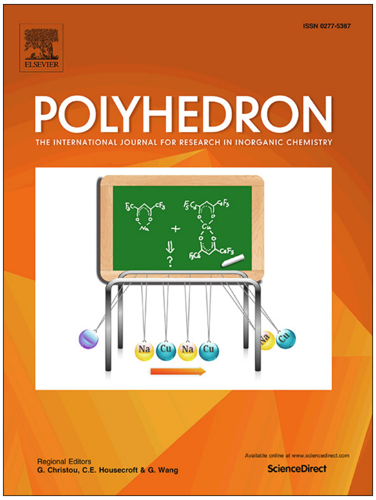

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Synthesis, structural diversity, luminescent properties and antibacterial effects of cadmium(II) and silver(I) coordination compounds with bis(1,2,3-benzotriazol-1-yl)alkanes

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Abstract

A series of bis(benzo-1,2,3-triazolyl)alkanes were prepared by the reaction of 1,2,3-benzotriazole with the corresponding dibromoalkanes. Individual isomers of these flexible polydentate ligands were separated by selective copper(II) chloride complex formation. Seven new coordination compounds of 1,3-bis(benzo-1,2,3-triazol-1-yl)propane (L_3), 1,4-bis(benzo-1,2,3-triazol-1-yl)butane (L_4) and 1,6-bis(benzo-1,2,3-triazol-1-yl)hexane (L_6) with cadmium(II) or silver(I) nitrates were prepared, characterized by single crystal X-Ray diffraction, IR spectroscopy, thermogravimetric analysis and luminescence studies. It was found that depending on the solvent used, cadmium(II) nitrate forms discrete binuclear complex with the ligand L_3 in acetone and 1D coordination polymer in acetonitrile. Ligands L_4 and L_6 with longer linkers formed 2D coordination polymers with silver nitrate both in acetone and acetonitrile. Silver coordination polymer with L_6 demonstrated bactericidal effect towards *Staphylococcus albus*, *Pseudomonas aeruginosa* and *Klebsiella pneumonia* bacteria.

Keywords: benzotriazole; cadmium; silver; coordination polymers; crystal structure

Introduction

Bis(benzotriazolyl)alkanes possess a range of valuable biological and chemical properties. Presence of four potential donor nitrogen atoms and conformational flexibility allows them to form coordination compounds demonstrating a wide variety of structures [1]. Most of these compounds are coordination polymers [2–4], but several examples of discrete complexes of 1,2-bis(benzotriazol-1-yl)ethane (**L_2**) [5–7] and 1,3-bis(benzotriazol-1-yl)propane (**L_3**) [8,9] were reported. The majority of coordination compounds reported in the literature contain ligands with relatively short linkers (1 to 4 methylene groups, **L_1-L_4**) and only several coordination polymers with penta- (**L_5**) of hexamethylene (**L_6**) linkers are known. Thus, 1D copper(I) bromide [10,11], cadmium(II) bromide [7] and 3D copper(I) chloride [12] coordination polymers with **L_6** were prepared and structurally characterized Quan-Guo Zhai et al. Very recently 1D copper(I) iodide coordination polymers with promising photophysical properties making them excellent candidates for yellow-emitting phosphors were prepared [13]. Copper(I) [14] and palladium(II) [15] *in situ* formed complexes were used as catalysts for C-N and C-C cross-coupling reactions. A variety of cadmium(II) [7,16], copper(I) [17,18] and silver(I) [6] coordination polymers demonstrated luminescent properties. Two-dimensional silver coordination polymer with **L_3** exhibited third-order non-linear optical properties [19]. In most of coordination compounds bis(benzotriazol-1-yl)alkanes adopt a $N^3,N^{3'}$-bridging coordination mode, but in some cases they act as $N^3,N^2,N^{2'},N^{3'}$-tertradentate bridging two metallocenters in a coordination polymer chain. All previously reported and structurally characterized coordination compounds with **L_3-L_6** ligands are listed in Table 1. The ligands themselves were tested as antibacterial agents [20,21]. Compounds **L_2**, **L_4** and **L_6** were more potent corrosion inhibitors compared to 1,2,3-benzotriazole and anticorrosion activity increased with hydrocarbon linker elongation [22].

Table 1. Coordination compounds of bis(1,2,3-benzotriazolyl)alkanes reported in the literature

Compound (dimensionality)	Benzotriazole ligand coordination mode	Properties studied	Reference
$[(CdI_2)_2(\mathbf{L_3})]_\infty$ (1D)	$N^3,N^{3'}$-bridging	photoluminescence	[7]
$[(CdBr_2)_2(\mathbf{L_4})]_\infty$ (2D)	$N^3,N^{3'}$-bridging, $M_6L_4Br_2$ 48-membered cycles	photoluminescence	[7]
$[(CdBr_2)_2(\mathbf{L_6})_2]_\infty$ (1D)	$N^3,N^{3'}$-bridging, M_2L_2 26-membered cycles	photoluminescence	[7]
$[(CdI_2)_4(\mathbf{L_6})_4]_\infty$ (1D)	$N^3,N^{3'}$-bridging, M_4L_4 52-membered cycles	photoluminescence	[7]
$[Cu(N(CN)_2)_2(\mathbf{L_3})]_\infty$ (1D)	$N^3,N^{3'}$-bridging	–	[8]
$[Cu_2(N(CN)_3)_2(\mathbf{L_3})_4](ClO_4)_2$ (0D)	$N^3,N^{3'}$-bridging, M_2L_4 cycles	–	[8]
$[Co(N(CN)_2)_2(\mathbf{L_3})]_\infty$ (3D)	$N^3,N^{3'}$-bridging	magnetic susceptibility	[8]
$[Ni(N(CN)_2)_2(\mathbf{L_3})]_\infty$ (3D)	$N^3,N^{3'}$-bridging	magnetic susceptibility	[8]
$[Cu(N(CN)_2)_2(\mathbf{L_4})]_\infty$ (2D)	$N^3,N^{3'}$-bridging	magnetic susceptibility	[8]
$[Cu(\mathbf{L_3})Cl_2]_2 \cdot CH_3OH$ (0D)	$N^3,N^{3'}$-bridging	cyclic voltammetry	[9]
$[Cu(\mathbf{L_4})_{1.5}Cl_2]_\infty$ (2D)	$N^3,N^{3'}$-bridging	cyclic voltammetry	[9]
$[K(Cu_6Br_7)(\mathbf{L_6})]_\infty$ (2D)	$N^3,N^2,N^{2'},N^{3'}$-bridging	photoluminescence	[10]
$[(CuBr)_4(\mathbf{L_6})]_\infty$ (2D)	$N^3,N^2,N^{2'},N^{3'}$-bridging	photoluminescence	[10]

[(C[illegible] (3D)	N^3,N^2,N$^{2'}$,N$^{3'}$-bridging	[illegible]	[10]
$[K(Cu_6Br_7)(\mathbf{L_6})]_\infty$ (2D)	N[illegible],N[illegible],N[illegible],N[illegible]-bridging	semiconducting	[11]
$[(CuCl)_2(\mathbf{L_6})]_\infty$ (3D)	N^3,N$^{3'}$-bridging	photoluminescence	[12]
$[Cu_2I_2(\mathbf{L_4})]_\infty$ (1D)	N^3,N$^{3'}$-bridging	photoluminescence	[13]
$[Cu_2I_2(\mathbf{L_5})]_\infty$ (1D)	N^3,N$^{3'}$-bridging	photoluminescence	[13]
$[Cu_4I_4(\mathbf{L_5})]_\infty$ (1D)	N^3,N$^{3'}$-bridging	white LED prototype	[13]
$[(CuCl)_2(\mathbf{L_3})]_\infty$ (1D)	N^3,N^2,N$^{2'}$,N$^{3'}$-bridging	photoluminescence	[17]
$[(CuI)_2(\mathbf{L_4})]_\infty$ (1D)	N^3,N$^{3'}$-bridging	photoluminescence	[17]
$[(CuBr)_2(\mathbf{L_4})]_\infty$ (2D)	N^3,N$^{3'}$-bridging	photoluminescence	[17]
$[(CuBr)_3(\mathbf{L_3'})]_\infty$ (2D)	N^1,N$^{1'}$-bridging	photoluminescence	[17]
$[(CuCl)_2(\mathbf{L_4})]_\infty$ (3D)	N^3,N^2,N$^{2'}$,N$^{3'}$-bridging	photoluminescence	[17]
$[[Ag_2(\mathbf{L_3})_3](NO_3)_2]_\infty$ (2D)	N^3,N$^{3'}$-bridging	non-linear optical properties	[19]
$[Co(\mathbf{L_3})Cl_2]_\infty$ (1D)	N^3,N$^{3'}$-bridging	–	[23]
$[Cu(\mathbf{L_3})Cl_2]_\infty$ (2D)	N^3,N$^{3'}$-bridging	–	[23]
$[Cu_2(\mathbf{L_3''})_2Cl_2]_\infty$ (1D)	N^1,N$^{1'}$-bridging, M_2L_2 16-membered cycles	–	[23]
$[Zn(\mathbf{L_3})(NCS)_2]_\infty$ (1D)	N^3,N$^{3'}$-bridging	nonlinear optical properties	[24]
$[Zn(\mathbf{L_4})(NCS)_2]_\infty$ (1D)	N^3,N$^{3'}$-bridging	nonlinear optical properties	[24]
$[Ni(\mathbf{L_3})_2(NCS)_2]_\infty$ (1D)	N^3,N$^{3'}$-bridging	nonlinear optical properties	[25]
$[Co(\mathbf{L_3})_2(NCS)_2]_\infty$ (1D)	N^3,N$^{3'}$-bridging	nonlinear optical properties	[25]
$[Co(\mathbf{L_4})_2(NCS)_2]_\infty$ (2D)	N^3,N$^{3'}$-bridging, M_4L_4 44-membered cycles	nonlinear optical properties	[26]
$[Mn(\mathbf{L_4})_2(NCS)_2]_\infty$ (2D)	N^3,N$^{3'}$-bridging, M_4L_4 44-membered cycles	nonlinear optical properties	[26]
$[Cd(\mathbf{L_4})_2(NCS)_2]_\infty$ (2D)	N^3,N$^{3'}$-bridging, M_4L_4 44-membered cycles	nonlinear optical properties	[26]
$[CdI_2(\mathbf{L_4})(CH_3OH)]_\infty$ (1D)	N^3,N$^{3'}$-bridging	–	[27]

