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Research Article

One-Pot Synthesis of Metallopyrazinoporphyrazines Using 2,3-Diaminomaleonitrile and 1,2-Dicarbonyl Compounds Accelerated by Microwave Irradiation

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A one-pot microwave-assisted synthesis of metallopyrazinoporphyrazines as porphyrazine derivatives carrying six-membered pyrazine rings annulated at the periphery of the tetrapyrrolic macrocycle is described starting from 2,3-diaminomaleonitrile, 1,2-dicarbonyl compounds, metal salts, and urea.

1. Introduction

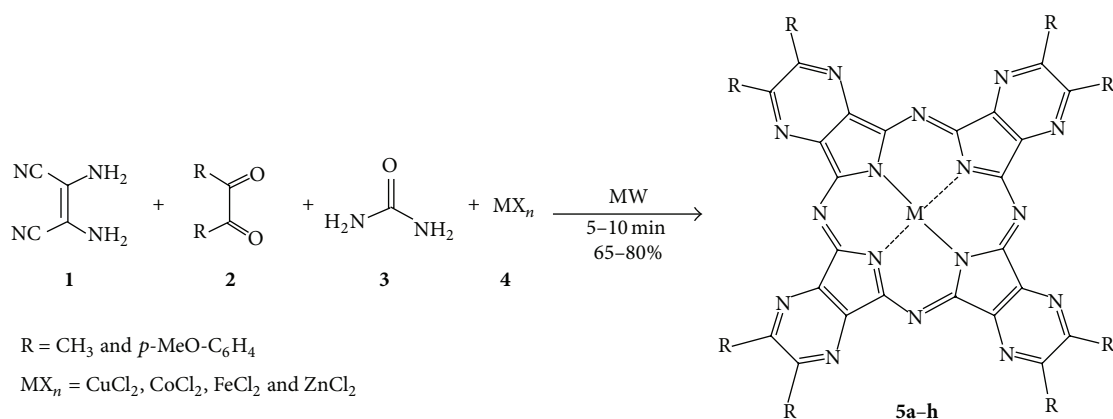
Tetrapyrrolic macrocycles of porphyrins, phthalocyanines, and related compounds, modified by the attachment of peripheral substituents, have attracted significant attention for many years because of their industrial applications in diverse areas, especially in modern technologies [1–4], such as elaboration of Langmuir-Blodgett films [5–7], chemical sensors [8, 9], nonlinear optical materials [10–12] biomedical agents for diagnosis, and therapy [13] as well as sensitizers in solar cells [14–16].

Porphyrazines (Pzs), as an important class of phthalocyanine analogues or porphyrinoid macrocycles, carrying heterocyclic rings, such as diazepine, pyridine, and pyrazine rings, directly annulated to the pyrrole rings of the porphyrazine core, have been presented in recent years as optical agents with clear advantages over the porphyrins [17–25]. Porphyrins are either naturally occurring molecular systems or original synthetic products, whereas Pzs are derived exclusively from synthetic laboratory work. An area of further expansion of new Pzs macrocycles can be directed to the synthesis of new phthalocyanines-like macrocycles opening a route to new forms of investigation and promising potential practical applications [26].

Metal complexes of Pzs (MPzs) ligands have been at the focus of interest because of their high electronic delocalization, biological significance, and numerous potential technological applications such as electronic, magnetic, photophysical, and photosensitizing properties of Pzs [27–31]. It has been found that functional groups fused to the peripheral positions of MPzs are integrated to the macrocyclic core more effectively than that of phthalocyanines [32–34]. It implies that the modification of the structure influences the photosensitizing properties [35].

There are only a few reports for the synthesis of Pzs under mild and efficient conditions. On the other hand, attempts for direct synthesis of Pzs carrying unprotected vicinal NH₂ groups from 2,3-diaminomaleonitrile were unsuccessful [17–20]. Due to the importance of these macrocycles, introduction of new, efficient, and inexpensive protocol for this purpose is of prime importance.

Microwave-assisted organic reactions are well known as environmentally benign transformations that can improve a diverse area of chemical processes. In particular, the reaction time and energy input of these processes are assumed to be mostly reduced in comparison with reactions of a long duration at high temperatures under conventional heating conditions [36].

SCHEME 1: Synthesis of MPPzs **5a-h**.

In continuation of our study to develop new procedures in various types of chemical transformations [37–41], herein, we wish to study the synthesis of MPPzs (**5a-h**) by a one-pot coupling reaction of 2,3-diaminomaleonitrile (**1**), various 1,2-dicarbonyl compounds (**2**), urea (**3**), and metal salts (**4**) under microwave irradiation conditions (Scheme 1).

