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Synthesis of and Ion Recognition by the Novel Schiff Base Macrocyclic Compounds Containing Triazine[1]

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Abstract—Several novel Schiff base macrocyclic compounds containing triazine were synthesized from cyanuric chloride, diethylamine, *p*-nitrophenol, *p*-phthalaldehyde, *m*-phthalaldehyde, and *o*-phthalaldehyde. Triazine macrocycles were synthesized using the high dilution method and their structures were elucidated by IR, NMR and electrospray ionization-mass spectrometry (ESI-MS).

Keywords: ion recognition, macrocycles, Schiff base, triazin

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INTRODUCTION

Design and synthesis of new molecular recognition receptors for metal ions has been the important aspect of organic and supramolecular chemistry [1–4]. Due to their unique spatial configuration macrocyclic compounds play an important role in molecular recognition [5–8]. Since the earliest study reported by Pilkington and Robson [9] great progress has been done in research [10–13] of Schiff base macrocycles particularly those based on coordination of N, O and other hetero atoms.

Triazine macrocyclic compounds demonstrated high potential application in molecular recognition [14–19]. However, this did not refer to Schiff base containing macrocycles [20, 21]. In the current publication we present synthesis of several triazine-containing Schiff base macrocyclic compounds (Scheme 1) that have high potential in metal ions recognition.

RESULTS AND DISCUSSION

Method. There are two synthetic approaches to Schiff base macrocyclic compounds: the template method [22, 23] and the high dilution method [24, 25]. Stability of Schiff base macrocycles was supported by a template ion. In our experiments the compounds **II–IV** were synthesized according to the high dilution method and stabilized by template ions.

Concentration of reagents and the method of addition of those had significant impact on the products. For example, the direct addition of reagents in the concentration of 0.01 mol/L gave a complex mixture (Fig. 1a). Drop wise addition of dialdehyde to compound **I** (0.01 mol/L) gave the product **II** with some impurities (Fig. 1b). The highest purity of the product was achieved by the direct addition of compound **I** (0.005 mol/L) and dropwise addition of dialdehyde (Fig. 1c). Therefore, the conditions were used in the cyclization reaction.

IR spectra of compounds **II–IV** demonstrated no bands in the area of 1605–1800 cm^{-1} indicating the complete cyclization of dialdehyde and diamine.

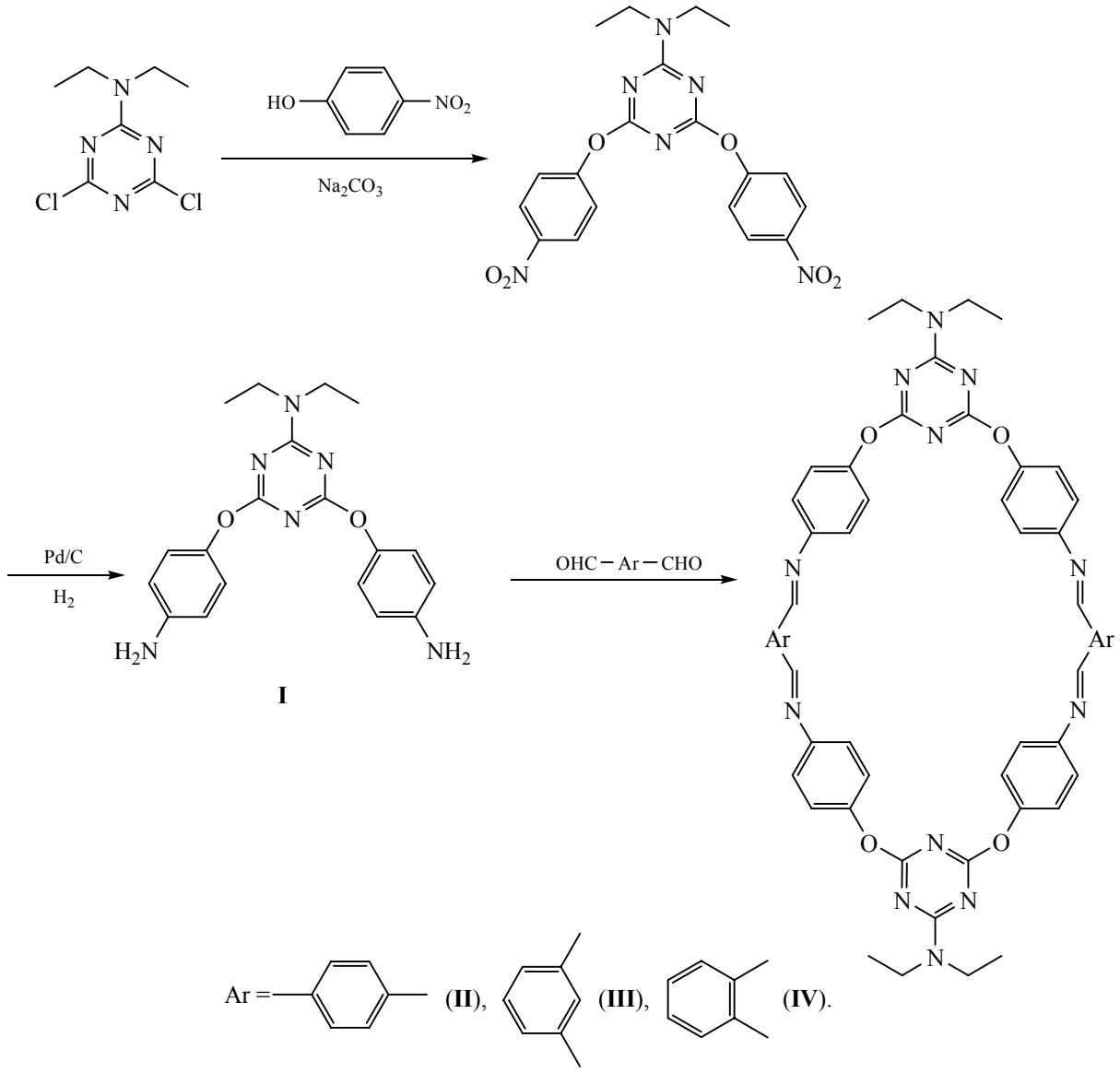
Because of poor solubility of compound **II** in $CHCl_3$ and DMSO its ^{13}C NMR spectrum could not be measured accurately.