Bis(benzotriazolyl)alkanes can be prepared by the reactions between 1,2,3-benzotriazole and dibromoalkanes in the presence of K_2CO_3 and PEG under microwave irradiation conditions [21] or phase-transfer conditions (tetra-n-butylammonium bromide / base) [28]; lithiated 1-alkylbenzotriazoles and iodine [29]. Xiaodong Shi et al. reported the reaction of 1,2,3-benzotriazole with diols in Mitsunobu reaction conditions (diisopropyl azodicarboxylate/ Ph_3P in THF) which favored the formation of 2-substituted derivatives [30]. Bis(benzotriazol-1-yl)methane was selectively obtained by the reaction of sodium benzotriazolate and 1-chloromethylbenzotriazole [31], by the condensation of 1-hydroxymethylbenzotriazole with benzoyl chloride [32], or by the thermal decomposition of 1-methylenebenzotriazol-1-ium [33]. However, alkylation in the superbasic medium (NaOH or preferably KOH in DMSO) [13,34,35] seems to be the most general method for the synthesis of bis(benzotriazolyl)alkanes, since the process does not require any specific, highly-dangerous or expensive reagents, equipment and proceeds under mild conditions. Herein we report the synthesis of individual isomers of bis(benzotriazolyl)alkanes **L_3-L_8**, synthesis and crystal structures of their discrete and polymeric cadmium(II) and silver(I) coordination compounds, as well as antibacterial and antifungal activity of silver(I) coordination polymers and luminescent properties of cadmium complexes.

Materials and Methods

General methods

NMR spectra were recorded using Bruker AC300 and Bruker AVANCE III HD instruments operating at 300 and 400 MHz for ^{1}H and 75 and 100 MHz for ^{13}C.

Chromato-mass spectrometric analysis was carried out using Agilent 7890A gas chromatograph with Agilent 5975C mass-selective detector with quadrupole mass-analyzer (electron impact ionization energy 70 eV). The injector temperature was maintained at 300 °C and the injection volume was 1 µL (split 40:1). The instrument was equipped with a HP-5ms capillary column of 30 m length, 0.25 mm i.d. and 0.25 µm film thickness. The carrier gas was helium at a constant flow rate of 1 ml/min. The GC oven program started at 79 °C (1.0 min hold) ramped up to 300 °C (heating rate 13 °C/min) for 10 min, total chromatogram time was 28 min. Transfer line temperature was 300 °C, MS Source – 230 °C and MS Quadrouple – 150 °C. The electron energy was 70 eV. From 0 min to 4 min the MS was switched off (solvent delay). Data analysis and instrument control was carried out with MSD 5975C software.

Infrared spectra of solid samples as KBr pellets were recorded using a VERTEX 80 (4000-400 cm^{-1}) and Nicolet 5700 (4000-400 cm^{-1}) instruments.

The elemental analyses were obtained on an analyzer «Vario Micro-Cube».

The powder X-ray diffraction data were obtained on «Shimadzu XRD 7000S» powder diffractometer (Cu-Kα irradiation).

The thermogravimetric analyses were carried out in O_2/Ar atmosphere on NETZSCH TG 209 F1 thermoanalyzer with the heating rate of 10 deg/min.

The luminescence spectra were recorded on Horiba Jobin Yvon Fluorolog 3 Photoluminescence Spectrometer, equipped by 450 W xenon lamp, excitation/emission monochromator, and FL-1073 PMT detector. The excitation was performed with λ_{ex} = 330 nm, the emission was recorded at λ_{em} = 400 nm.

Single-Crystal X-ray Diffraction

Diffraction data for single-crystals **1**–**7** were obtained on an automated Agilent Xcalibur diffractometer equipped with an area AtlasS2 detector (graphite monochromator, λ(MoKα) = 0.71073 Å, ω-scans). Integration, absorption correction, and determination of unit cell parameters were performed using the CrysAlisPro program package [36]. The structures were solved by dual space algorithm (SHELXT [37]) and refined by the full-matrix least squares technique (SHELXL [38]) in the anisotropic approximation (except hydrogen atoms). Positions of hydrogen atoms of organic ligands were calculated geometrically and refined in the riding model. The crystallographic data and details of the structure refinements are summarized in Table S1.

General procedure and analytical data for α,ω-bis(benzotriazolyl)alkanes

Po[illegible] 1). Benzotriazole (1.19 g, 10 mmol) was added to Solution 1. α,ω-Dibromoalkane (5 mmol) was dissolved in 5 ml of DMSO (Solution 2). Solution 1 was stirred on a magnetic stirrer at 80 °C during 30 minutes. Solution 2 was added drop wise to a cold (10-20 °C) Solution 1 under cooling. The reaction mixture was stirred and heated at 80 °C for an hour. The product was precipitated by a ten-fold volume of water, filtered and washed by water. In case of hexane derivative an oily product was obtained and it was extracted by ethyl acetate (20 ml x 3), the solvent was removed on a rotary evaporator. The product was air-dried.

1,3-Bis(benzo-1,2,3-triazolyl)propane mixture of isomers. Yield 80 %, colorless crystals. Anal. Calc. for $C_{15}H_{14}N_6$ (%): C, 64.73; H, 5.07; N, 30.20. Found: C, 64.99; H, 4.94; N, 30.47.

1,3-Bis(benzo-1,2,3-triazol-1-yl)propane (L$_3$). Yield 20 %, colorless crystals, m.p. 138-141 °C. m/z: $(M)^+$ 278.1 (0.7%), 250.1 (4.7%) $[C_{15}H_{14}N_4]^+$, 221.1 (31.1%) $[C_{15}H_{13}N_2]^+$, 193.1 (28.2%), 180.1 (8.6%), 167.1 (30.6%), 160.1$[C_9H_{10}N_3]^+$, 132.1 (33.5%), 131.1 (33.6%) , 130.1 (45.2%), 104.1 (17.4%) $[C_6H_4N_2]^+$, 78.1 (13.5%) $[C_6H_6]^+$, 77.1 (100%) $[C_6H_5]^+$. ^{1}H NMR (CDCl$_3$) δ 2.87 quint (2H, CH$_2$-$C\underline{H}_2$-CH$_2$, J=6.6 Hz), 4.68 t (4H, Bta-$C\underline{H}_2$-CH$_2$-$C\underline{H}_2$-Bta, J=6.5 Hz), 7.34-7.47 m (6H, Bta), 8.05-8.07 d (2H, Bta, J=6 Hz). ^{13}C NMR (CDCl$_3$) δ 29.4, 44.9, 109.3, 120.3, 124.3, 127.8, 133.2, 146.1. IR (cm^{-1}): 3070, 2947, 2923, 2866, 1616, 1566, 1496, 1460, 1451, 1336, 1278, 1201, 1095, 1087, 746.

1-(Benzo-1,2,3-triazol-1-yl)-3-(benzo-1,2,3-triazol-2-yl)propane (L$_3$'). Yield 40 %, colorless crystals, m.p. 79-80 °C. m/z: $(M)^+$ 278.1 (0.8%), 249.1 (5.6%) $[C_{15}H_{13}N_4]^+$, 221.1 (9.2%) $[C_{15}H_{13}N_2]^+$, 193.1 (15.6%), 181.1 (3.2%), 166.1 (9.3%), 159.1 (17.3%) $[C_9H_9N_3]^+$, 132.1 (38.2%), 131.1 (72.8%), 130.1 (100%), 104.1 (20.1%) $[C_6H_4N_2]^+$, 78.1 (20.0%) $[C_6H_6]^+$, 77.1 (70.6%) $[C_6H_5]^+$. ^{1}H NMR (CDCl$_3$) δ 2.86 quint (2H, Bta-CH$_2$-$C\underline{H}_2$-CH$_2$-Bta, J=6 Hz), 4.73 t (2H, Bta^2-CH$_2$-CH$_2$-$C\underline{H}_2$-Bta^1, J=8 Hz), 4.80 t (2H, Bta^2-$C\underline{H}_2$-CH$_2$-CH$_2$-Bta^1, J=6 Hz), 7.33-7.50 m (5H, Bta), 7.84-7.86 m (2H, Bta), 8.03-8.05 d (1H, Bta, J=8 Hz). ^{13}C NMR (CDCl$_3$) δ 29.77, 45.13, 53.43, 109.34, 118.06, 120.12, 124.11, 126.66, 127.57, 133.15, 144.49, 145.99. IR (cm^{-1}): 3433, 3057, 2961, 2943, 1608, 1569, 1496, 1458, 1450, 1323, 1286, 1268, 1204, 1160, 1116, 1044, 748.