2. Results and Discussion

In a typical experiment, the synthesis of MPPzs was carried out by mixing 2,3-diaminomaleonitrile **1** (1 mmol) with 1,2-dicarbonyl compounds **2** (1 mmol), urea **3** (4 mmol), and metal salts **4** (0.5 mmol) under microwave irradiation conditions. In this step, the reaction conditions were optimized with various molar ratios of raw materials. It was found that, the molar ratio of 1 : 1 : 4 : 0.5 from **1** : **2** : **3** : CuCl₂·2H₂O obtained the best results under microwave irradiation conditions. As the reaction proceeded after 5 min colorful solid gradually appeared at medium power level option of microwave oven. After completion of the reaction, the crude product was washed with water and filtered off and the solid residue purified further by washing with EtOH to give pure MPPz of **5a** in 80% yield. It is important to note that in the absence of CuCl₂·2H₂O or urea the yield of reaction intensively decreased. In addition, excess amounts of them did not increase the yield of the reaction considerably.

To explore the scope and limitations of the reaction, the optimized protocol was applied to other substrates. The procedure was extended to various raw materials and different metal salts such as CoCl₂, FeCl₂·4H₂O, and ZnCl₂. As can be seen from Table 1, the different starting materials are converted to MPPzs in good yields after 5–10 min. In general, these results showed that the CuCl₂·2H₂O among metal salts and 1,2-*bis*(4-methoxyphenyl) ethane-1,2-dione within dicarbonyl compounds produce the best yields.

PPzs of metal salt are prepared efficiently from 1,2-*bis*(4-methoxyphenyl) ethane-1,2-dione. However, synthesis of these compounds from biacetyl was not so successful and yields of the reaction were lower than the other derivatives. As a result, the reaction gave excellent results in the cases of using aromatic 1,2-dione, independently of the metal salts.

In comparison with the previously reported multistep procedures [17, 18, 26, 42], this work has some advantages such as higher yields, atom economy, and mild reaction conditions. Furthermore, our protocol does not require any protection/deprotection of functional groups (Scheme 2) [42].

In summary, we have described an efficient microwave-assisted procedure for the synthesis of porphyrazine derivatives carrying six membered pyrazine rings annulated at the periphery of the tetrapyrrolic macrocycle starting from simple and readily available precursors including 2,3-diaminomaleonitrile, 1,2-dicarbonyl compounds, metal salts, and urea. This new multicomponent protocol for the preparation of synthetically, biologically, and technologically relevant MPPzs includes some important aspects like the fast and simple reaction, easy workup procedure, and high atom economy.

