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Synthesis and characterization of 1,4-dihydropyridine-substituted metallophthalocyanines

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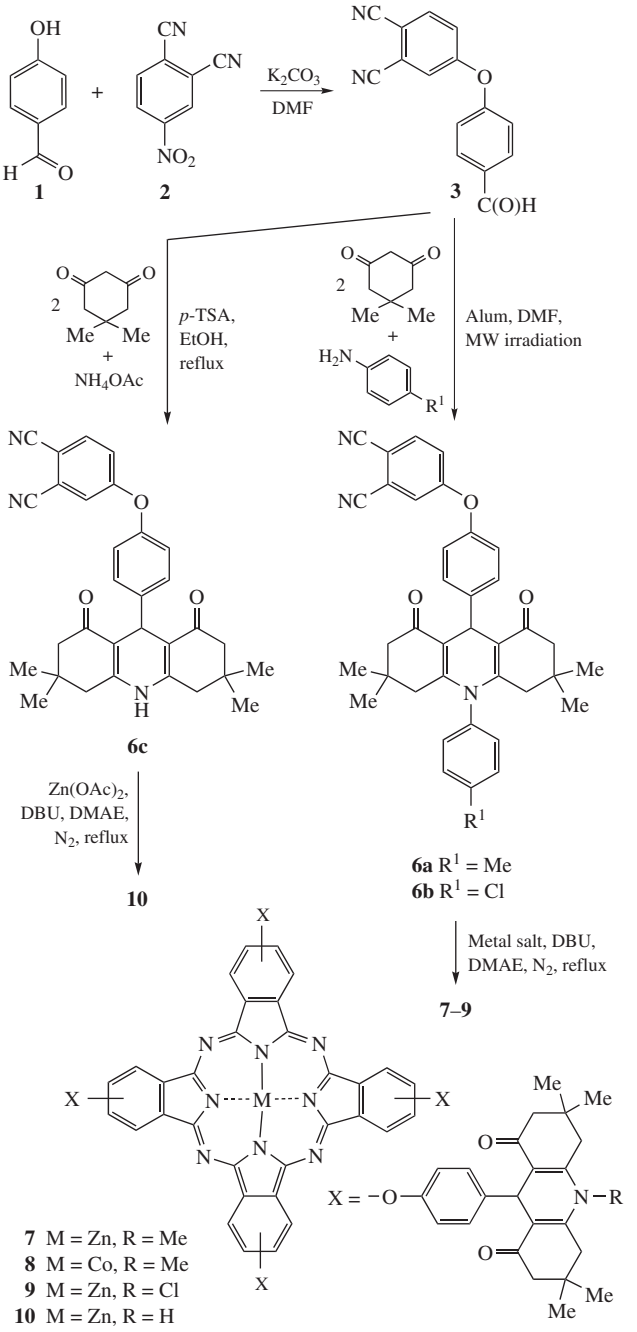
New phthalocyanines bearing 1,4-dihydropyridine fragments were synthesized by cyclotetramerization of phthalonitrile derivatives and the corresponding metal salts.

Phthalocyanines bearing heterocyclic group have received considerable attention due to their chemistry, biochemistry and photochemistry.[1] Among them phthalocyanines with xanthenes,[2] L-prolinol,[3] imidazole,[4] bis(indolyl)methane,[5] thiophene,[6] pyridine,[7] triazol[8] *etc.* are known. These compounds showed interesting electrical, electrochemical and electrochromic properties.[9] Thus, synthesis of phthalocyanines bearing other heterocycles, with the aim to develop new bioactive molecules is an active area of research.

1,4-Dihydropyridines (DHPs) and their derivatives have attracted strong interest for the treatment of cardiovascular diseases, such as angina pectoris[10] and hypertension.[11] They are also an interesting class of photochromic materials, for example, the coloured form of DHP in the solid state is very stable.[12] Recently, 1,4-dihydropyridines were reported as compounds possessing ability to scavenge $^1O_2$.[13]

In continuation of our previous work on the synthesis of heterocycle-functionalized phthalocyanines[2,4,5] and 1,4-dihydropyridines[14] and due to the resultant pharmacological interest in compounds which belong to these families, here we describe the synthesis and characterization of a new class of metallophthalocyanines containing DHPs (Scheme 1).

Phthalonitrile derivatives **6a–c** were synthesized in two steps.† The first involves the nucleophilic aromatic nitro substitution in 4-nitrophthalonitrile under the action of 4-hydroxybenzaldehyde in the presence of anhydrous K_2CO_3 as the base in DMF.[5] The



Scheme 1

† *General procedure for the preparation of* **6a**,**b**. A solution of 4-(4-formylphenoxy)phthalonitrile **3** (1 mmol), dimedone (2 mmol) and Alum (0.1 mmol), in 1 ml DMF was stirred at room temperature. Then 4-methylaniline (1 mmol) or 4-chloroaniline (1 mmol) was added and the mixture was irradiated in a microwave oven at 300 W for 4 min. After completion of the reaction, the mixture was cooled to room temperature. Ethanol (2 ml) and water (1 ml) were added to the reaction mixture, the resulting precipitate was separated and washed with hot water and ethanol.

