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PYRAZINE-2,3-DICARBONITRILES SUBSTITUTED WITH MALEIMIDE DERIVATIVES

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Syntheses and spectroscopic characteristics are reported for eight pyrazine-2,3-dicarbonitriles substituted with maleimide residue in addition to phenyl, 2-thienyl, or 2-furyl substituent.

Keywords: 2-furyl, maleimide, pyrazine-2,3-dicarbonitrile, 2-thienyl, zinc azaphthalocyanine.

Pyrazine-2,3-dicarbonitrile may be used for preparation of azaphthalocyanines (AzaPcs) or, more accurately, tetrapyrazinoporphyrazines [1]. Substituents in positions 5 and 6 of pyrazine-2,3-dicarbonitrile may affect, for instance, solubility and UV-vis absorption of the target AzaPcs. However, as compared to phthalocyanines, there is limited knowledge of substituent effects on AzaPcs.

Previously we have prepared metal, i.e., Cu, Ni, Mg, and Zn, complexes of AzaPcs with sulphanyl, oxo, or amino substituents [2-4]. We observed the exchange of both oxo and some sulphanyl substituents with nucleophiles during cyclotetramerizations, whereas amino substituents caused slow cyclizations due to a strong electron donation by nitrogen. Maleimide substituents are not expected to cause either of the mentioned problems, but two maleimide substituents in adjacent positions at the pyrazine ring would certainly induce a steric strain. Therefore, we decided to test a combination of one maleimide substituent and either one phenyl, 2-thienyl, or 2-furyl substituent. The two unsaturated substituents at the pyrazine ring are expected to cause the chromophoric system extension of a target AzaPc.

Compounds **1a–c**, *viz.*, 5-chloro-6-phenylpyrazine-2,3-dicarbonitrile (**1a**), 5-chloro-6-(2-thienyl)pyrazine-2,3-dicarbonitrile (**1b**), and 5-chloro-6-(2-furyl)pyrazine-2,3-dicarbonitrile (**1c**) are known [5]. We used compounds **1** for the preparation of compounds **2**–**4,** which are shown below.

The dimethylmaleimide substituent of compounds **2** was used as a reference for maleimide, but is expected to give somewhat better solubility in organic solvents. The introduction of sulfur in conjugation with the maleimide carbonyl groups of compounds **3** is expected to induce interesting electronic effects on the maleimide chromophoric system. Many years ago the diimino derivative of 5,6-dihydro-1,4-dithiin- 2,3-dicarboximide was found to be a reactive monomer for the reactions of porphyrazines [6]. More recently, the same monomer was used to prepare mixed porphyrazines [7]. The electronic spectra of these compounds were found to have an additional absorption band at 525-595 nm due to the $n \rightarrow n^*$ excitation of the *n*-electrons on sulfur. As for compounds **4**, our original intention was to introduce two thiomorpholine substituents into 3,4-dichloromaleimide. However, other researchers have pointed out that only one amino substituent will be introduced into 3,4-dichloromaleimide [8]. We decided to use monosubstituted thiomorpholinyl maleimide, since the electronic effects of this group might be of interest as well.

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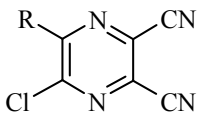

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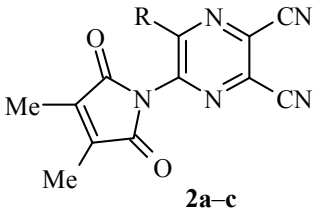
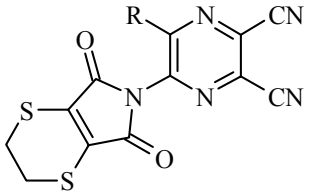
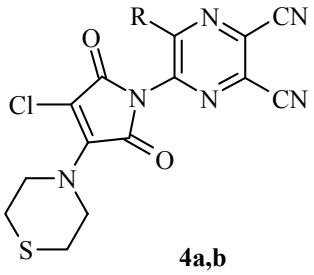


2a–c



3a–c



4a,b

1–4 **a** R = Ph, **b** R = 2-thienyl, **c** R = 2-furyl

For preparations of compounds **2–4** from **1**, the maleimide anions were prepared. We have chosen the 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU) salts due to their good solubility, except for one reaction of compound **1c** where the dimethylmaleimide DBU salt caused extensive decomposition. Therefore, the potassium salt of dimethylmaleimide was used to prepare **2c**. However, compounds **2** were obtained in merely 20% yields, and consequently will be of little interest for further reactions.