High resolution mass spectra of compounds **II–IV** indicated the [2+2] cyclization mode of compound **I** and dialdehyde.

Recognition of metal ions. UV-Vis absorption of compounds **II–IV** were recorded with simple cationic species such as Cd^{2+}, Co^{2+}, Cu^{2+}, Fe^{3+}, Li^{+}, Mg^{2+}, Mn^{2+}, Na^{+}, Ni^{2+}, and Zn^{2+}. Spectra of macrocyclic

[1] The text was submitted by the authors in English.

Scheme 1. Synthesis of compounds **I–IV**.



compounds **III** and **IV** demonstrated a significant shift in chloroform–ethanol solutions in the presence of Fe^{3+}, Cu^{2+}, and Zn^{2+}(Figs. 2b and 2c). The spectrum of macrocyclic compound **II** displayed a substantial shift only with Fe^{3+} (Fig. 2a) indicating its specific recognition of Fe^{3+}.

UV-Vis titration experiments for compound **II** demonstrated that the increase in Fe^{+3} concentration caused the absorption intensity at 350 nm to decrease and eventually disappear. The effect was accompanied by the rise of a new peak at 258 nm (Fig. 3a), which indicated formation of a stable complex of the macrocycle with Fe^{3+}. In the experiment the limit of detection of Fe^{+3} was 1×10^{-6} mol/L. At 350 nm the value of K_s was determined to be 1.18×10^9.

The Job's plot between the product **II** and Fe^{3+} (Fig. 3b) disclosed that the binding ratio of compound **II** to Fe^{3+} was 1 : 2.

EXPERIMENTAL

All reagents were commercially available and used without further purification. Melting points were measured with XT-4 Microscopic melting point apparatus. IR spectra (KBr discs) were recorded on an EQUINOX55 FT-IR spectrophotometer. NMR spectra

