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Synthesis and characterization of metal-free and metallophthalocyanines containing N_2S_2-type macrocyclic moieties linked ferrocenyl groups

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Abstract

The new metal-free (**4**) and metallophthalocyanines (**5**) carrying macrocyclic moieties linked ferrocenyl groups have been synthesized by direct cyclotetramerization of the pre-cursor, 12,13-dicyano-4,7-bis(ferrocenylmethyl)-2,3,4,5,6,7,8,9-octahydrocyclobenzo[*k*]-4,7-diaza-1,10-dithiacyclododecine (**3**) which has been prepared by the macrocyclization reaction of 1,2-bis(2-iodoethylmercapto)-4,5-dicyanobenzene (**1**) with *N*,*N*′-ethylenebis-(ferroceneylmethyl)amine (**2**), in the presence of 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU) as a strong organic base. Nickel (II) phthalocyanine (**5**) was synthesized by the reaction of metal-free phthalocyanine with anhydrous $NiCl_2$ in dry quinoline. The target compound and its intermediates have been characterized by a combination of elemental analysis and ^1H, ^{13}C NMR, IR, UV–Vis and MS spectral data.

Keywords: Phthalocyanine; Mixed-donor macrocycle; Ferrocene; Macrocyclization; Template effect; Nickel (II)

1. Introduction

Phthalocyanines are 18 π-electron aromatic planar macrocycles constituted by four isoindoline units linked together in the 1,3-positions by aza bridges [1]. These compounds and their macrocyclic analogues continue to attract considerable attention, due in part to their characteristic optical properties [2] and applications including medicinal therapeutic agents [3], field effect transistors [4], photosensitizers [5], photoconductors [6], organic light-emitting diodes [7], nonlinear optical devices [8], catalysts [9], dye industry and gas sensors [10] have been demonstrated. Owing to their rigid geometry as well as their unique electronic and photonic properties, phthalocyanines and their metal complexes are attractive and excellent building components. Many derivatives of these compounds can be prepared not only by changing the nature of the central metal atom, but also by formally fusing additional aromatic rings to the central core; or by forming planar or linear groups [11]. Phthalocyanine-based multicomponent systems have been explored, including porphyrins, ferrocenes, crown ethers [12], tetrathiafulvalenes, oligopridyl-metal complexes, dendrimers, and C_{60} [13]. Furthermore, Pcs have long been known to undergo electron transfer reactions, both to and from their excited states, and strong electron donors such as ferrocene are able to quench the Pc fluorescence by intermolecular electron transfer [14].

The fascinating structural properties of ferrocene and its derivatives have been the subject of increasing interest in all fields of organometallic chemistry, since the discovery of ferrocene in 1950 [15]. A sandwich structured compound ferrocene is suitable to functionalization by direct electrophilic substitution of the 6π-cyclopentadienide ring, like benzene. On the other hand ferrocene reacts 3×10^6 times faster than benzene [16]. Because of the high stability, ease

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of functionalization, and well defined electrochemistry, ferrocene has been widely used as a redox-active center which is linked together with a wide variety of structural units [17]. Furthermore, the combination of an electron donor unit such as ferrocene and an electron acceptor moiety such as phthalocyanine may give rise to inter-molecular charge transfer that may enhance the second order response. So far, only a few examples of Pcs covalently linked to one or more ferrocene units have been described, and also their NLO properties have not been studied adequately [18]. Therefore, to investigate phthalocyanine–ferrocene conjugates is worthwhile.

In the present paper we have synthesized a 12-membered N_2S_2-type macrocycle which connected two ferrocene units via methylene bridges and a metal-free and metallophthalocyanine compound.

2. Experimental

2.1. General and Instrumental

The reagents were used as supplied while the solvents were purified according to the standard procedure before use [19]. The IR spectra were recorded on a Perkin Elmer Spectrum One FTIR Spectrophotometer, using KBr pellets or NaCl disc. ^1H and ^{13}C NMR spectra were recorded on a Varian Mercury 200 MHz spectrometer in $CDCl_3$, and chemical shifts are reported (δ) relative to Me_4Si as internal standard. Mass spectra were measured on a Micromass Quatro LC/ULTIMA LC–MS MS spectrometer. Elemental analysis and metal contents of these compounds were determined by a LECO elemental analyzer and Unicam 929 AA spectrophotometer, respectively. Electronic spectra were recorded at room temperature on a Unicam UV–Vis spectrophotometer. Melting points were determined in open capillaries on an Electrothermal apparatus and were uncorrected. 1,2-Bis(2-iodomercapto-ethyl)-4,5-dicyanobenzene (**1**) [20] and *N*,*N*′-ethylenebis(ferrocenylmethyl)amine (**2**) [21] were synthesized according to reported procedures.