Compounds **3** and **4** are yellow fluorescent powders, and the UV-vis absorptions of the thienyl and furyl derivatives are found at λ_{max} 365 nm, whereas the phenyl derivatives show broad absorptions with shoulders from 410 to approximately 300 nm.

Cyclotetramerizations of compounds **3** and **4** with zinc(II) acetate and quinoline gave ZnAzaPcs with λ_{max} 655 nm for phenyl-substituted compounds, and at 675 nm for the thienyl- or furyl-substituted macrocycles. The low solubilities of these compounds made purification difficult, and only the macrocyclic products **5a** and **5b** from the 2-thienyl-substituted monomers **3b** and **4b** are reported. These products are mixtures of four constitutional isomers due to unsymmetrical monomers. The elemental analyses for compounds **5a** and **5b** are unsatisfactory, with too high zinc level and low values for both sulfur and nitrogen.

We have reported syntheses and spectroscopic analyses of compounds **2–4**, pyrazine-2,3-dicarbonitriles, which are substituted with one maleimide derivative in addition to phenyl-, 2-thienyl-, or 2-furyl substituents. These compounds are not well suited for the intended purpose, i.e., preparation of ZnAzaPcs. Two zinc complexes **5a–b** were prepared from cyclotetramerizations of compounds **3b** and **4b**, but purification and separation of the expected product isomers was not successful due to low solubility in organic solvents. However, compounds **2–4** are well characterised and might find some alternative use.

EXPERIMENTAL

EI mass spectra of compounds **1–4** were obtained on a Finnigan MAT 95XL spectrometer at 70 eV electron energy and 1.0 mA electron current. IR spectra were obtained on a Nicolet 20-SXC FT IR spectrometer in KBr. ^{1}H and ^{13}C NMR spectra were recorded on a Bruker Avance DPX 400 NMR spectrometer at 399 and 100 MHz, respectively, in $CDCl_3$ (compounds **1a–c**, **2a**,**b**, **4a**,**b**) and $(CD_3)_2CO$ (compounds **2c**, **3a–c**). UV-vis spectra were

obtained on a Cary 50 UV-vis spectrophotometer in DCM (compounds **2**–**4**) and pyridine (compounds **5a**,**b**). Melting points were obtained on a Büchi 530 melting point apparatus and are uncorrected. Microanalyses were performed by Analytische Laboratorien GmbH, Lindlar, Germany. The analytical samples were dried at 50°C/HV prior to analyses. Merck Kieselgel 60F 254 was used for TLC and Merck silica 63-200: was used for column chromatography. Compounds **1a–c** were prepared similarly to [5].

Compounds 1 (General Method). A mixture of equimolar amounts of diaminomaleonitrile and phenylglyoxylic acid, 2-thienylglyoxylic acid, or 2-furylglyoxylic acid, dissolved in water, were stirred at ambient temperature for 1-2 h. The crude hydroxypyrazines, which were obtained in 70-90% yields, were heated with phosphorus oxychloride and pyridine at mp 90°C for 2 h, poured on ice, extracted with DCM, and chromatographed on silica with dichloromethane.

5-Chloro-6-phenylpyrazine-2,3-dicarbonitrile (**1a**). Yield 64%; mp 138-139°C (mp 139-141°C [5]). ^{1}H NMR spectrum, δ, ppm: 7.60 (3H, s); 7.93 (2H, s). ^{13}C NMR spectrum, δ, ppm: 112.48 (CN), 112.81 (CN), 129.38, 130.47, 132.79, 129.95, 131.27 (C-2, pyrazine), 133.30 (C-3, pyrazine), 150.62 (C-5, pyrazine), 157.35 (C-6, pyrazine).

5-Chloro-6-(2-thienyl)pyrazine-2,3-dicarbonitrile (**1b**). Yield 61%; mp 124-125°C (mp 115-117°C [5]). ^{1}H NMR spectrum, δ, ppm (*J*, Hz): 7.29 (1H, dd, J_{34} = 4, J_{45} = 5, H-4, thiophene); 7.86 (1H, dd, J_{45} = 5, J_{35} = 1, H-5); 8.47 (1H, dd, J_{34} = 4, J_{35} = 1, H-3). ^{13}C NMR spectrum, δ, ppm: 112.32 (CN), 112.39 (CN), 127.25, 129.69, 130.64 (C-4, thiophene), 135.25 (C-5), 136.51 (C-3), 146.28, 149.93.