1,3-Bis(benzo-1,2,3-triazol-2-yl)propane (L$_3$''). Yield 20 %, colorless crystals, m.p. 120-122 °C. m/z: $(M)^+$ 278.1 (2.7%), 159.1 (100%) $[C_9H_9N_3]^+$, 146.1 (20.3%) $[C_8H_8N_3]^+$, 132.1 (7.7%), 131.1 (15.7%), 130.1 (58.0%), 104.1 (32.7%) $[C_6H_4N_2]^+$, 78.1 (22.5%) $[C_6H_5]^+$, 77.1 (29.7%) $[C_6H_5]^+$. ^{1}H NMR (CDCl$_3$) δ 2.93 quint (2H, Bta-CH$_2$-$C\underline{H}_2$-CH$_2$-Bta, J=7 Hz), 4.87 t (4H, Bta-$C\underline{H}_2$, J=6 Hz), 7.35-7.38 m (4H, Bta), 7.83-7.85 m (4H, Bta). ^{13}C NMR (CDCl$_3$) δ 30.03, 53.64, 118.09, 126.55, 144.53. IR (cm^{-1}): 3441, 3091, 3069, 3001, 2960, 2927, 2856, 1564, 1496, 1458, 1445, 1439, 1327, 1284, 1191, 1142, 1069, 1061.

1,4-Bis(benzo-1,2,3-triazolyl)butane mixture of isomers. Yield 80 %, colorless crystals. Anal. Calc. for $C_{16}H_{16}N_6$ (%): C, 65.74; H, 5.52; N, 28.75. Found: C, 65.60; H, 5.78; N, 28.30.

1,4-Bis(benzo-1,2,3-triazol-1-yl)butane (L_4). Yield 30 %, colorless crystals, m.p. 146-147 °C. m/z: 263.1 (8.8%) $[C_{16}H_{15}N_4]^+$, 235.1 (17.8%) $[C_{16}H_{15}N_2]^+$, 207.1 (20.2%), 193.1 (13.7%), 180.1 (11.9%), 173.1 (46.0%) $[C_{10}H_{11}N_3]^+$, 145.1 (26.7%), 132.1 (71.2%), 104.1 (24.2%) $[C_7H_6N]^+$, 77.1 (100%) $[C_6H_5]^+$. ^{1}H NMR ($CDCl_3$) δ 2.04 quint (4H, Bta-CH_2-$\mathit{C}\underline{\mathit{H}}_2$, J=3 Hz), 4.66 t (4H, Bta-$\mathit{C}\underline{\mathit{H}}_2$-$CH_2$, J=6 Hz), 7.34-7.45 m (6H, Bta), 8.02-8.08 d (2H, Bta, J=8 Hz). ^{13}C NMR ($CDCl_3$) δ 26.45, 47.11, 109.14, 120.08, 124.06, 127.54, 132.78, 145.96. IR (cm^{-1}): 3431, 3068, 2949, 2879, 1495, 1467, 1455, 1326, 1273, 1213, 1166, 1074, 737.

1-(Benzo-1,2,3-triazol-1-yl)-4-(benzo-1,2,3-triazol-2-yl)butane (L_4’). Yield 40 %, colorless crystals, m.p. 84-86 °C. m/z: 264.1 (17.1%) $[C_{16}H_{16}N_4]^+$, 263.1 (51.5%) $[C_{16}H_{15}N_4]^+$, 235.1 (3%) $[C_{16}H_{15}N_2]^+$, 207.1 (9.5%), 173.1 (100%) $[C_{10}H_{11}N_3]^+$, 145.1 (60.1%), 144.1 (31.6%), 132.1 (67%), 120.1 (23.0%), 104.1 (24.3%) $[C_7H_6N]^+$, 91.1 (29.1%) $[C_6H_5N]^+$, 77.1 (91.4%) $[C_6H_5]^+$. ^{1}H NMR ($CDCl_3$) δ 1.90 quint (2H, Bta^1-CH_2-$\mathit{C}\underline{\mathit{H}}_2$-$CH_2$-$CH_2$-$Bta^2$, J=7 Hz), 2.04 quint (2H, Bta^1-CH_2-CH_2-$\mathit{C}\underline{\mathit{H}}_2$-$CH_2$-$Bta^2$, J=7 Hz), 4.54 t (2H, Bta^1-$\mathit{C}\underline{\mathit{H}}_2$-$CH_2$-$CH_2$-$CH_2$-$Bta^2$, J=8 Hz), 4.65 t (2H, Bta^1-CH_2-CH_2-CH_2-$\mathit{C}\underline{\mathit{H}}_2$-$Bta^2$, J=6 Hz), 7.20-7.36 m (5H, Bta), 7.70-7.74 m (2H, Bta), 7.91-7.93 d (1H, Bta, J=8 Hz). ^{13}C NMR ($CDCl_3$) δ 26.39, 26.86, 47.10, 55.36, 109.14, 117.87, 119.93, 123.86, 126.33, 127.26, 132.73, 144.24, 145.86. IR (cm^{-1}): 3064, 2934, 2858, 1566, 1455, 1460, 1323, 1274, 1194, 1052, 738.

1,4-Bis(benzo-1,2,3-triazol-2-yl)butane (L_4’’). Yield 20 %, colorless crystals, m.p. 110-111 °C. m/z: 173.1 (100%) $[C_{10}H_{11}N_3]^+$, 172.1 (17.1%) $[C_{10}H_{10}N_3]^+$, 145.1 (49.3%), 132.1 (5.6%), 120.1 (7.7%), 105.1 (8.3%) $[C_7H_7N]^+$, 78.1 (12.4%) $[C_6H_6]^+$, 77.1 (25.9%) $[C_6H_5]^+$. ^{1}H NMR ($CDCl_3$) δ 2.15 quint (4H, Bta-CH_2-$\mathit{C}\underline{\mathit{H}}_2$-$\mathit{C}\underline{\mathit{H}}_2$-$CH_2$-Bta, J=7 Hz), 4.77 t (4H, Bta-$\mathit{C}\underline{\mathit{H}}_2$-$CH_2$-$CH_2$-$\mathit{C}\underline{\mathit{H}}_2$-Bta, J=4 Hz), 7.33-7.37 m (4H, Bta), 7.81-7.85 m (4H, Bta). ^{13}C NMR ($CDCl_3$) δ 26.96, 55.60, 118.02, 126.39, 144.38. IR (cm^{-1}): 2964, 2929, 1567, 1466, 1326, 1279, 1242, 1140, 1094, 848, 746.

1,5-Bis(benzo-1,2,3-triazolyl)pentane mixture of isomers. Yield 83 %, colorless crystals. Anal. Calc. for $C_{17}H_{18}N_6$ (%): C, 66.65; H, 5.92; N, 27.43. Found: C, 66.42; H, 5.68; N, 27.65.

1,5-Bis(benzo-1,2,3-triazol-1-yl)pentane (L_5). Yield 20%, colorless crystals, m.p. 103-105 °C. m/z: 277.1 (6.4%) $[C_{17}H_{17}N_4]^+$, 249.1 (33.4%) $[C_{17}H_{17}N_2]^+$, 221.1 (16.7%), 167.1 (21.7%), 158.1 (32.9%), 146.1 (13.8%), 132.1 (27.6%), 119.1 (22.0%), 104.1 (25.9%) $[C_7H_6N]^+$, 91.1 (44.1%) $[C_6H_5N]^+$, 77.1 (100%) $[C_6H_5]^+$. ^{1}H NMR ($CDCl_3$) δ 1.32-1.34 d (2H, CH_2-CH_2-$\mathit{C}\underline{\mathit{H}}_2$-$CH_2$-$CH_2$, J=8 Hz), 2.03 m (4H, CH_2-$\mathit{C}\underline{\mathit{H}}_2$-$CH_2$-$\mathit{C}\underline{\mathit{H}}_2$-$CH_2$), 4.51-4.57 q (4H, $\mathit{C}\underline{\mathit{H}}_2$-$CH_2$-$CH_2$-$CH_2$-$\mathit{C}\underline{\mathit{H}}_2$, J=8 Hz), 7.29-7.42 m (6H, Bta), 7.99 t (2H, Bta, J=8 Hz). ^{13}C NMR ($CDCl_3$) δ 20.99, 23.85, 28.96, 47.70, 109.23, 119.85, 123.98, 127.37, 145.73. IR (cm^{-1}): 3064, 2941, 2864, 1614, 1591, 1496, 1456, 1325, 1261, 1228, 1174, 1049, 742.

1-(Benzo-1,2,3-triazol-1-yl)-5-(benzo-1,2,3-triazol-2-yl)pentane (L_5’). Yield 42 %, colorless crystals, mp 75-76 °C. m/z: 278.2 (45.0%) $[C_{17}H_{18}N_4]^+$, 277.2 (76.0%) $[C_{17}H_{17}N_4]^+$, 249.1 (6.1%) $[C_{17}H_{17}N_2]^+$, 221.1 (6.6%), 193.1 (21.5%), 187.1 (67.6%) $[C_{11}H_{13}N_3]^+$, 167.1 (12.3%), 159.1 (26.8%), 146.1 (14.7%), 132.1 (45.5%), 130.1 (24.0%), 120.1 (55.1%), 104.1 (36.9%) $[C_7H_6N]^+$, 93.1 (46.1%) $[C_6H_7N]^+$, 91.1

(45.4%) [illegible]$^+$, 78.1 (27.2%) $[C_6H_6]^+$, 77.1 (100%) $[C_6H_5]^+$. ^{1}H NMR (CDCl$_3$) δ 1.12 m (2H, CH$_2$-CH$_2$-$C\underline{H}_2$-CH$_2$-CH$_2$), 1.74-1.87 m (4H, CH$_2$-$C\underline{H}_2$-CH$_2$-$C\underline{H}_2$-CH$_2$), 4.29-4.43 m (4H, $C\underline{H}_2$-CH$_2$-CH$_2$-CH$_2$-$C\underline{H}_2$), 7.07-7.26 m (5H, Bta), 7.58-7.78 m (3H, Bta). ^{13}C NMR (CDCl$_3$) δ 23.09, 28.38, 28.68, 47.15, 55.41, 108.85, 117.37, 119.18, 123.29, 125.67, 126.65, 132.28, 143.66, 145.27. IR (cm^{-1}): 3444, 3051, 2954, 2871, 1496, 1464, 1454, 1323, 1286, 1224, 1186, 1160, 1111, 1053, 850, 752, 743.