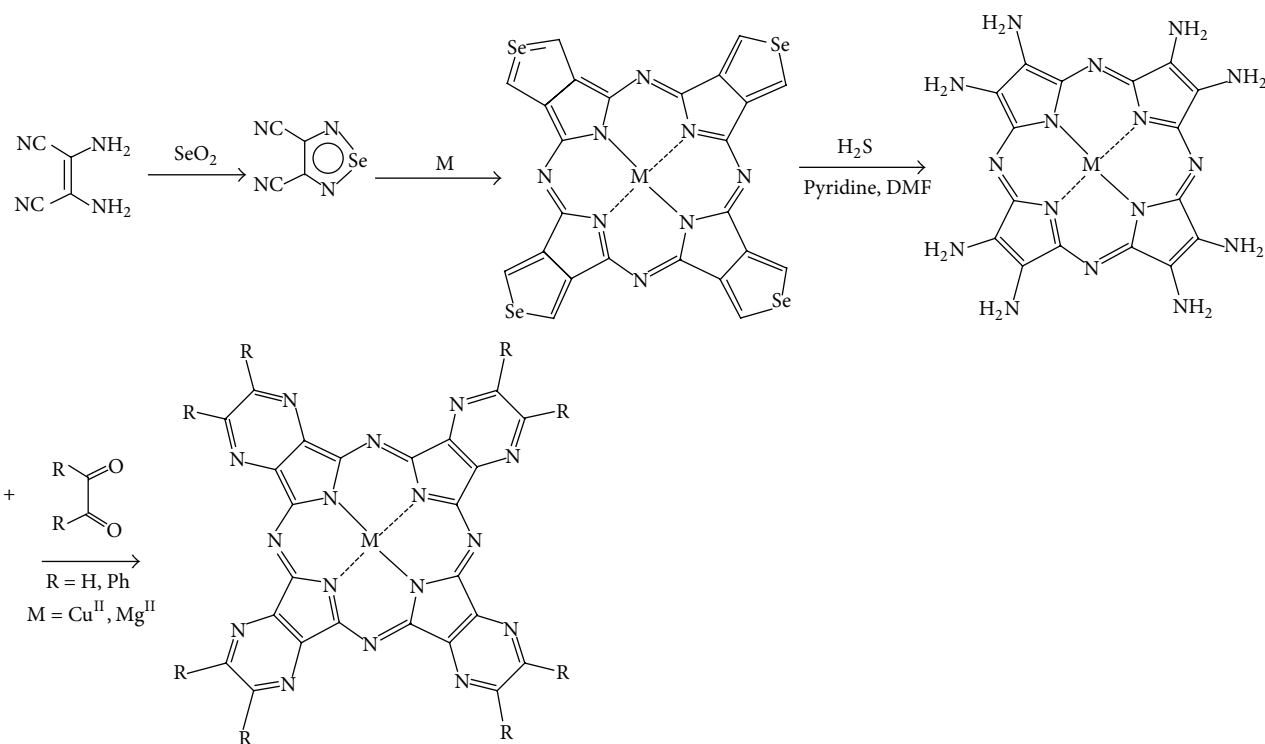
3. Experimental

3.1. Materials and Equipment. All solvents, chemicals, and reagents were purchased from Merck, Fluka, and Sigma-Aldrich international chemical companies. Melting points were measured on an Electrothermal 9200 apparatus and are uncorrected. IR and UV-Vis spectra were recorded with a Shimadzu IR-470 spectrometer and UV-Vis Shimadzu 2100, respectively. The elemental analyses were performed with an Elementar Analysensysteme GmbH VarioEL. The microwave oven was a Samsung model GE-4020W (max. 900 W) with five power level options (option used for this experiment: medium 50% power).

3.2. General Procedure for the Preparation of MPPzs (5a-h). 2,3-Diaminomaleonitrile (1 mmol), 1,2-dicarbonyl compound (1 mmol), metal salt (0.5 mmol), and urea (4 mmol) were taken in a round bottomed flask. Then, the resulting mixture was irradiated in a domestic microwave oven at medium state for appropriate time. As the reaction proceeded, colorful solid gradually appeared. After completion of the reaction, the crude product was washed with water (4 × 10 mL) to give dark-green solid. Then, the precipitated solid

TABLE 1: Microwave-assisted synthesis of MPPzs 5a-h.

Product	R	MX_n	Time (min)	Yield ^a (%)
5a	CH ₃	CuCl ₂ ·2H ₂ O	5	80
5b	<i>p</i> -CH ₃ O-C ₆ H ₄	CuCl ₂ ·2H ₂ O	6	78
5c	CH ₃	CoCl ₂	10	68
5d	<i>p</i> -CH ₃ O-C ₆ H ₄	CoCl ₂	7	74
5e	CH ₃	FeCl ₂ ·4H ₂ O	10	65
5f	<i>p</i> -CH ₃ O-C ₆ H ₄	FeCl ₂ ·4H ₂ O	8	73
5g	CH ₃	ZnCl ₂	10	66
5h	<i>p</i> -CH ₃ O-C ₆ H ₄	ZnCl ₂	8	70

^aIsolated yield.

SCHEME 2: Reported multistep synthesis of MPPzs.

was dried under vacuum and the solid residue was purified by washing three times in boiling EtOH (3 × 5 mL) until the filtrate was colorless. The solid was dissolved in DMF and filtered through a cartridge filter to remove any inorganic impurities that may have been present. Concentration of the filtrate afforded **5a-h** as dark green to blue solids.

The prepared compounds were known and the data are comparable to the literature reports [17, 18, 26, 42].

3.3. Characterization of the Products. **5a:** Dark blue solid; mp > 200°C. IR (KBr): ν , cm⁻¹ 1604 (m), 1500 (w), 1457 (m), 1415 (m), 1328 (w), 1282 (m), 1166 (s), 1085 (m), 1067 (m), 897 (m), 871 (m), 799 (s), 775 (m), 752 (w). UV-Vis (DMSO): λ_{max} , nm 638, 556, 445. Anal. Calcd for C₃₂H₂₄CuN₁₆: C, 55.21; H, 3.47; N, 32.19. Found C, 55.34; H, 3.56; N, 32.10.

5b: Dark blue solid; mp > 200°C. IR (KBr): ν , cm⁻¹ 1602 (m), 1500 (w), 1457 (m), 1415 (s), 1328 (w), 1282 (m), 1166 (s), 1085 (m), 1067 (m), 897 (m), 871 (m), 799 (s), 775 (w), 752 (w). UV-Vis (DMSO): λ_{max} , nm 655, 564, 457. Anal. Calcd for C₈₀H₅₆CuN₁₆O₈: C, 67.05; H, 3.94; N, 15.64. Found C, 67.12; H, 4.08; N, 15.53.