5-Chloro-6-(2-furyl)pyrazine-2,3-dicarbonitrile (**1c**)**.** Yield 80%; mp 121-122°C (mp 118–119°C [5]). ^{1}H NMR spectrum, δ, ppm (*J*, Hz): 6.57 (1H, dd, J_{34} = 3.7, J_{45} = 1.7, H-4, furan); 7.67 (1H, d, J_{34} = 3.7, H-3); 7.68 (1H, dd, J_{45} = 1.7, J_{35} = 0.6, H-5). ^{13}C NMR spectrum, δ, ppm: 112.12 (CN), 112.24 (CN), 113.84, 121.96, 127.22, 130.76, 145.07, 145.68, 146.58, 149.04.

Compounds 2. **Dimethylmaleimide and its DBU and Potassium Salts**. Dimethylmaleimide was prepared from dimethylmaleic anhydride and ammonium acetate [9], mp 110-114°C.

The reaction of equimolar amounts of dimethylmaleimide and DBU in acetone gave an oil upon removal of the solvent. Trituration with diethyl ether and hexane gave a white powder (54%), mp 69-71°C.

The reaction of equimolar amounts of dimethylmaleimide and potassium *t*-butoxide in methanol gave a white powder (58%), mp >300°C.

Compounds 2a,**b** were prepared from acetone solutions of the DBU-imide salt and compound **1a** or **1b**. Acetone was removed from the dark blue reaction mixture, and the residue was chromatographed on silica with DCM. Compound **2c** was prepared from the potassium-imide salt, the phase transfer catalyst "Aliquat" and compound **1c** dissolved in DCM.

5-(3,4-Dimethyl-2,5-dioxopyrrolin-1-yl)-6-phenylpyrazine-2,3-dicarbonitrile (**2a**). A white powder; yield 20%; mp 158-160°C. IR spectrum, ν, cm^{-1}: 2237 (w, CN), 1715 (s, C=O), 1397 (s), 1415, 1339, 1290, 1074, 1008, 814, 764, 729, 709, 694. ^{1}H NMR spectrum, δ, ppm: 2.02 (6H, s); 7.55 (5H, m). ^{13}C NMR spectrum, δ, ppm: 9.31, 112.44 (CN), 112.77 (CN), 128.17, 129.53, 130.23, 131.98, 132.14, 133.78, 139.78, 142.59, 156.44, 168.36. Mass spectrum, *m*/*z* (I_{rel}, %): 329 [M] (100), 330 (21.1). Found, M: 329.0913. $C_{18}H_{11}N_5O_2$. Calculated, M: 329.0913.

5-(3,4-Dimethyl-2,5-dioxopyrrolin-1-yl)-6-(2-thienyl)pyrazine-2,3-dicarbonitrile (**2b**). A yellow fluorescent powder; yield 21%, mp 172-173°C. IR spectrum, ν, cm^{-1}: 2235 (w, CN), 1731 (s, C=O), 1711 (s, C=O), 1524, 1414 (s), 1387 (s), 1353, 1330, 1278, 1073, 856, 792, 730. UV-vis, λ_{max}, nm (ε): 365 (23 000). ^{1}H NMR spectrum, δ, ppm (*J*, Hz): 2.13 (6H, s); 7.19 (1H, dd, J_{34} = 4, *J* = 5, H-4, thiophene); 7.69 (1H, dd, J_{45} = 5, J_{35} = 1, H-5); 7.91 (1H, dd, J_{34} = 4, J_{35} = 1, H-3). ^{13}C NMR spectrum, δ, ppm: 112.35 (CN), 112.49 (CN), 128.24, 129.39, 132.37, 133.45, 134.73, 135.25, 139.72, 140.26, 150.43, 168.74. Mass spectrum, *m*/*z* (I_{rel}, %): 335 [M] (100), 336 (16.0), 337 (5.4). Found, M: 335.0478. $C_{16}H_9N_5O_2S$. Calculated, M: 335.0477.