2.2. Synthesis

2.2.1. 12,13-Dicyano-4,7-bis(ferrocenylmethyl)-2,3,4,5,6,7,8,9-octahydrocyclobenzo[k]-4,7-diaza-1,10-dithiacyclododecine (3)

A three-necked flask containing dry acetonitrile (150 ml) and fitted with condenser was evacuated, refilled three times with argon, and connected to vacuum line. Under argon, the flask was charged with **1** (3.325 g, 5 mmol) and three-fold excess of finely ground anhydrous Na_2CO_3 (2.23 g, 21 mmol), anhydrous NaI (0.3 g, 2 mmol) and the mixture was stirred at 40 °C for 1 h. A solution of **2** (3.185 g, 7 mmol) in dry acetonitrile (120 ml) was added to this mixture under argon atmosphere and the reaction mixture was refluxed and stirred for 210 h. The reaction was monitored by thin layer chromatography [silica gel (chloroform:methanol) (95:5)]. At the end of this period, the mixture was cooled to room temperature and filtered using Celite as the filtering agent and washed with dry acetonitrile and then solvent was evaporated to dryness under reduced pressure. Brown oily crude product was purified by using column chromatography technique [silica gel (chloroform:methanol) (95:5)]. After combining the appropriate fractions, the solvent was removed under reduced pressure and the pale brown oily product was obtained. Yield: 1.68 g (34.3%).

Anal. Calc. for $C_{36}H_{36}N_4S_2Fe_2$: C, 61.71; H, 5.14; N, 8.00. Found: C, 61.47; H, 4.88; N, 8.36%. IR (NaCl disc, cm^{-1}): 3076 (Ar–H), 2919–2846 $(C–H)_{alip.}$, 2229 ($C\equiv N$), 1568, 1514 (C=C), 1459, 1415, 1333, 1265, 1117, 771. ^1H NMR ($CDCl_3$): δ 7.46 (m, 2 H, Ar–H), 4.05 (m, 18 H, C_5H_5), 3.37 (s, 8H, NCH_2), 2.68 (s, 4H, CH_2), 2.58 (s, 4H, SCH_2). ^{13}C NMR ($CDCl_3$): δ 115.10 (ArC), 117.50 ($ArC\equiv N$), 132.80 (ArCH), 138.10 (ArCS), 82.28 (C_5H_5), 68.87 (C_5H_5), 68.21 (C_5H_5), 68.11 (C_5H_5), 52.56 (NCH_2), 47.38 (CH_2), 28.67 (SCH_2). MS (*m*/*z*): 701 $[M+1]^+$.

2.2.2. Metal-free phthalocyanine (4)

Dinitrile derivative **3** (1.485 g, 1.08 mmol), 1.8 ml of dry *n*-pentanol, 0.33 ml of DBU and catalytic amount of pyridine was placed under argon atmosphere in a standard Schlenk tube and degassed several times. The reaction mixture was heated and stirred at 170 °C for 24 h under argon. After cooling to room temperature, the mixture was filtered and washed with dry methanol.The filtrate was evaporated to dryness under reduced pressure and chromatographed on a silica column [eluent chloroform:petroleum ether (60:40)] to give dark green solid product which dried in vacuo. Yield: 0.2 g (% 26.3), m.p. >300 °C.

Anal. Calc. for $C_{144}H_{146}N_{16}S_8Fe_8$: C, 61.70; H, 5.20; N, 7.99. Found: C, 61.63; H, 5.31; N, 7.58%. IR (KBr pellets, cm^{-1}): 3202(N–H), 3084(Ar–H), 2925–2854 $(C–H)_{alip.}$,1646 (C=N), 1585, 1511, 1444, 1367, 1322, 1261, 1204, 1105. ^1H NMR ($CDCl_3$): δ 7.64 (s, 4H, Ar–H), 7.47 (s, 4H, Ar–H), 4.21–4.01 (m, 72H, C_5H_5), 3.21 (m, 32H, CH_2N), 2.44 (m, 16H, CH_2S), 1.59 (s, 16H, CH_2). ^{13}C NMR ($CDCl_3$): δ 163.04 (C=N), 135.55 (ArCS), 131.35 (ArCH), 129.23 (ArC), 82.05(C_5H_5), 68.93 (C_5H_5), 68.38 (C_5H_5), 68.17(C_5H_5), 53.39 (NCH_2), 48.61 (CH_2), 29.75 (SCH_2). UV–Vis [(in $CHCl_3 \lambda_{maks}$/nm $10^{-5}\varepsilon$ (mol^{-1} cm^{-1}))] : 696 (5.27), 676 (5.29), 630 (4.88), 355 (4.67), 270 (4.95), 243 (5.01). MS (m/z) = 2826 $[M+Na+1]^+$.

2.2.3. Nickel(II) Phthalocyanine (5)

A mixture of the metal-free phthalocyanine **4** (0.12 g, 0.043 mmol), anhydrous $NiCl_2$ (0.0055 g, 0.043 mmol) and 1 ml of dry quinoline was added into a sealed tube under argon atmosphere and then the reaction mixture was heated and stirred for 15 h at 210 °C After cooled to room temperature, the crude product was diluted with 5 ml of methanol and filtered off, washed with dry methanol and then dried *in vacuo*. The solid product was purified on a silicagel column using pyridine:methanol (100:1) as