1,5-Bis(benzo-1,2,3-triazol-2-yl)pentane (L$_5$’’). Yield 21 %, colorless crystals, m.p. 42-44 °C. m/z: 187.1 (100%) $[C_{11}H_{13}N_3]^+$, 174.1 (6.1%) $[C_{10}H_{12}N_3]^+$, 159.1 (13.3%), 146.1 (19.2%), 133.1 (16.2%), 132.1 (14.1%), 120.1 (27.4%), 104.1 (22.9%) $[C_7H_6N]^+$, 91.1 (19.2%) $[C_6H_7N]^+$, 78.1 (18.3%) $[C_6H_6]^+$, 77.1 (30.5%) $[C_6H_5]^+$. ^{1}H NMR (CDCl$_3$) δ 1.38 quint (2H, CH$_2$-CH$_2$-$C\underline{H}_2$-CH$_2$-CH$_2$, J=7 Hz), 2.16 quint (4H, CH$_2$-$C\underline{H}_2$-CH$_2$-$C\underline{H}_2$-CH$_2$, J=7 Hz), 4.69 t (4H, $C\underline{H}_2$-CH$_2$-CH$_2$-CH$_2$-$C\underline{H}_2$, J=6 Hz), 7.33-7.35 m (4H, Bta), 7.80-7.82 dd (4H, Bta, J$_1$=6 Hz, J$_2$=3 Hz). ^{13}C NMR (CDCl$_3$) δ 23.58, 29.39, 56.11, 117.98, 126.27, 144.31. IR (cm^{-1}): 2947, 2923, 2866, 1566, 1466, 1450, 1326, 1278, 1201, 1096, 1087, 979, 850, 830, 746.

1,6-Bis(benzo-1,2,3-triazolyl)hexane mixture of isomers. Yield 81%, yellow oil. Anal. Calc. for $C_{18}H_{20}N_6$ (%): C, 67.48; H, 6.29; N, 26.23. Found: C, 67.53; H, 6.13; N, 25.94.

1,6-Bis(benzo-1,2,3-triazol-1-yl)hexane (L$_6$). Yield 20 %, colorless crystals, m.p. 97-99 °C. m/z: 291.1 (3.4%) $[C_{18}H_{19}N_4]^+$, 263.1 (13.1%) $[C_{18}H_{19}N_2]^+$, 249.1 (24.2%), 235.1 (10.0%), 221.1 (12.2%), 208.1 (10.4%), 193.1 (9.1%), 174.1 (15.6%), 172.1 (15.8%), 167.1 (10.7%), 158.1 (6.2%), 145.1 (20.3%), 132.1 (33.3%), 119.1 (57.1%), 104.1 (28.6%) $[C_7H_6N]^+$, 91.1 (49.7%) $[C_6H_5N]^+$, 77.1 (100%) $[C_6H_5]^+$. ^{1}H NMR (CDCl$_3$, 400 MHz) δ 1.38 quint (4H, CH$_2$-CH$_2$-$C\underline{H}_2$-$C\underline{H}_2$-CH$_2$-CH$_2$, J=3.6 Hz), 1.9 t (4H, CH$_2$-$C\underline{H}_2$-CH$_2$-CH$_2$-$C\underline{H}_2$-CH$_2$, J=6.7 Hz), 4.61 t (4H, $C\underline{H}_2$-CH$_2$-CH$_2$-CH$_2$-CH$_2$-CH$_2$-$C\underline{H}_2$, J=7 Hz), 7.33-7.39 m (2H, Bta), 7.46-7.47 dd (4H, Bta, J$_1$=3.5 Hz, J$_2$=0.9 Hz), 8.04-8.06 dd (2H, Bta, J$_1$=8.4 Hz, J$_2$=0.8 Hz). ^{13}C NMR (CDCl$_3$) δ 26.25, 29.49, 48.01, 109.33, 120.21, 123.97, 127.38, 133.02, 146.14. IR (cm^{-1}): 3069, 2936, 2864, 1616, 1585, 1495, 1468, 1456, 1319, 1312, 1265, 1260, 1200, 1167, 1070, 777, 761, 733, 761, 733, 428.

1-(Benzo-1,2,3-triazol-1-yl)-6-(benzo-1,2,3-triazol-2-yl)hexane (L$_6$’). Yield 41 %, yellow oil. m/z: (M)$^+$ 320.2 (11.2%), 292.2 (27.3%) $[C_{18}H_{20}N_4]^+$, 291.2 (52.3%) $[C_{18}H_{19}N_4]^+$, 263.1 (6%), 249.1 (24.2%) $[C_{17}H_{18}N_2]^+$, 235.1 (5.4%), 221.1 (9.7%), 208.1 (13.4%), 207.1 (13.0%), 195.1 (7.8%), 188.1 (21.6%) $[C_{11}H_{14}N_3]^+$, 173.1 (16.8%), 146.1 (16.8%), 133.1 (28.9%), 132.1 (48.6%), 120.1 (80.2%), 119.1 (28.2%), 105.1 (21.3%) $[C_7H_7N]^+$, 104.1 (38.6%) $[C_7H_6N]^+$, 91.1 (56.2%) $[C_6H_5N]^+$, 78.1 (27.1%) $[C_6H_6]^+$, 77.1 (100%) $[C_6H_5]^+$. ^{1}H NMR (CDCl$_3$, 400 MHz) δ 1.39 quint (4H, CH$_2$-CH$_2$-$C\underline{H}_2$-$C\underline{H}_2$-CH$_2$-CH$_2$, J=3.5 Hz), 2.0 quint (2H, ^{1}CH$_2$-$C\underline{H}_2$-CH$_2$-CH$_2$-CH$_2$-CH$_2$, J=7.2 Hz), 2.09 quint (2H, ^{2}CH$_2$-$C\underline{H}_2$-CH$_2$-CH$_2$-CH$_2$-CH$_2$, J=7.1 Hz), 4.61 t (2H, $^1C\underline{H}_2$-CH$_2$-CH$_2$-CH$_2$-CH$_2$-CH$_2$, J=7 Hz), 4.7 t (2H, $^2C\underline{H}_2$-CH$_2$-CH$_2$- CH$_2$-CH$_2$-CH$_2$, J=6.9 Hz), 7.36-7.49 m (5H, Bta), 7.83-7.86 dd (2H, Bta, J$_1$=6.5 Hz, J$_2$=3.1 Hz), 8.05-8.07 d (1H, Bta, J=8.3 Hz). ^{13}C NMR (CDCl$_3$) δ 26.10, 26.25, 29.51, 29.83, 48.16, 56.42, 109.29, 118.05, 120.94, 124.19, 126.27, 127.47, 144.39. IR (cm^{-1}): 2925, 2858, 1614, 1566, 1495, 1452, 1323, 1268, 1224, 1158, 1111, 1053, 999, 849, 740, 668.

1,6-Bis(benzo-1,2,3-triazol-2-yl)hexane (L_6’’). Yield 20 %, colorless crystals, m.p. 93-95 °C. m/z: $(M)^+$ 320.2 (23.0%), 263.1 (7.4%) $[C_{18}H_{19}N_2]^+$, 201.1 (45.2%) $[C_{12}H_{15}N_3]^+$, 188.1 (22.6%) $[C_{11}H_{14}N_3]^+$, 173.1 (54.1%), 159.1 (13.1%), 146.1 (37.0%), 145.1 (31.1%), 132.1 (33.3%), 120.1 (100%), 104.1 (47.9%) $[C_7H_6N]^+$, 91.1 (56.7%) $[C_6H_5N]^+$, 77.1 (57.9%) $[C_6H_5]^+$. ^{1}H NMR ($CDCl_3$, 400 MHz) δ 1.41 quint (4H, CH_2-CH_2-$C\underline{H}_2$-$C\underline{H}_2$-CH_2-CH_2, J=3.5 Hz), 2.11 quint (4H, CH_2-$C\underline{H}_2$-CH_2-CH_2-$C\underline{H}_2$-CH_2, J=7 Hz), 4.7 t (4H, $C\underline{H}_2$-CH_2-CH_2-CH_2-CH_2-$C\underline{H}_2$, J=7 Hz), 7.35-7.38 dd (4H, Bta, J_1=6.5 Hz, J_2=3 Hz), 7.83-7.85 dd (4H, Bta, J_1=6.5 Hz, J_2=3 Hz). ^{13}C NMR ($CDCl_3$) δ 26.14, 29.91, 56.47, 118.07, 126.34, 144.39. IR (cm^{-1}): 3067, 2947, 2918, 2857, 1566, 1467, 1438, 1369, 1322, 1281, 1239, 1119, 980, 913, 853, 735, 668.