5-(3,4-Dimethyl-2,5-dioxopyrrolin-1-yl)-6-(2-furyl)pyrazine-2,3-dicarbonitrile (**2c**). Yield 20%, mp 210-212°C. IR spectrum, ν, cm^{-1}: 2238 (w, CN), 1732 (s, C=O), 1708 (s, C=O), 1575, 1527, 1465 (s), 1432 (s),

1300, 1086, 1009, 795, 723, 706. UV-vis, λ_{max}, nm (ε): 365 (19 000). ^{1}H NMR spectrum, δ, ppm (*J*, Hz): 2.10 (6H, s); 6.76 (1H, dd, J_{34} = 3.7, J_{45} = 1.8, H-4, furan); 7.59 (1H, m, H-3); 7.88 (1H, m, H-5). ^{13}C NMR spectrum, δ, ppm: 8.13, 113.23 (CN), 113.36 (CN), 113.62, 119.10, 128.98, 132.86, 138.27, 139.38, 144.38, 148.04, 148.57. Mass spectrum, *m*/*z* (I_{rel}, %) 319 [M] (100), 320 (17.7), 321 (2.2). Found, M: 319.0701. $C_{16}H_9N_5O_3$ Calculated, M: 319.0705.

Compounds 3. 5,6-Dihydro-1,4-dithiin-2,3-dicarboximide and its DBU Salt. Dichloromaleimide was prepared by heating dichloromaleic anhydride and urea in acetic acid for 10 min. Yield 56%; mp 172–174°C (mp 173-174°C [10]). A solution of dichloromaleimide (1.66 g, 10 mmol) and ethane-1,2-dithiol (0.94 g, 10 mmol) in DMF (10 ml) was heated at mp 170-180°C for 1.5 h. The solvent was removed under reduced pressure and the residue was treated with DCM and water. 5,6-Dihydro-1,4-dithiin-2,3-dicarboximide, a yellow powder, insoluble in both phases, was obtained. Yield 1.1 g (59%); mp 190-205°C (mp 217°C [6]). ^{1}H NMR spectrum, ($CDCl_3$), δ, ppm: 3.33 (4H, s). 5,6-Dihydro-1,4-dithiin-2,3-dicarboximide (1.1 g, 5.9 mmol) and DBU (0.9 g, 6 mmol) were stirred in acetone (30 ml) at ambient temperature for 1 h. Most of the solvent was removed under reduced pressure, diethyl ether was added, and the product was filtered off. Yield 1.9 g (95%), mp 138-144°C (dec).

Compounds 3 (General procedure). Compounds **1** were stirred with an equimolar amount of the DBU-salt of 5,6-dihydro-1,4-dithiin-2,3-dicarboximide in acetone at ambient temperature for 1 h. The crude products were chromatographed on silica with DCM.

5-(4,7-Dioxo-4,5,6,7-tetrahydro-1,4-dithiino[2,3-*c*]pyrrol-2-yl)-6-phenylpyrazine-2,3-dicarbonitrile (**3a**). A yellow fluorescent powder; yield 64%, mp 325°C (dec). IR spectrum, ν, cm^{-1}: 2241 (w, CN), 1713 (s, C=O), 1542, 1396 (s), 1336, 1289, 1203, 1137, 1091, 1066, 982, 921, 855, 783, 699 (s). UV-vis, λ_{max}, nm (ε): 420 (6 000), 352 sh (11 000), 323 sh (15 000), 285 (20 000). ^{1}H NMR spectrum, δ, ppm: 3.63 (4H, s); 7.69 (3H, m); 7.88 (2H, m). ^{13}C NMR spectrum, δ, ppm: 26.23, 113.41 (CN), 128.01, 129.20, 131.34, 132.39, 134.15, 142.0, 156.0, 163.10. Mass spectrum, *m*/*z* (I_{rel}, %): 391 [M] (100), 392 (21.9), 393 (11.7). Found, M; 391.0187. $C_{18}H_9N_5O_2S_2$ Calculated, M: 391.0198.