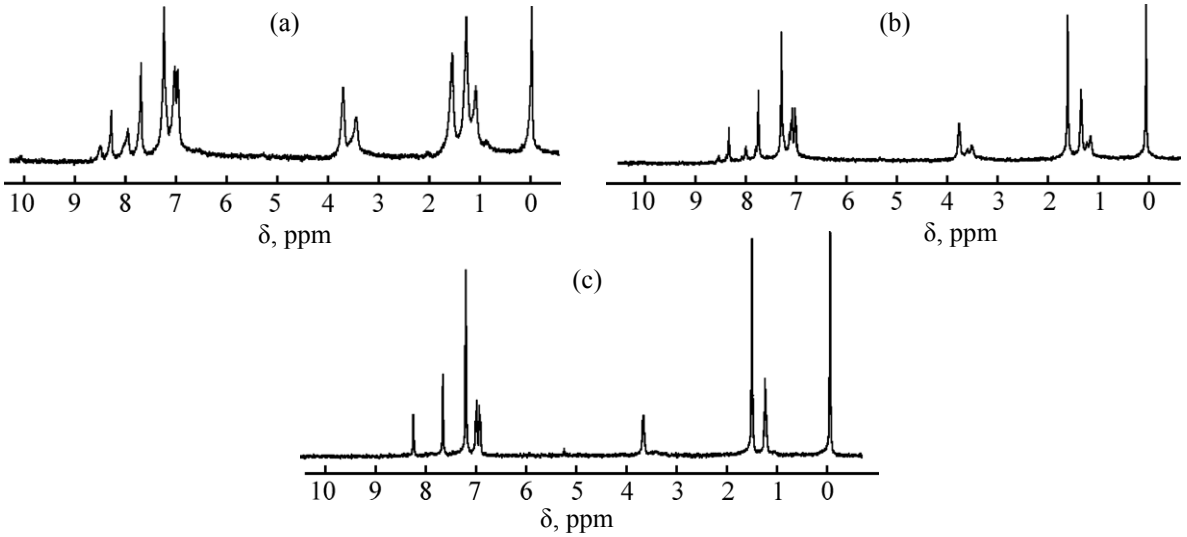


Fig. 1. [1]H NMR spectra of compound **II** formed under different experimental conditions. (a) solvent: MeOH, concentration of the reactants: 0.01 mol/L, compound **I** and 1,4-phthalaldehyde were added directly under reflux; (b) solvent: MeOH, concentration of the reactants: 0.01 mol/L, compound **I** was added directly while the 1,4-phthalaldehyde was added dropwise into the solution under reflux; and (c) solvent: MeOH, concentration of the reactants: 0.005 mol/L, compound **I** was added directly while the 1,4-phthalaldehyde was added dropwise into the solution under reflux.

