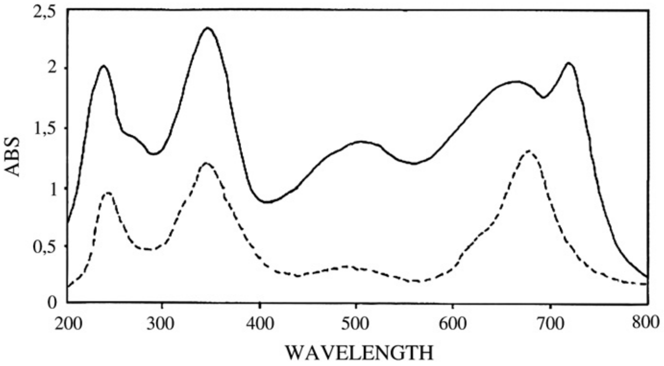


Fig. 4. UV–vis spectra of **4** (---) and **5** (—) in chloroform.

the split Q bands at 717 and 659 nm. This is due to the lowering of symmetry from four-fold to two-fold symmetry for the metal-free porphyrazine and removal of the degeneracy of the e_g LUMOs [14,21]. This spectrum also shows a slight red-shift at the Soret band which is similar to that reported for the other porphyrazines [22]. The intense absorption around 350 nm can be attributed to the so-called N-band, which is strengthened with respect to the Soret B band. The intense absorptions, in addition to characteristic porphyrazine core, at 240 nm could be attributed to the $\pi \rightarrow \pi^*$ transition of iminostilbene groups.

3. Experimental

Proton and carbon-13 NMR spectra were recorded on a Varian Mercury 200 Spectrometer, using tetramethylsilane as the internal standard. Mass spectra of the compounds were measured on a Micromass Quatro LC/ULTIMA LC–MS MS Spectrometer. IR spectra were recorded on a Perkin–Elmer Spectrum One FTIR Spectrometer at room temperature. Electronic absorption spectra were recorded using a Unicam UV2-100 Spectrophotometer. Measurement was made in a 1 ml quartz cuvette sealed with a septum. The elemental analysis of the compounds was determined on a Hewlett–Packard 185 CHN analyzer. Melting points were determined by an electrothermal melting point apparatus and are uncorrected. 1,10-Diiodo-5,6-dicyano-4,7-dithia-6-decene [11] was prepared by literature method. The reactions were followed by TLC, which was carried out on precoated plates. Merck Kieselgel 60 (70–230 mesh) was used in column chromatography. All reactions were carried out under argon atmosphere using Standard Schlenck techniques. Solvents were purified according to standard procedure [23].

*3.1. 1,2-Bis(dibenz[b,f]azepinepropylthio)maleonitrile (**3**)*

A round-bottom flask containing dry acetonitrile (120 ml) and fitted with condenser was evacuated, refilled three times with argon and connected to a vacuum line. Under argon, the flask was charged with **1** (1.16 g, 6 mmol), excess amount of finely ground anhydrous Na_2CO_3 (1.56 g, 15 mmol) and the mixture was heated and stirred at 80 °C for 1 h. The dicyano compound (**2**) (1.43 g, 3 mmol) in dry acetonitrile (20 ml) was added to this reaction mixture at the same temperature and refluxed for 6 days. At the end of this period, the mixture was cooled to room temperature and filtered using Celite as standard filtering agent and washed with dry acetonitrile. The combined solution was evaporated to dryness under reduced pressure and the residue was subjected to chromatography on silica gel (eluent: hexanes/chloroform, 5:1). Yield: 1.575 g (86.34%), m.p. > 300 °C. IR (KBr): 3058 (Ar–H), 2925–2852 (C–H), 2208 (C≡N), 1593, 1571 (Ar–H), 1484, 1460, 1436, 1313, 1241, 1177, 1116, 1044 cm^{-1}. ^1H NMR ($CDCl_3$): $\delta = 7.28$ (d, 2H, ArH), 7.02 (t, 4H, ArH), 6.77 (d, 2H, ArH), 6.10 (s, 2H, =CH), 3.82 (t, 4H, NCH_2), 3.11 (t, 4H, SCH_2), 1.91 (m, 4H, CH_2). ^{13}C NMR ($CDCl_3$): δ 149.83 (C_8), 133.82 (C_{13}), 132.04 (C_{14}), 129.22 (C_{12}), 128.82 (C_{11}), 123.59 (C_{10}), 121.24 (C_9), 120.18 (C_2), 112.07 (C_1), 47.97 (C_6), 32.45 (C_4), 29.60 (C_5). Anal. Calcd for $C_{38}H_{32}N_4$ S_2: C, 75.00; H, 5.26; N, 9.21. Found: C, 74.81; H, 5.09; N, 9.35. MS (m/z) = 609 $[M+1]^+$, 631 $[M+Na]^+$.