1,7-Bis(benzo-1,2,3-triazolyl)heptane mixture of isomers. Yield 92 %, yellow oil. ^{1}H NMR ($CDCl_3$): δ 1.28-1.29 m (6H, $(CH_2)_2$-$(C\underline{H}_2)_3$-$(CH_2)_2$), 1.91-2.02 m (4H, CH_2-$C\underline{H}_2$-$(CH_2)_3$-$C\underline{H}_2$-CH_2), 4.54 t (2H, Bta^1-$C\underline{H}_2$-$(CH_2)_6$, J=7 Hz), 4.64 t (2H, Bta^2-$C\underline{H}_2$-$(CH_2)_6$, J=7 Hz), 7.28-7.43 m (5H, Bta), 7.77-7.80 dd (2H, Bta, J_1=6.6 Hz, J_2=3 Hz), 7.96-7.99 dd (1H, Bta, J_1=0.75 Hz, J_2=4.12 Hz). Anal. Calc. for $C_{19}H_{22}N_6$ (%): C, 68.24; H, 6.63; N, 25.13. Found: C, 68.33; H, 6.37; N, 25.19.

1,7-Bis(benzo-1,2,3-triazol-1-yl)heptane (L_7). m/z: $(M)^+$ 334.2 (2.7%), 305.1 (2.8%) $[C_{19}H_{21}N_4]^+$, 277.1 (3.9%) $[C_{19}H_{23}N_2]^+$, 249.1 (11.7%) $[C_{19}H_{21}]^+$, 223.1 (8.2%), 207.1 (7.0%), 193.1 (11.7%), 188.1 (23.6%), 167.1 (15.1%), 146.1 (17.2%), 132.1 (39.2%), 119.1 (84.6%), 104.0 (31.0%) $[C_7H_6N]^+$, 91.0 (47.4%) $[C_6H_5N]^+$, 77.0 (100%) $[C_6H_5]^+$.

1-(Benzo-1,2,3-triazol-1-yl)-7-(benzo-1,2,3-triazol-2-yl)heptane (L_7’). m/z: $(M)^+$ 334.2 (26.8%), 305.2 (8.7%) $[C_{19}H_{21}N_4]^+$, 249.1 (9.9%) $[C_{19}H_{21}]^+$, 202.1 (20.4%) $[C_{12}H_{16}N_3]^+$, 193.1 (21.1%), 174.1 (10.2%), 167.1 (8.2%), 158.1 (8.9%), 146.1 (25.4%), 133.1 (57.9%), 132.1 (45.1%), 120.1 (100%), 104.1 (38.4%) $[C_7H_6N]^+$, 91.1 (54.0%) $[C_6H_5N]^+$, 77.1 (90.0%) $[C_6H_5]^+$.

1,7-Bis(benzo-1,2,3-triazol-2-yl)heptane (L_7’’). m/z: $(M)^+$ 334.2 (16.1%), 277.2 (12.8%) $[C_{19}H_{21}N_2]^+$, 215.1 (13.0%) $[C_{13}H_{18}N_3]^+$, 202.1 (15.7%) $[C_{12}H_{16}N_3]$+, 187.1 (15.1%), 173.1 (22.7%), 159.1 (14.2%), 146.1 (32.8%), 133.1 (32.1%), 120.1 (100%), 104.1 (34.7%) $[C_7H_6N]^+$, 91.1 (48.0%) $[C_6H_5N]^+$, 78.1 (26.8%) $[C_6H_6]^+$, 77.1 (41.7%) $[C_6H_5]^+$.

1,8-Bis(benzo-1,2,3-triazolyl)octane mixture of isomers. Yield 81 %, colorless crystals. ^{1}H NMR ($CDCl_3$): 1.27-1.29 m (8H, $(CH_2)_2$-$(C\underline{H}_2)_4$-$(CH_2)_2$), 1.95-2.08 m (4H, CH_2-$C\underline{H}_2$-$(CH_2)_4$-$C\underline{H}_2$-CH_2), 4.57 t (2H, Bta^1-$C\underline{H}_2$-$(CH_2)_7$, J=7 Hz), 4.67 t (2H, Bta^2-$C\underline{H}_2$-$(CH_2)_7$, J=7 Hz), 7.30-7.49 m (4H, Bta), 7.81-7.84 dd (2H, Bta, J_1=6.3 Hz, J_2=3 Hz), 8.01-8.04 d (2H, Bta, J=8.4 Hz). Anal. Calc. for $C_{20}H_{24}N_6$ (%): C, 68.94; H, 6.94; N, 24.12. Found: C, 68.70; H, 7.20; N, 23.90.

1,8-Bis(benzo-1,2,3-triazol-1-yl)octane (L_8). m/z: $(M)^+$ 348.2 (0.5%), 319.2 (4.7%) $[C_{20}H_{23}N_4]^+$, 291.2 (5.7%) $[C_{20}H_{23}N_2]^+$, 277.2 (5.1%), 263.1 (6.0%), 249.1 (19.4%), 202.1 (31.8%), 200.1 (14.3%), 193.1

(9.0%), 167.1 (13.0%), 158.1 (6.8%), 146.1 (31.3%), 133.1 (43.7%), 120.1 (43.5%), 119.1 (88.1%), 104.1 (33.7%) $[C_7H_6N]^+$, 91.1 (64.7%) $[C_6H_5N]^+$, 78.1 (15.2%) $[C_6H_6]^+$, 77.1 (100%) $[C_6H_5]^+$.

1-(Benzo-1,2,3-triazol-1-yl)-8-(benzo-1,2,3-triazol-2-yl)octane (L_8'). m/z: $(M)^+$ 348.2 (48.7%), 319.2 (12.1%) $[C_{20}H_{23}N_4]^+$, 291.2 (5.1%) $[C_{20}H_{23}N_2]^+$, 277.2 (4.2%), 263.1 (6.0%), 249.1 (15.5%), 229.2 (9.4%) $[C_{14}H_{19}N_3]^+$, 216.2 (29.7%) $[C_{13}H_{18}N_3]^+$, 208.1 (11.5%), 202.1 (9.4%), 193.1 (15.0%), 188.1 (22.7%), 180.1 (9.5%), 172.1 (11.6%), 160.1 (13.1%), 147.1 (21.5%), 146.1 (34.3%), 133.1 (53.6%), 132.1 (54.3%), 120.1 (100%), 119.1 (37.5%), 104.1 (47.2%) $[C_7H_6N]^+$, 91.1 (69.3%) $[C_6H_5N]^+$, 78.1 (24.5%) $[C_6H_6]^+$, 77.1 (97.6%) $[C_6H_5]^+$.

1,8-Bis(benzo-1,2,3-triazol-2-yl)octane (L_8''). m/z: $(M)^+$ 348.2 (30.1%), 319.2 (5.1%) $[C_{20}H_{23}N_4]^+$, 291.2 (15.3%) $[C_{20}H_{23}N_2]^+$, 249.1 (5.1%), 229.2 (11.6%) $[C_{14}H_{19}N_3]^+$, 216.2 (10.7%) $[C_{13}H_{18}N_3]^+$, 201.1 (13.6%), 188.1 (11.8%), 172.1 (24.2%), 161.1 (14.1%), 146.1 (34.3%), 133.1 (34.6%), 132.1 (28.2%), 120.1 (100%), 119.1 (23.8%), 105.1 (19.2%) $[C_7H_7N]^+$, 104.1 (37.4%) $[C_7H_6N]^+$, 91.1 (45.8%) $[C_6H_5N]^+$, 78.1 (25.9%) $[C_6H_6]^+$, 77.1 (41.3%) $[C_6H_5]^+$.

Preparation of 1,3-Bis(benzotriazolyl)propane under solvent-free conditions

Powdered potassium hydroxide (0.168 g, 3 mmol), 1,2,3-benzotriazole (0.238 g, 2 mmol) and 1,3-dibromopropane (0.102 ml, 1 mmol) were loaded into a sealed flask and heated at 110 °C. After 1 hour, the reaction mixture was suspended in water, the product was extracted by dichloromethane (5 ml x 5); the extract was washed by water; the solvent was removed by distillation; the product was air-dried. The yield was 67 %, which contained 33 % of $\mathbf{L_3}$, 28% of $\mathbf{L_3}$**'**, 6% of $\mathbf{L_3}$**''**.

Preparation of copper chloride (II) complexes for the separation of isomers

Portions of isomer mixtures and copper chloride (II) dihydrate were dissolved in acetone separately; the solutions were mixed and allowed to stand for an hour. The precipitate of the complex was filtered and washed by acetone. Yield 66-88 %.The complexes were degraded by a small amount of DMSO. The resulting solutions were diluted by ten-fold excess of water and left to coagulate overnight. Precipitates of the ligands were filtered using a glass filter, washed by NH_4OH solution and water, then dried. When compounds $\mathbf{L_5}$, $\mathbf{L_6}$ and $\mathbf{L_7}$ were isolated after precipitation by water, oily products were obtained, they were extracted by dichloromethane (20 ml x 5); the extracts were washed by NH_4OH solution and water; the solvent was removed by distillation and the products were dried.

Synthesis of coordination compounds

*Synthesis of $[Cd(L_3)_2(NO_3)_2]_\infty$ (**1**)*

Cadmium(II) nitrate tetrahydrate $Cd(NO_3)_2{\cdot}4H_2O$ **(**0.015 g, 0.05 mmol) was dissolved in 1 ml of acetone. L^I (0.042 g, 0.15 mmol) was dissolved in 4.5 ml of acetone. The ligand solution was added dropwise to the cadmium nitrate solution under stirring. The resulting solution was opaque, so, 2 ml of acetone was added to the reaction system. The vial with the reaction solution was left at room temperature for slow evaporation. In two days plate crystals were formed, they were washed with acetone (3×6.5 ml) and dried in air. Yield 0.0134 g (78 %). Anal. Calc. for [illegible] (%): C 45.44, H 3.56, N 24.72 %. Found: C 45.3, H 3.55, N 24.5. IR data (cm^{-1}): 3561 (m), 3100 (w), 3070 (w), 3036 (w), 2951 (m), 1615 (w), 1594 (w), 1496 (w), 1461 (m), 1436 (m), 1385 (s), 1330 (w), 1310 (w), 1293 (w), 1273 (m), 1225 (m), 1183 (m), 1169 (w), 1145 (w), 1116 (w), 1037 (m), 1026 (w), 1004 (w), 988 (w), 942 (w), 743 (s), 432 (w).