5-(4,7-Dioxo-4,5,6,7-tetrahydro-1,4-dithiino[2,3-*c*]pyrrol-2-yl)-6-(2-thienyl)pyrazine-2,3-dicarbonitrile (**3b**). Yield 70%; mp 286-290°C (dec). IR spectrum, ν, cm^{-1}: 2238 (w, CN), 1717 (s, C=O), 1546, 1525 (s), 1420 (s), 1387 (s), 1325, 1198 (s), 1127, 1061, 918, 846, 730 (s), 696, 670. UV-vis, λ_{max}, nm (ε): 437 sh (5 000), 365 (20 000). ^{1}H NMR spectrum, δ, ppm (*J*, Hz): 3.51 (4H, s); 7.30 (1H, dd, J_{45} = 5, J_{34} = 4, H-4, thiophene); 7.99 (1H, dd, J_{34} = 4, J_{35} = 1.1 , H-3); 8.08 (1H, d, J_{35} = 1.1, H-5). ^{13}C NMR spectrum, δ, ppm: 26.21, 113.50 (CN), 113.62 (CN), 128.92, 129.98, 132.78, 132.96, 133.22, 135.40, 135.46, 137.41, 148.22, 163.72. Mass spectrum, *m*/*z* (I_{rel}, %): 397 [M] (100), 398 (17.4), 399 (14.4), 400 (2.6). Found, M: 396.9759. $C_{17}H_7N_5O_2S_3$. Calculated, M: 396.9762.

5-(4,7-Dioxo-4,5,6,7-tetrahydro-1,4-dithiino[2,3-*c*]pyrrol-2-yl)-6-(2-furyl)pyrazine-2,3-dicarbonitrile (**3c**). Yield 57%; mp 270°C (dec). IR spectrum, ν, cm^{-1}: 2235 (w, CN), 1714 (s, C=O), 1574, 1523, 1464, 1394 (s), 1332, 1203 (s), 1016, 894, 857, 775 (s), 730 (s), 698. UV-vis, λ_{max}, nm (ε): 350 (17 000). ^{1}H NMR spectrum, δ, ppm: 3.71 (4H, s); 6.93 (1H, dd, J_{34} = 3.7, J_{45} = .7, H-4, furan); 7.76 (1H, dd, J_{34} = 3.7, J_{35} = 0.8, H-3); 8.07 (1H, dd, J_{45} = 1.8, J_{35} = 0.8, H-5). ^{13}C NMR spectrum, δ, ppm: 26.3, 113.7 (CN), 119.2, 132.4, 148.6, 163.7 (CO). Mass spectrum, *m*/*z* (I_{rel}, %); 381 [M] (100), 382 (17.7), 383 (9.5). Found, M: 380.9983. $C_{16}H_7N_5O_3S_2$ Calculated, M: 380.9990.

Compounds 4. 2-Chloro-3-(thiomorpholin-4-yl)maleimide. A solution of 2,3-dichlo-romaleimide (1.66 g, 10 mmol), thiomorpholine (2.1 g, 20 mmol), and triethylamine (2.2 g, 22 mmol) in acetone (40 ml) was left at ambient temperature for 1 week. Triethylammonium chloride was removed by filtration, the solvent was removed from the filtrate, and the residue was triturated with diethyl ether. An orange powder; yield 1.91 g (91%); mp 180-185°C. ^{1}H NMR spectrum, δ, ppm: 2.78 (4H, s); 4.17 (4H, s). ^{13}C NMR spectrum, δ, ppm: 28.02, 50.89, 141.41, 165.29, 165.54. Mass spectrum, *m*/*z* (I_{rel}, %): 232 [M] (100), 233 (11.2), 234 (35.2). Found, M: 232.0067. $C_8H_9ClN_2O_2S$. Calculated, M: 232.0073.

The DBU-salt of 2-chloro-3-(thiomorpholin-4-yl)maleimide was prepared in acetone and precipitated with diethyl ether. Yield 91%; mp 100-109°C.

Compounds **4** were prepared from compounds **1** and DBU-salt of 2-chloro-3-(thiomorpholin-4-yl)maleimide by the same general procedure as for compounds **3**.