*3.2. [2,3,7,8,12,13,17,18-Octakis(dibenz[b,f]-azepinepropylthio)porphyrazinato]Mg(II) (**4**)*

Magnesium turnings (0.046 g, 1.93 mmol) and a small chip of iodide were added to *n*-butanol (21 ml) under an argon atmosphere; the mixture was refluxed until the magnesium had completely reacted to form a suspension of magnesium butoxide for 24 h [caution required]. A solution of maleonitrile containing dibenz[*b*,*f*]azepine (**3**) (0.5 g, 0.82 mmol) in *n*-butanol (25 ml) was added dropwise to the refluxing reaction mixture for 1 h and the mixture was refluxed and stirred for 24 h and then filtered while hot and the residue was washed with acetone several times. The solution was evaporated to dryness under reduced pressure. The dark blue residue was purified by chromatography on silica gel using chloroform/hexane (3:2) mixture as the eluent. Yield: 0.30 g (61.2%), m.p. > 300 °C. IR (KBr): 3060 (Ar–H), 2942–2852 (C–H), 1634 (C=N), 1593 (Ar–H), 1574, 1483, 1459, 1432, 1313, 1239, 1115, 1042 cm^{-1}. ^1H NMR ($CDCl_3$): δ 7.25 (m, 8H, ArH), 6.99 (m, 16H, ArH), 6.73 (m, 8H, ArH), 6.14 (m, 8H, =CH), 3.85 (m, 16H, NCH_2), 3.14 (m,16H, SCH_2), 1.95 (m, 16H, CH_2). ^{13}C NMR ($CDCl_3$): δ 155.53 (C_1), 149.93 (C_8), 133.95 (C_{13}), 132.13 (C_{14}), 129.31 (C_{12}), 129.21 (C_2), 128.90 (C_{11}), 123.69 (C_{10}), 121.33 (C_9), 48.10 (C_6), 31.95 (C_4), 29.70 (C_5). UV–vis [chloroform, λ_{max}/nm (log ε)]: 674 (3.86), 623 (3.22), 491 (3.12), 344 (3.82), 321 (3.79), 246 (3.74). Anal. Calcd for $C_{152}H_{128}N_{16}S_8Mg$: C, 74.25; H, 5.21; N, 9.11. Found: C, 74.03; H, 5.48; N, 8.87. MS (m/z) = 2456.90 $[M]^+$.

*3.3. 2,3,7,8,12,13,17,18-Octakis(dibenz-[b,f]azepinepropylthio)H^{21},H^{23} porphyrazine (**5**)*

Porphyrazinomagnesium (**4**) (0.22 g, 0.09 mmol) was dissolved in 2.8 ml of trifluoroacetic acid under argon atmosphere. After stirring for 3 h at room temperature the solution was added dropwise into iced water at 0 °C in order to precipitate the target compound and then neutralized with aqueous solution of ammonia (10%). The crude product was obtained by extraction with chloroform (3×40 ml) and dried over anhydrous $MgSO_4$ overnight and then finally the solvent was evaporated to dryness under reduced pressure. The dark purple product was purified by column chromatography on silica gel using chloroform/hexane (1:1) mixture as the eluent. Yield: 0.13 g (59.9%), m.p. > 300 °C. IR (KBr): 3276 (N–H), 3060 (Ar–H), 2925–2854 (C–H), 1641 (C=N), 1593 (Ar–H), 1571, 1483, 1459, 1376, 1289, 1239, 1173, 1116, 1043 cm^{-1}. ^{1}H NMR ($CDCl_3$): δ 7.25 (m, 16H, ArH), 7.02 (m, 32H, ArH), 6.71 (m, 16H, ArH), 6.09 (m, 8H, =CH), 3.81 (m, 16H, NCH_2), 3.11 (m, 16H, SCH_2), 1.90 (m, 16H, CH_2). ^{13}C NMR ($CDCl_3$): δ 154.97 (C_1), 149.96 (C_8), 133.96 (C_{13}), 132.14 (C_{14}), 129.38 (C_{12}), 129.24 (C_2), 128.91 (C_{11}), 123.50 (C_{10}), 120.29 (C_9), 48.13 (C_6), 31.94 (C_4), 29.71 (C_5). UV–vis [chloroform, λ_{max}/nm (log ε)]: 717 (4.38), 659 (4.34), 506 (3.94), 350 (4.52), 273 (3.97), 240 (4.37). Anal. Calcd. for $C_{152}H_{130}N_{16}S_8$: C, 74.93; H, 5.34; N, 9.20. Found: C, 75.21; H, 5.24; N, 9.05. MS (m/z) = 2435.17 $[M+1]^+$.

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