Synthesis of $[Cd_2(L_3)_2(NO_3)_4(H_2O)_4]$ ***(2)***

Cadmium(II) nitrate tetrahydrate $Cd(NO_3)_2{\cdot}4H_2O$ **(**0.015 g, 0.05 mmol) was dissolved in 1 ml of acetonitrile. **L_3** (0.042 g, 0.15 mmol) was dissolved in 4.5 ml of acetonitrile. The ligand solution was added dropwise to the cadmium nitrate solution under stirring. The vial with the reaction solution was left at room temperature for slow evaporation. In six days plate crystals were formed, they were washed with acetonitrile (3×5.5 ml) and dried in air. Yield 0.0276 g (85 %). Anal. Calc. for $C_{30}H_{36}Cd_2N_{16}O_{16}{\cdot}3.5CH_3CN{\cdot}2.5H_2O$ (%): C 34.4, H 4.0, N 21.17. Found: C 34.6, H 3.9, N 20.75. IR data (cm^{-1}): 3461 (s), 3097 (w), 3071 (w), 2950 (w), 1637 (m), 1592 (w), 1494 (w), 1452 (w), 1400 (w), 1385 (s), 1331 (s), 1330 (w), 1310 (w), 1279 (w), 1244 (w), 1228 (w), 1203 (m), 1183 (w), 1139 (w), 1117 (m), 1081 (w), 1037 (m), 998 (w), 943 (w), 858 (w), 820 (m), 780 (m), 753 (s), 743 (s), 664 (w), 575 (w), 539 (w) 503 (w), 432 (m), 409 (w).

Synthesis of $[Cd_2(L_3)_2(NO_3)_4(H_2O)_2]$ ***(3)***

When Cd^{2+}:L_3 ratio was less than 3, hexagonal plates were formed as an impurity to **1** (when the synthesis was carried out in acetone) or to **2** (when acetonitrile was used as a solution). Their crystal structure and chemical composition were established by a single-crystal X-ray diffraction method.

Synthesis of $[Ag(L_4)(NO_3)]_\infty$ ***(4)***

Silver nitrate $AgNO_3$ (0.0085 g, 0.05 mmol) was dissolved in 1 ml of acetonitrile. **L_4** (0.015 g, 0.05 mmol) was dissolved in 2 ml of acetonitrile. The ligand solution was added dropwise to the silver nitrate solution under stirring. The vial with the reaction solution was closed with a screw cap and left at room temperature in the dark. In two weeks plate crystals were formed, they were washed with acetonitrile (3×3 ml) and dried in air. Yield 0.0034 g (15 %).

Synthesis of $[Ag(L_4)(NO_3)]_\infty$ ***(5)***

Silver nitrate $AgNO_3$ (0.0085 g, 0.05 mmol) was dissolved in 6 ml of acetone. L_4 (0.029 g, 0.10 mmol) was dissolved in 4 ml of acetone. The ligand solution was added dropwise to the silver nitrate solution under stirring. Then 5 ml of N,N-dimethylformamide was added dropwise to the vial with the solution under stirring. The vial was closed with a screw cap and left at room temperature in the dark. In two weeks plate rhombohedral crystals were formed, they were filtered, washed with acetone (3×14 ml) and dried in air. Yield 0.0095 (40 %). Anal. calc. for $C_{16}H_{16}AgN_7O_3$ (%): C 41.58, H 3.49, N 21.21. Found: C 41.6, H 3.2, N 21.3 %. IR data (cm^{-1}): 3468 (w), 3091 (w), 3068 (w), 3034 (w), 2953 (w), 1614 (w), 1593 (w), 1496 (w), 1457 (m), 1448 (w), 1411 (w), 1385 (s), 1286 (s), 1215 (s), 1185 (m), 1164 (w), 1061 (s), 1032 (m), 935 (m), 820 (m), 759 (w), 743 (s), 671 (w), 543 (w), 489 (w) 429 (s).

Synthesis of [Ag(L$_6$)(NO$_3$)]$_\infty$ (6)

Silver nitrate AgNO$_3$ (0.0336 g, 0.20 mmol) was dissolved in 4 ml of acetonitrile. **L$_6$** (0.064 g, 0.20 mmol) was dissolved in 12 ml of acetonitrile. The ligand solution was added dropwise to the silver nitrate solution under stirring. The vial with the reaction solution was closed with a screw cap and left at room temperature in the dark. In two weeks square prismatic crystals were formed, they were filtered, washed with acetonitrile (3×16 ml) and dried in air. Yield 0.0245 g (25 %). Anal. calc. for $C_{18}H_{20}AgN_7O_3$ (%): C 44.10, H 4.11, N 20.00. Found: C 44.0, H 4.0, N 19.7 %. IR data (cm^{-1}): 3063 (w), 2945 (w), 2928 (m), 2920 (w), 2853 (m), 2434 (w), 2336 (w), 1612 (w), 1593 (w), 1496 (w), 1456 (m), 1406 (s), 1360 (w), 1311 (s), 1276 (w), 1221 (s), 1162 (s), 1148 (w), 1130 (w), 1066 (s), 1041 (m), 1000 (m), 941 (m), 903 (w), 823 (m), 779 (w), 771 (m), 760 (w), 752 (s), 735 (w), 703 (w), 667 (w), 574 (w), 515 (w), 435 (m).

*Synthesis of [Ag(L$_6$)(NO$_3$)]$_\infty$ (**7**)*

Silver nitrate AgNO$_3$ (0.0085 g, 0.05 mmol) was dissolved in 1 ml of acetonitrile. **L$_6$** (0.0326 g, 0.10 mmol) was dissolved in 4 ml of acetonitrile. The ligand solution was added dropwise to the silver nitrate solution under stirring. The vial with the reaction solution was closed with a screw cap and left at room temperature in the dark. In two weeks plate crystals were formed, they were filtered, washed with acetonitrile (3×5 ml) and dried in air. Yield 0.0086 g (35 %). Anal. calc. for $C_{18}H_{20}AgN_7O_3$ (%): C 44.10, H 4.11, N 20.00. Found: C 44.4, H 3.8, N 20.1 %. IR data (cm^{-1}): 3454 (w), 3092 (w), 3063 (w), 3035 (w), 2944 (w), 2929 (w), 2915 (w), 2855 (w), 1740 (w), 1611 (w), 1590 (w), 1494 (m), 1462 (m), 1385 (s), 1362 (w), 1318 (s), 1217 (s), 1162 (s), 1139 (w), 1070 (m), 1038 (s), 1004 (w), 942 (w), 902 (w), 822 (m), 778 (s), 762 (m), 736 (m), 704 (w), 669 (w), 528 (w), 441 (m).

Antibacterial and antifungal activity determination

All measurements were conducted in accordance with the Guidelines for Antimicrobial Susceptibility Testing [39]. The inhibitory, bactericide and fungicide efficiency of compounds **L$_4$** and **L$_6$** were assayed *in vitro* in the nutrient broth. *Staphylococcus albus*, *Escherichia coli*, *Pseudomonas aeruginosa*, *Klebsiella pneumonia* bacteria and *Candida albicans* yeast strains were used as test cultures. The bactericidal activity is defined as a reduction of 99% of the total count of colony-forming units (CFU) in 1 ml the original inoculum, whereas the bacteriostatic activity is defined as maintenance of a reduction of less than 99% of the total count of CFU/ml in the original inoculum.

The meat infusion broth was poured into five test tubes (0.5 ml) for each microorganism. **L$_4$** and **L$_6$** were dissolved in DMSO and added to the broth (0.5 ml). The range of concentrations was from 1024 μg/ml to 64 μg/ml. Analyses were conducted with a sequential dilution assay. Inoculums were prepared from the daily culture; microorganism suspensions were compared to 0.5 McFarland standards (1.5×10^8 CFU/ml). The culture medium was inoculated with the test microbes (0.5 ml) and cultivated 24 h at 35-37 ºC under aerobic conditions. *Candida albicans* was cultivated by the same method in the Sabouraud dextrose broth.

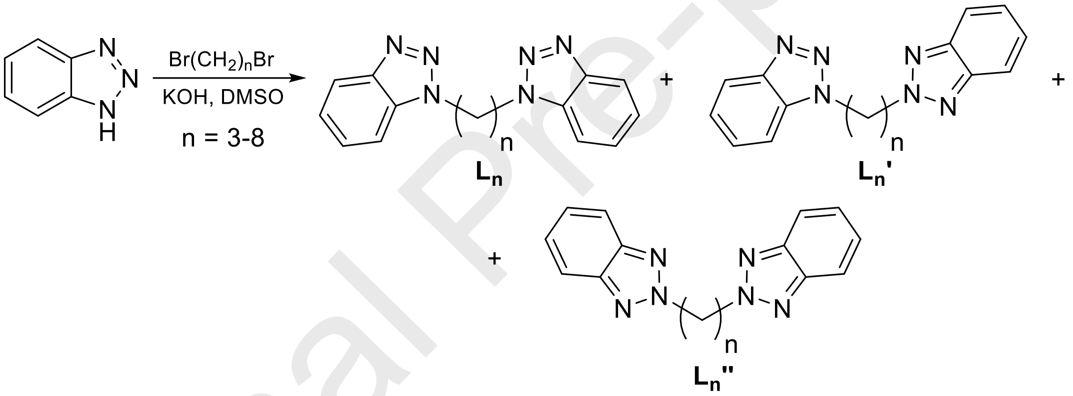
M re inoculated in the meat-peptone agar and fish peptone agar for bacterium and yeast respectively. After 24 h at 35-37 ºC under aerobic conditions the cultivation CFU was calculated. Purity control of the cultures was carried out with Gram's staining of microorganisms and microscopy at each stage.