General procedure for preparation of **6c**. A solution of 4-(4-formylphenoxy)phthalonitrile **3** (1 mmol), dimedone (2 mmol), *p*-TSA (0.1 mmol), ammonium acetate (1.5 mmol) in ethanol (20 ml) was refluxed at 80 °C for 12 h. Then to the resulting solution some water was added to precipitate the product. The resulting solid residue was filtered off and washed with hot water and hot ethanol.

4-{4-[3,3,6,6-Tetramethyl-10-(4-methylphenyl)-1,8-dioxo-1,2,3,4,5,6,7,8,9,10-decahydro-9-acridinyl]phenoxy}phthalonitrile **6a**: yield 83%. IR (KBr, ν_{max}/cm^{-1}): 3043, 2928, 2960, 2231, 1641, 1574, 1498, 1359, 1621, 850, 570. ^{1}H NMR (300 MHz, DMSO-d_6) δ: 7.65 (d, 1H, H_{arom}, J 8.4 Hz), 7.46 (d, 2H, H_{arom}, J 8.4 Hz), 7.29 (d, 2H, H_{arom}, J 6.0 Hz), 7.22 (s, 1H, H_{arom}), 7.15 (d, 1H, H_{arom}, J 8.1 Hz), 7.06 (d, 2H, H_{arom}, J 6.0 Hz), 6.91 (d, 2H, H_{arom}, J 8.1 Hz), 5.24 (s, 1H, CH), 2.44 (s, 3H, Me), 2.20–1.83 (m, 8H, CH_2), 0.94 (s, 6H, Me), 0.77 (s, 6H, Me).

product of this step was reacted with 2 equiv. of dimedone and 4-methylaniline, 4-chloroaniline or ammonium acetate to access **6a–c**. The desired metallophthalocyanines **7–10** were obtained by cyclotetramerization of dinitrile compounds **6a–c** (3 mmol) in the presence of anhydrous metal salts [$CoCl_2$ and $Zn(OAc)_2$] (1 mmol) using DBU as a base in 2-(dimethylamino)ethanol (DMAE) under reflux.‡ These complexes showed good thermal stability (Table S1, Online Supplementary Materials). The primary weight loss is related to the residual solvent and water which is a typical of a TGA heating run. The initial decomposition temperatures of the compounds are in the order: **9** > **7** > **10** > **8**.

Phthalocyanine **7** is soluble in THF, chloroform and DMF, phthalocyanine **8** is soluble in chloroform and DMF, whereas phthalocyanines **9**, **10** show good solubility in DMSO and DMF. The UV-VIS spectra of compounds **7–10** in DMF are shown in Figure 1.

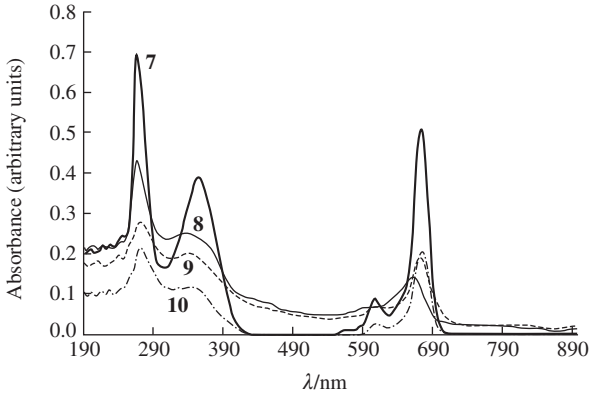


Figure 1 Absorption spectra of complexes **7–10** in DMF (C = 30 μmol dm^{-3}).

4-{4-[10-(4-Chlorophenyl)-3,3,6,6-tetramethyl-1,8-dioxo-1,2,3,4,5,6,7,8,9,10-decahydro-9-acridinyl]phenoxy}phthalonitrile **6b**: yield 78%. IR (KBr, ν_{max}/cm^{-1}): 3086, 3047, 2962, 2935, 2879, 2231, 1641, 1593, 1487, 1361, 1284, 850, 524. ^{1}H NMR (300 MHz, DMSO-d_6) δ: 7.66 (d, 2H, H_{arom}, J 7.5 Hz), 7.48 (m, 2H, H_{arom}), 7.19 (m, 4H, H_{arom}), 6.91 (m, 3H, H_{arom}), 5.48 (s, 1H, CH), 1.99 (m, 8H, CH_2), 0.95 (s, 6H, Me), 0.78 (s, 6H, Me).