5-[(3-Chloro-2,5-dioxo-4-(thiomorpholin-4-yl)pyrrolin-1-yl]-6-phenylpyrazine-2,3-dicarbonitrile (**4a**). A yellow fluorescent powder; yield 73%; mp 183-185°C. IR spectrum, ν, cm^{-1}: 2236 (w, CN), 1723 (s, C=O), 1621 (s), 1418 (s), 1394 (s), 1338, 1292, 1250, 1215, 952, 816, 755, 730, 703, 689. UV-vis, λ_{max}, nm (ε): 412 sh (8 000), 363 sh (11 000), 320 (16 000). ^{1}H NMR spectrum, δ, ppm: 2.74 (4H, s); 4.12 (4H, s); 7.56 (5H, m). ^{13}C NMR spectrum, δ, ppm: 28.07, 51.36, 97.56, 112.11 (CN), 112.45 (CN), 127.94, 129.40, 129.97, 131.80, 133.43, 141.50, 156.16, 162.21, 162.32. Mass spectrum, *m/z* (I_{rel}, %) 436 [M] (100), 437 (24.5), 438 (37.5). 439 (9.0). Found, M: 436.0497. $C_{20}H_{13}ClN_6O_2S$. Calculated, M: 436.0509.

5-[(3-Chloro-2,5-dioxo-4-(thiomorpholin-4-yl)pyrrolin-1-yl]-6-(2-thienyl)pyrazine-2,3-di-carbonitrile (**4b**). A yellow fluorescent powder; yield 62%; mp 207-208°C (dec). IR spectrum, ν, cm^{-1}: 2235 (w, CN), 1720 (s, C=O), 1614 (s), 1414 (s), 1393, 1350, 1219, 952, 815, 725 (s). UV-vis, λ_{max}, nm (ε): 365 (25 000). ^{1}H NMR spectrum, δ, ppm (*J*, Hz): 2.85 (4H, m); 4.27 (4H, m); 7.25 (1H, dd, J_{45} = 5, J_{34} = 4, H-4, thiophene); 7.75 (1H, dd, J_{45} = 5, J_{35} = 1, H-5); 7.98 (1H, dd, J_{34} = 4, J_{35} = 1, H-3). ^{13}C NMR spectrum, δ, ppm: 28.17, 51.45, 97.96, 112.19 (CN), 112.34 (CN), 128.07, 129.42, 132.49, 133.57, 134.84, 135.00, 138.79, 142.02, 150.37, 162.58, 163.05. Mass spectrum, *m/z* (I_{rel}, %): 406 (11.7), 407 [M–Cl] (19.2), 408 (17.6), 442 [M] (27.2), 443 (6.2), 444 (11.6). Found, M: 442.0063. $C_{18}H_{11}ClN_6O_2S_2$ Calculated, **M**: 442.0074.

Unsymmetrically substituted zinc azaphthalocyanines 5. Compounds 5 were obtained from heating the dicarbonitriles 3b or 4b with Zn(II) acetate and freshly distilled quinoline under a nitrogen blanket at 170-180°C for 10–15 min. The crude products were repeatedly triturated and washed with methanol, water, and acetone until colorless filtrates.

Tetrakis{(4,7-dioxo-4,5,6,7-tetrahydro-1,4-dithiino[2,3-*c*]pyrrol-2-yl)}tetrakis(2-thienyl)octaazaphthalocyaninatozinc(II) (**5a**). A dark-green powder; yield 97%. UV-vis, λ_{max}, nm (ε): 675 (119 000), 610 (29 000), 385 (95 000). Found, %: C 44.67; H 2.27; N 16.07; S 19.00; Zn 6.08. $C_{64}H_{28}N_{20}O_8S_{12}Zn$. Calculated, %: C 46.44; H 1.71; N 16.92; S 23.25; Zn 3.95.

Tetrakis[3-chloro-2,5-dioxo-4-(thiomorpholin-4-yl)pyrrolin-1-yl]tetrakis(2-thienyl)octaazaphthalocyaninatozinc(II) (**5b**). A dark powder; yield 85%. UV-vis, λ_{max}, nm (ε): 675 (142 000), 610 (40 000), 390 (126 000). Found, %: C 46.24; H 3.21; Cl 5.92; N 17.73; S 10.62; Zn 5.78. $C_{72}H_{44}Cl_4N_{24}O_8S_8Zn$. Calculated, %: C 47.08; H 2.41; Cl 7.72; N 18.30; S 13.96; Zn 3.56. TOF-SIMS (Ar^+): A solution of **5b** in $CHCl_3$ was prepared on a clean Ag-substrate. Molecular ion cluster centered at 1837 amu corresponding to $C_{72}H_{45}Cl_4N_{24}O_8S_8Zn$, $[M + H]^+$ was observed. Additional ion at $[M–H]^-$ was found.

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