The biological activity of coordination compound **6** was studied in a heterogenious system due to extremely low solubility of the compound. 2 mg of powdered complex was added to 10 ml of broth with inoculum of microorganisms. It was cultivated at 35-37 ºC during 72 h with stirring. Sampling and broth renewal (9 ml of medium removed and 9 ml new broth with inoculum added) were carried out each 24 h.

Results and discussion

Synthesis of bis(benzo-1,2,3-triazolyl)alkanes

Benzotriazole was alkylated in a superbasic medium by terminal dibromoalkanes containing from two to eight methylene groups in hydrocarbon linker (Scheme 1). The proposed method of synthesis does not require highly toxic reagents, catalysts or solvents and special equipment and affords the products in high yields and can be carried out on a multigram scale.

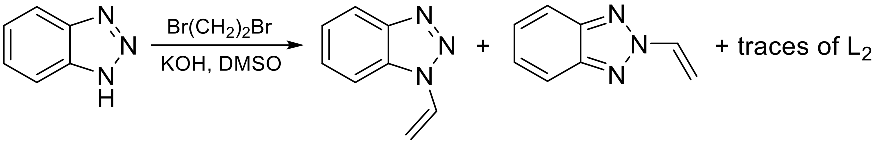


Scheme 1. Benzotriazole alkylation scheme

As a result of benzotriazole tautomerism [40], mixtures of isomers (1,x-bis(1,2,3-benzotriazol-1-yl)alkanes (**L_3-L_8**), 1-(1,2,3-benzotriazol-1-yl)-x-(1,2,3-benzotriazol-2-yl)alkanes (**L_3'-L_8'**), 1,x-bis(1,2,3-benzotriazol-2-yl)alkanes (**L_3''-L_8''**), further referred to as 1,1-, 1,2- and 2,2-isomers respectively) were obtained. The yields were 80-92%.

Qualitative analysis of mixtures was carried out using GC-MS technique, while the ratios of isomers were determined from ^{1}H and ^{13}C NMR. The isomer ratio was determined for **L_3** using the characteristic signals of Bta-CH_2- in the ^{1}H NMR spectrum (**L_3** – 4.68 t; **L_3'** – 4.73 t and 4.80 t; **L_3''** – 4.87 t). In spectra of products with longer hydrocarbon linkers, corresponding signals for different isomers overlap, this is probably because the induction effect of nitrogen atoms does not extend over a distance exceeding three methylene groups.

In case of the reaction with 1,2-dibromoethane, the desired product was detected only in trace amounts, since the elimination process proceeds predominantly with the formation of more stable Nvi ble change in the composition of the products.



Scheme 2. Elimination to form N-vinylbenzo1,2,3-triazole

To optimize the synthesis of **L3**, the temperature and the excess of base were varied (Table S2). It was found that the length of hydrocarbon linker and KOH excess did not have significant effect on the amount and composition of the products. Reaction temperature of 80 °C was found to be optimal for the synthesis of **L3**. In all cases, the ratio of 1,1-, 1,2- and 2,2-isomers is close to statistically expected 1:2:1.

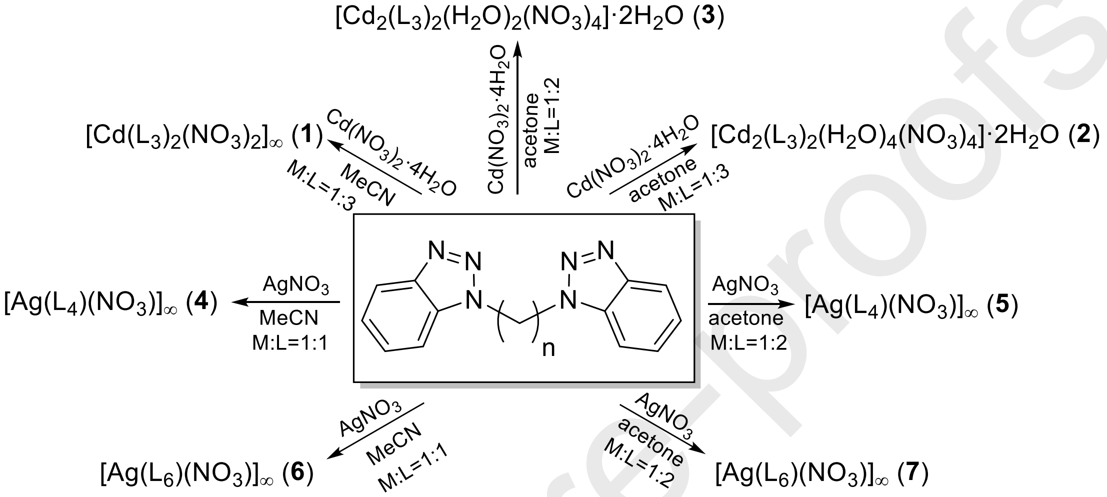
We investigated the possibility of synthesizing bis(1,2,3-benzotriazol-1-yl)alkanes without a solvent on the example of **L3**. Although the yield was lower compared to the reaction in DMSO solution (67 %), formation of 1,1-isomer was more favorable and the ratio of 1,1-, 1,2- and 2,2-isomers was found to be 49:42:9. Presence of the base in this reaction was found to be necessary, since in the absence of KOH after 24 hours of reaction only trace amounts of the product were formed.

Separation of bis(benzo-1,2,3-triazolyl)alkane isomers by selective complex formation

The conventional method of column chromatography requires significant amounts of eluent and thus is poorly suited for separation of large quantities of products. We explored the possibility of the separation of isomers by complex formation with copper(II) chloride. Previously, we have studied the complex formation of bis(benzotriazol-1-yl)methane with copper(II) ions and found that that the complex formation is a competitive process and the formation of the complexes by benzotriazol-1-yl fragments is much more favorable [2]. 1,1-Isomer forms the most stable complex with copper(II) ions, the asymmetric 1,2-isomer is capable of forming a complex, and the 2,2-isomer does not form a complex at all. These complexes are probably coordination polymers, but their structures could not be determined, since it was not possible to obtain the single crystals. Selective complex formation and subsequent complex digestion by an excess of a strong ligand (e.g. DMSO) can be used to enrich the mixture with a certain isomer before further separation or to isolate individual isomers by two sequential separations. Separations of the isomers of ligands with a linker length from three to seven methylene groups at various ligand-metal ratios were carried out. By selecting the optimal ratio, we were able to obtain the 1,1-isomer with a purity of 95-100 % for various ligands (Table S3).

Synthesis and crystal structures of coordination polymers

Coordination compounds of bis(benzotriazolyl)alkanes were prepared by their reactions with cadmium(II) or silver(I) nitrates in acetone or acetonitrile. It should be noted that we were able to isolate and metal-to-ligand ratio discrete complexes and coordination polymers were obtained. The crystal structures and chemical composition of the prepared coordination compounds were established by the single crystal X-ray crystallography. The powder X-ray diffraction was used to confirm the phase purity of the compounds (see Supplementary materials), and elemental analysis was carried to confirm their chemical purity. In addition, the complexes were characterized by IR spectroscopy (see Supplementary materials) and thermogravimetric analysis (see Supplementary materials). General synthesis routes for all of the prepared coordination compounds are shown in Scheme 3.



Scheme 3. Synthesis of the complexes with bis(benzotriazol-1-yl)alkanes.

The colorless plate crystals of $[Cd(L_3)_2(NO_3)_2]_\infty$ (**1**) were formed in the reaction mixture of $Cd(NO_3)_2$ and **L3** in acetonitrile upon solvent evaporation. The asymmetric unit of **1** contains a cadmium(II) cation, the coordination environment of which consists of three N atoms of three **L3** ligands and four O atoms of two nitrate anions coordinated in a bidentate fashion (Fig. S1, a). The Cd–O distances are in range 2.3716(15)–2.5282(17) Å and the Cd–N distances are in the range 2.2880(17)–2.3133(18) Å, typical for cadmium(II) nitrate and cadmium-benzotriazole complexes correspondingly. One **L3** molecule connects two Cd(II) cations forming a polymeric chain. Another L_3 molecule acts as a terminal ligand and connects to Cd(II) cation only by one triazole ring (Fig. 1). The second heterocycle of the ligand remains uncoordinated and disordered in two positions (Fig. S1, *b*). The TG curve demonstrates no weight loss till 280 °C, which testifies to the absence of guest molecules (see Supplementary materials).