4-[4-(3,3,6,6-Tetramethyl-1,8-dioxo-1,2,3,4,5,6,7,8,9,10-decahydro-9-acridinyl)phenoxy]phthalonitrile **6c**: yield 68%. IR (KBr, ν_{max}/cm^{-1}): 3313, 3205, 3061, 3040, 2985, 2931, 2872, 2231, 1628, 1593, 1485, 1423, 1392, 572, 524. ^{1}H NMR (300 MHz, DMSO-d_6) δ: 11.94 (s, 1H, NH), 7.70 (d, 1H, H_{arom}, J 8.4 Hz), 7.30 (d, 2H, H_{arom}, J 2.1 Hz), 7.18 (m, 2H, H_{arom}), 6.67 (d, 2H, H_{arom}, J 8.4 Hz), 5.53 (s, 1H, CH), 2.45 (m, 8H, CH_2), 1.23 (s, 6H, Me), 0.89 (s, 6H, Me).

‡ *General procedure for preparation of metallophthalocyanines* **7–10**. A mixture of compound **6** (3 mmol), metal salt [anhydrous $Zn(OAc)_2$ or $CoCl_2$] (1 mmol), DBU (3 drops) and DMAE (10 ml) was refluxed under nitrogen for 12 h. The reaction mixture was then cooled to room temperature. Ethanol was then added and the product was filtered under suction. The green solid was washed several times with hot ethanol.

Zinc(II) phthalocyanine **7**: yield 42%. IR (KBr, ν_{max}/cm^{-1}): 3055, 2957, 2872, 1716, 1639, 1601, 1502, 1473, 1363, 1300, 1261, 1224, 1165, 1122, 954, 846. ^{1}H NMR (300 MHz, DMSO-d_6) δ: 7.56–6.95 (m, 44H, H_{arom}), 5.29 (4H, CH), 2.45 (12H, Me), 2.25–1.90 (m, 32H, CH_2), 0.99–0.84 (48H, Me). MS (MALDI-TOF), m/z: 2392 (M$^+$).

Cobalt(II) phthalocyanine **8**: yield 39%. IR (KBr, ν_{max}/cm^{-1}): 2957, 2918, 2850, 1641, 1500, 1471, 1363, 1222, 1097, 1016, 956, 848, 729. MS (MALDI-TOF), m/z: 2385 (M$^+$).

Zinc(II) phthalocyanine **9**: yield 41%. IR (KBr, ν_{max}/cm^{-1}): 3041, 2943, 2874, 1714, 1635, 1599, 1491, 1473, 1394, 1365, 1228, 1163, 1091, 1014, 943, 746. MS (MALDI-TOF), m/z: 2474 (M$^+$).

Zinc(II) phthalocyanine **10**: yield 45%. IR (KBr, ν_{max}/cm^{-1}): 3383, 3261, 3043, 2951, 1714, 1602, 1504, 1473, 1394, 1369, 1232, 1176, 1085, 945, 837. ^{1}H NMR, δ: 7.70–7.19 (m, 4H + 28H, NH + H_{arom}), 5.40 (4H, CH), 2.50–2.09 (32H, CH_2), 1.04–0.98 (48H, Me). MS (MALDI-TOF), m/z: 2030 (M$^+$).

For more details, see Online Supplementary Materials.

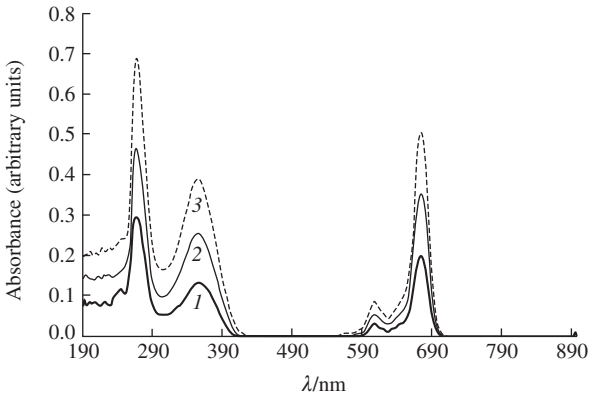


Figure 2 Absorption spectra of complex **7** in DMF at concentrations of (*1*) 10, (*2*) 20 and (*3*) 30 μmol dm^{-3}.

The aggregation behaviour of phthalocyanines **7–10** at five concentrations (50, 40, 30, 20 and 10 μmol dm^{-3}) in DMSO, DMF, chloroform and THF was studied. The intensity of the absorption bands was increased with growing concentration and there were no new bands due to the aggregated species. So, phthalocyanines **7–10** did not form aggregates in these solvents at different concentrations. Phthalocyanine **7** did not show aggregation in THF, DMF and $CHCl_3$ (Figure 2). The aggregation behaviours of synthesized compounds were initiated at concetration of 500 μmol dm^{-3}.

In conclusion, we have synthesized and characterized four new metallophthalocyanines **7–10** which possess good solubility and do not undergo aggregation in DMF, DMSO, THF and $CHCl_3$.

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Online Supplementary Materials

Supplementary data associated with this article can be found in the online version at doi:10.1016/j.mencom.2013.07.016.

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