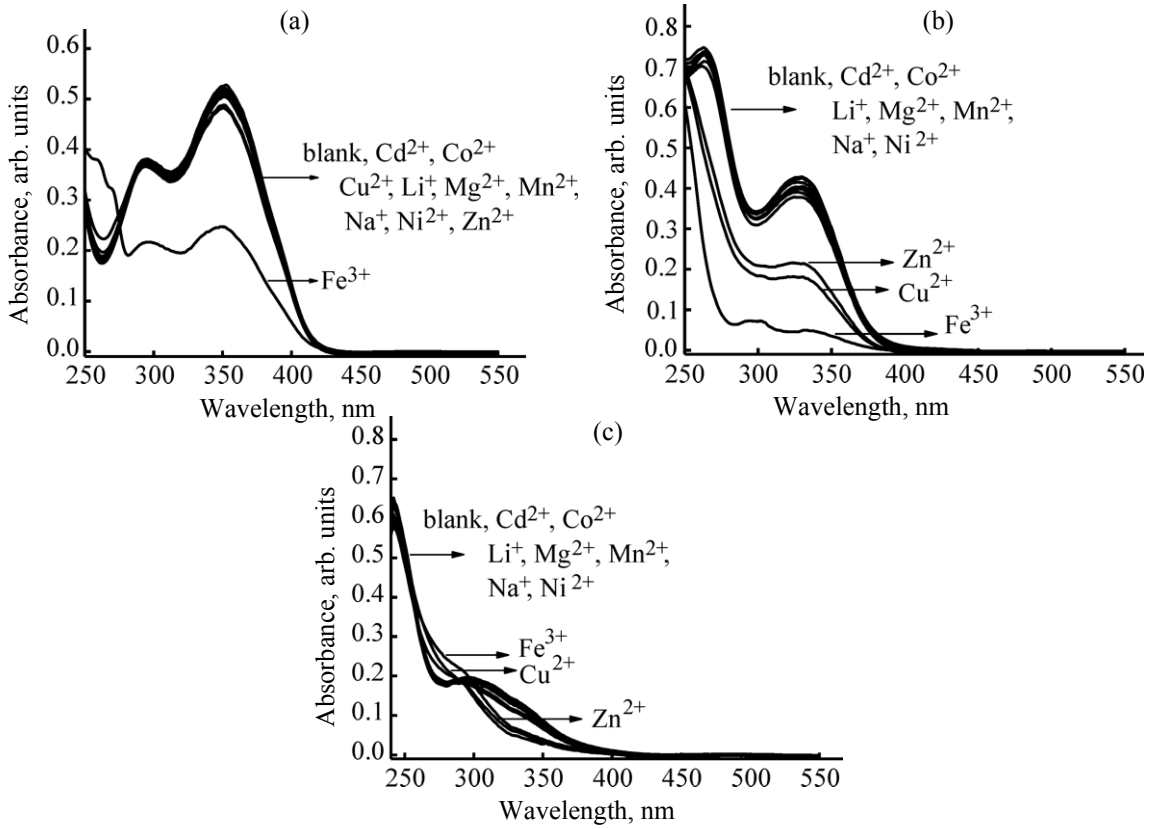


Fig. 2. UV-Vis spectra of the products (1×10^{-5} mol/L) in the presence of various metal cations (2×10^{-5} mol/L): (a) **II**, (b) **III**; and (c) **IV**.

were measured with a Varian INOVA-400MHz spectrometer. High resolution mass spectra (HRMS) were recorded on a Bruker MicrOTOF-QII electrospray ionization-mass spectrometer (ESI-MS). UV-Vis spectra were recorded with a Shimadzu WFH-203B spectrophotometer.

Synthesis of compound I. A solution of 4,6-dichloro-*N,N*-diethyl-1,3,5-triazin-2-amine [25] (3.30 g, 15 mmol) and *p*-nitrophenol (4.17 g, 30 mmol) in 1,4-dioxane (40 mL) was added to a solution of Na_2CO_3 (3.25 g) in water (20 mL). The reaction mixture was heated to reflux and stirred for 36 h. Upon cooling it down to room temperature the mixture was filtered off under vacuum and the yellow residue was recrystallized from THF to give a light yellow crystalline solid 5.67 g. The solid, Pd/C (5%, 1.75 g) and methanol–ethyl acetate (volume ratio 1 : 3) (60 mL) were added in the autoclave. The reaction mixture was heated to 70ºC at the pressure of 1.0 kPa and stirred for 12 h. The product **I** was obtained as dark red crystals upon the solvent removal under reduced pressure. Yield 84%, mp 199–200ºC. IR spectrum, ν, cm^{-1}: 3390, 3315, 2973, 2930, 1608, 1506, 1547, 1426, 1368, 1199, 1063, 832, 792. Found, %: C 62.45; H 6.33; N 22.67. $C_{19}H_{22}N_6O_2$. Calculated, %: C 62.30; H 6.01; N 22.95. ESI-MS, *m/z*. Found 367.1861. $C_{19}H_{23}N_6O_2$. Calculated 367.1877. [$M + H^+$].

Synthesis of compounds II–IV. A solution of phthalaldehyde (0.5 mmol) in anhydrous methanol (40 mL) was added dropwise to a solution of compound **I** (0.5 mmol) in anhydrous methanol (60 mL). The reaction mixture was heated to reflux and stirred under nitrogen for 8 h. The reaction mixture was filtered off and the filter cake was washed repeatedly with hot methanol and ethanol. The residue was dried naturally.

Compound **II** was synthesized from *p*-phthalaldehyde as a light yellow powder. Yield 36%, mp >300ºC. IR spectrum, ν, cm^{-1}: 2972, 2930, 2869, 1605, 1522, 1494, 1377, 1215, 1077, 841, 807. ^{1}H NMR (400 MHz, $CDCl_3$), δ, ppm: 1.29 t (12H, J = 6.2 Hz), 3.72 q (8H, J = 6.5 Hz), 7.02 d.d (16H, J = 7.7 Hz), 7.72 s (8H), 8.31 s (4H). Found, %: C 69.70; H 5.11; N 17. 98. $C_{54}H_{48}N_{12}O_4$. Calculated, %: C 69.83; H 5.17; N 18.10. ESI-MS, *m/z*. Found 929.3912. $C_{54}H_{49}N_{12}O_4$. Calculated 929.4000. [$M + H^+$].