5c: Dark greenish blue solid; mp > 200°C. IR (KBr): ν , cm⁻¹ 1604 (m), 1515 (w), 1485 (m), 1420 (s), 1326 (s), 1284 (m), 1153 (w), 1085 (s), 1024 (m), 948 (m), 910 (w), 871 (m), 778 (s), 756 (m). UV-Vis (DMSO): λ_{max} , nm 615, 597, 420. Anal. Calcd for C₃₂H₂₄CoN₁₆: C, 55.58; H, 3.50; N, 32.41. Found C, 55.63; H, 3.46; N, 32.58.

5d: Dark green solid; mp > 200°C. IR (KBr): ν , cm⁻¹ 1604 (m), 1516 (w), 1484 (m), 1420 (s), 1326 (m), 1284 (s), 1153 (m), 1115 (s), 1085 (w), 1024 (m), 948 (w), 912 (m), 871 (w), 778 (s), 756 (m). UV-Vis (DMSO): λ_{max} , nm 625, 617, 426. Anal.

Calcd for $C_{80}H_{56}CoN_{16}O_8$: C, 67.27; H, 3.95; N, 15.69. Found C, 67.36; H, 4.13; N, 15.52.

5e: Light olive gray solid; mp > 200°C. IR (KBr): ν , cm^{-1} 1601 (m), 1478 (w), 1448 (m), 1404 (s), 1327 (m), 1278 (s), 1152 (m), 1112 (w), 1087 (w), 884 (m), 775 (s), 748 (m). UV-Vis (DMSO): λ_{max} , nm 654, 645, 569. Anal. Calcd for $C_{32}H_{24}FeN_{16}$: C, 55.82; H, 3.51; N, 32.55. Found C, 55.93; H, 3.42; N, 32.67.

5f: Light olive gray solid; mp > 200°C. IR (KBr): ν , cm^{-1} 1601 (m), 1478 (w), 1448 (m), 1404 (s), 1327 (s), 1278 (m), 1150 (w), 1088 (m), 884 (w), 775 (s), 749 (m). UV-Vis (DMSO): λ_{max} , nm 668, 662, 575. Anal. Calcd for $C_{80}H_{56}FeN_{16}O_8$: C, 67.42; H, 3.96; N, 15.72. Found C, 67.56; H, 4.15; N, 15.67.

5g: Light greenish blue solid; mp > 200°C. IR (KBr): ν , cm^{-1} 1600 (m), 1462 (s), 1416 (s), 1325 (m), 1282 (w), 1158 (m), 1112 (m), 1065 (w), 948 (m), 864 (w), 775 (s), 752 (m). UV-Vis (DMSO): λ_{max} , nm 642, 563, 414. Anal. Calcd for $C_{32}H_{24}N_{16}Zn$: C, 55.06; H, 3.47; N, 32.10. Found C, 54.98; H, 3.52; N, 32.27.

5h: Dark greenish blue solid; mp > 200°C. IR (KBr): ν , cm^{-1} 1600 (m), 1462 (s), 1415 (m), 1325 (s), 1282 (m), 1158 (w), 1112 (m), 1065 (m), 948 (w), 864 (m), 775 (s), 752 (w). UV-Vis (DMSO): λ_{max} , nm 658, 602, 498, 388. Anal. Calcd for $C_{80}H_{56}N_{16}O_8Zn$: C, 66.97; H, 3.93; N, 15.62. Found C, 67.06; H, 4.10; N, 15.53.

Conflict of Interests

The authors declare that there is no conflict of interests regarding the publication of this paper.

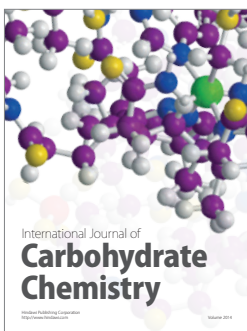
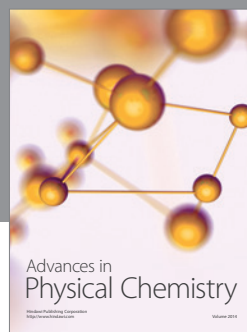
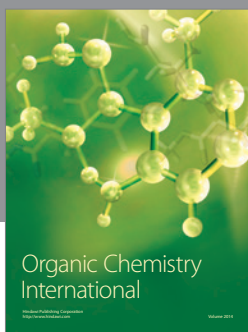
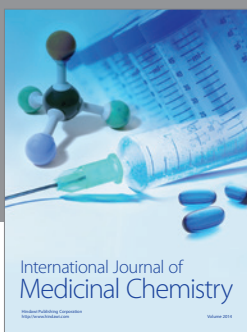
Acknowledgment

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