Compound **III** was synthesized from *m*-phthalaldehyde as a white powder. Yield 29%, mp 262-263ºC. IR spectrum, ν, cm^{-1}: 2973, 2932, 2867, 1585, 1528, 1493, 1457, 1374, 1193, 1092, 846, 804, 749, 689; ^{1}HNMR spectrum (400 MHz, $CDCl_3$), δ, ppm: 1.28 t (12H, J = 7.0 Hz), 3.71 q (8H, J = 6.9 Hz), 6.99 d.d (16H, J = 8.7 Hz), 7.51–7.58 m (2H), 8.24 s (4H), 7.60–7.67 m (4H), 8.05 s (2H). ^{13}CNMR spectrum (101 MHz, $CDCl_3$), δ_C, ppm: 172.3, 166.4, 159.4, 150.8, 148.9, 136.9, 134.3, 130.4, 129.7, 122.7, 121.7, 42.2, 13.1. Found, %: C 69.94; H 5.26; N 18.04. $C_{54}H_{48}N_{12}O_4$. Calculated, %: C 69.83; H 5.17; N 18.10. ESI-MS, *m/z*. Found 929.3933. $C_{54}H_{49}N_{12}O_4$. Calculated 929.4000. [$M + H^+$].

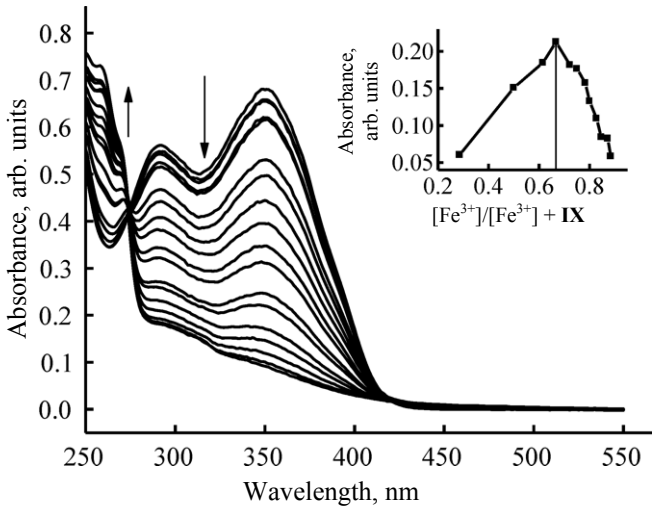


Fig. 3. (a) Titration curves of the compound **II** (1×10^{-5} mol/L) in $CHCl_3$–EtOH solution (volume ratio 4 : 1) upon addition of Fe^{3+}. (b) Job's plot between the compound **II** and Fe^{3+} in $CHCl_3$–EtOH solution.

Compound **IV** was synthesized from *o*-phthalaldehyde as a yellow powder. Yield 28%, mp 204–205ºC. IR spectrum, ν, cm^{-1}: 2967, 2931, 2868, 1571, 1533, 1496, 1454, 1377, 1218, 1090, 848, 814, 781, 756. ^{1}H NMR (400 MHz, $CDCl_3$), δ, ppm: 1.30 t (12H, J = 6.9 Hz), 3.71 q (8H, J = 6.8 Hz), 6.65–6.81 m (16H), 6.98–7.06 m (4H), 7.32–7.44 m (4H), 7.98 s (4H). ^{13}C NMR spectrum (101 MHz, $CDCl_3$), δ_C, ppm: 172.1, 166.3, 162.5, 151.1, 145.7, 133.3, 132.4, 122.9, 121.9, 119.2, 42.3, 13.0. Found, %: C 69.72; H 5.07; N 18.23. $C_{54}H_{48}N_{12}O_4$. Calculated, %: C 69.83; H 5.17; N 18.10. ESI-MS, *m/z*. Found 929.4024. $C_{54}H_{49}N_{12}O_4$. Calculated 929.4000. [$M + H^+$].

Ion recognition experiment. UV-Vis spectra were recorded on a Shimadzu WFH-203B spectrophotometer. The stock solution of each of compound **II–IV** was prepared in chloroform, concentration 1×10^{-4} mol/L. The stock solutions (1×10^{-4} mol/L) of Cd^{2+}, Co^{2+}, Cu^{2+}, Fe^{3+}, Li^+, Mg^{2+}, Mn^{2+}, Na^+, Ni^{2+}, and Zn^{2+} perchlorates in ethanol were used. UV-Vis test solutions were prepared by mixing 1 mL of a solution of a compound **II–IV** with 2 mL of a metal stock solution in a 10 mL colorimetrical cylinder. The cylinder was filled with chloroform. The spectra were recorded at 25ºC.

CONCLUSIONS

Several Schiff base macrocycles containing triazine were synthesized and characterized. Their specific recognition for ten metal ions has been tested. UV-Vis absorption spectra indicated the Schiff base macrocycle 2 specific potential in recognition of Fe^{3+}.

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