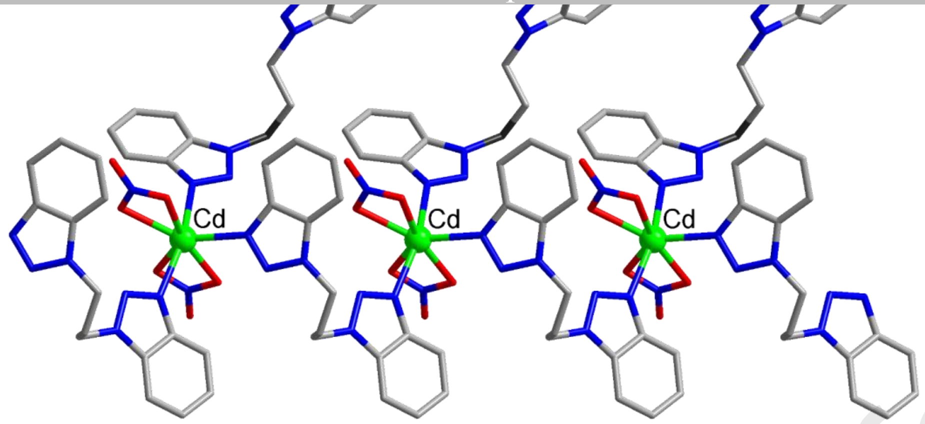


Fig. 1. Fragment of a polymeric chain in the structure **1**. Hydrogen atoms are omitted. Only one of the possible orientations of terminal **L**$_3$ ligand is shown.

The colorless plate crystals of $[Cd_2(L_3)_2(H_2O)_4(NO_3)_4]\cdot 2H_2O$ (**2**) were formed in the reaction mixture of $Cd(NO_3)_2$ and **L**$_3$ in acetone upon solvent evaporation. The compound **2** is a discrete binuclear complex consisting of two equivalent cadmium(II) cations, each of which coordinates two **L**$_3$ molecules, two nitrate anions and two aqua ligands (Fig. 2). One of NO_3^- anions is disordered over two orientations (Fig. S2). The Cd–O distances are in range 2.271(2)–2.3569(19) Å, the Cd–N distances are 2.2869(19) and 2.290(2) Å. The TG curve demonstrates 6% weight loss till 100 °C, corresponding to four H_2O molecules, and 3% weight loss till 170 °C corresponding to the remaining two H_2O molecules (see Supplementary materials).

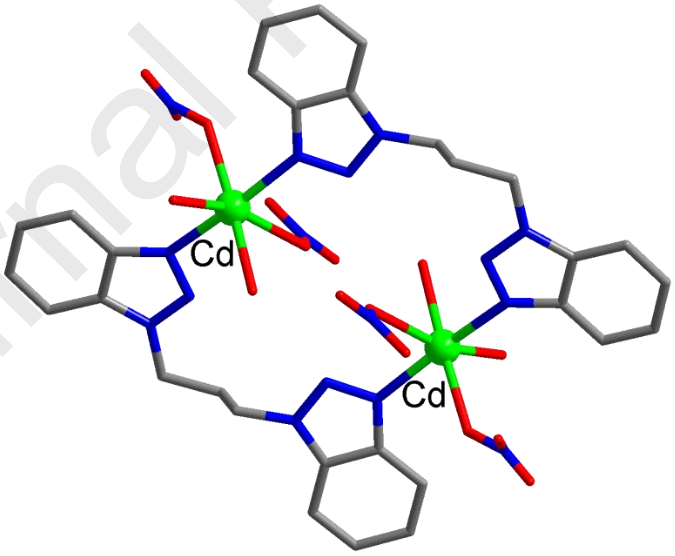


Fig. 2. Structure of the complex **2**. Hydrogen atoms are omitted. Only one of the possible orientations of NO_3^- anion is shown.

When Cd(II):**L**$_3$ ratio was less than 3, some amount of hexagonal plates of $[Cd_2(L_3)_2(H_2O)_2(NO_3)_4]\cdot 2H_2O$ (**3**) were formed as an impurity to the compound **1** (when the synthesis was carried out in acetone) or to the compound **2** (when acetonitrile was used as a solvent). Compound **3** is a binuclear complex similar to **2** (Fig. 3). The difference is that two of four nitrate anions adopt bri es only one H_2O molecule. The Cd–O distances are in range 2.243(9)–2.558(3) Å, the Cd–N distances are 2.281(3) and 2.305(3) Å. It should be noted that the bridging bidentate coordination mode of nitrate ions in binuclear cadmium(II) complexes is quite rare and is observed only in four other structures [41–44], only one of which is a discrete complex [41]. Terminal NO_3^- anion and aliphatic fragment of $\mathbf{L_3}$ ligand are disordered over two orientations (Fig. S3). Despite of numerical attempts, no pure phase of **3** could be obtained.

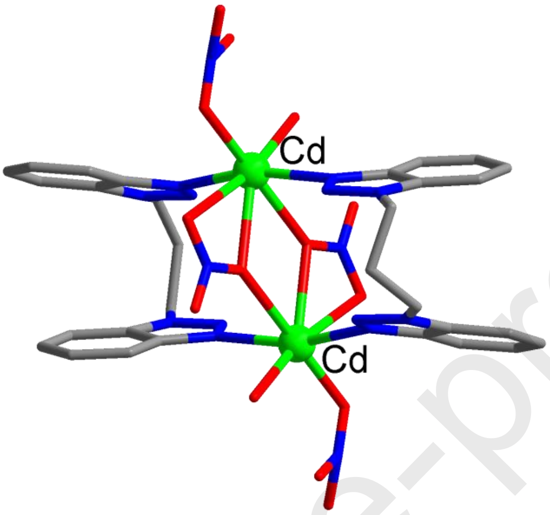


Fig. 3. Structure of the complex **3**. Hydrogen atoms are omitted. Only one of the possible orientations of NO_3^- anion and aliphatic fragment of L_3 ligand is shown.

The colorless plate crystals of $[Ag(L_4)(NO_3)]_\infty$ (**4**) were formed in the reaction mixture of $AgNO_3$ and L_4 in acetonitrile. The asymmetric unit of **4** contains two silver(I) cations. The coordination environment of Ag1 is a highly distorted tetrahedron consisting of two N atoms of two $\mathbf{L_4}$ ligands and two O atoms of two NO_3^- anions (Fig. S4). Ag1–N distances are 2.2109(18) and 2.2510(18) Å and Ag1–O distances are 2.4433(18) and 2.5199(17) Å. The coordination number of Ag2 is 4 + 1 and its coordination environment consists of two N atoms of two $\mathbf{L_4}$ ligands and three O atoms of two nitrate anions, one of which is coordinated in a bidentate fashion (Fig. S4). The Ag–O distances are 2.5203(19), 2.5743(16) and 2.7137(19) Å, the Ag2–N distances are 2.1992(17) and 2.2240(17) Å. Two Ag1 and Ag2 cations are bridged via two nitrate anions to form binuclear $\{Ag_2(L_4)_{4/2}(NO_3)_2\}$ units. The binuclear units are interconnected via bridging $\mathbf{L_4}$ ligands with the formation of a metal-organic layer (Fig. 4). The layers pack along (21−3) plane family.

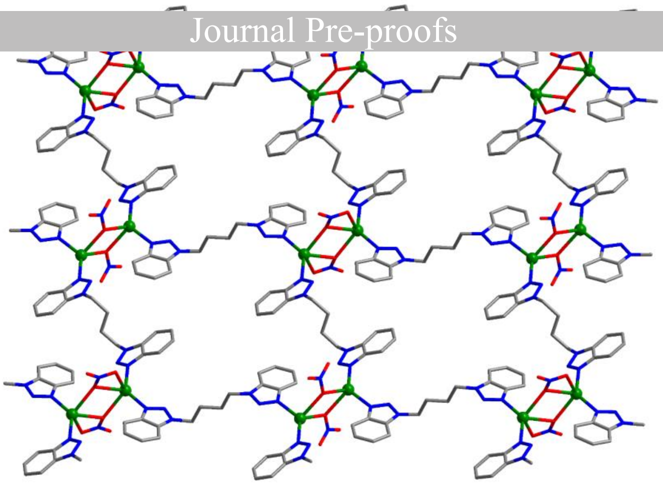


Fig. 4. Fragment of the polymeric layer in the structure **4** (projection on *bc* plane). Hydrogen atoms are omitted.

The colorless plate rhombohedral crystals of $[Ag(L_4)(NO_3)]_\infty$ (**5**) were formed in the reaction mixture of $AgNO_3$ and $\mathbf{L_4}$ in acetone. The asymmetric unit of **5** contains of a silver(I) cation in a highly distorted tetrahedral environment consisting of two N atoms of two $\mathbf{L_4}$ ligands and two O atoms of two nitrate anions (Fig. S5). The Ag–O distances are 2.3948(14) and 2.5084(13) Å, the Ag–N distances are 2.1989(15) and 2.2704(16) Å. Two silver(I) cations are interconnected via two bridging nitrate anions to form binuclear $\{Ag_2(L_4)_{4/2}(NO_3)_2\}$ building unit (Fig. 5). The binuclear units are connected to each other via bridging $\mathbf{L_4}$ ligands forming a metal-organic layer (Fig. 6, *a*). Two layers interweave to form supramolecular layers (Fig. 6, *b*), which alternate along [1−10] direction to form two-layered crystal packing. The TG curve demonstrates no weight loss up to 230 °C (see Supplementary materials), which testifies to the absence of guest molecules.

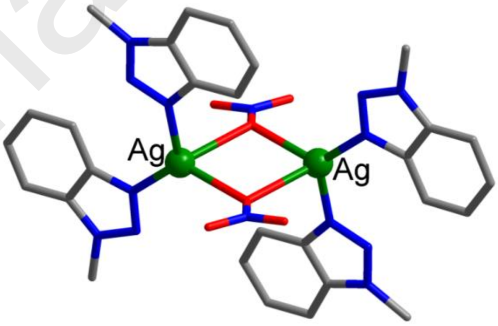


Fig. 5. Structure of the binuclear unit in the structure **5**. Hydrogen atoms are omitted.

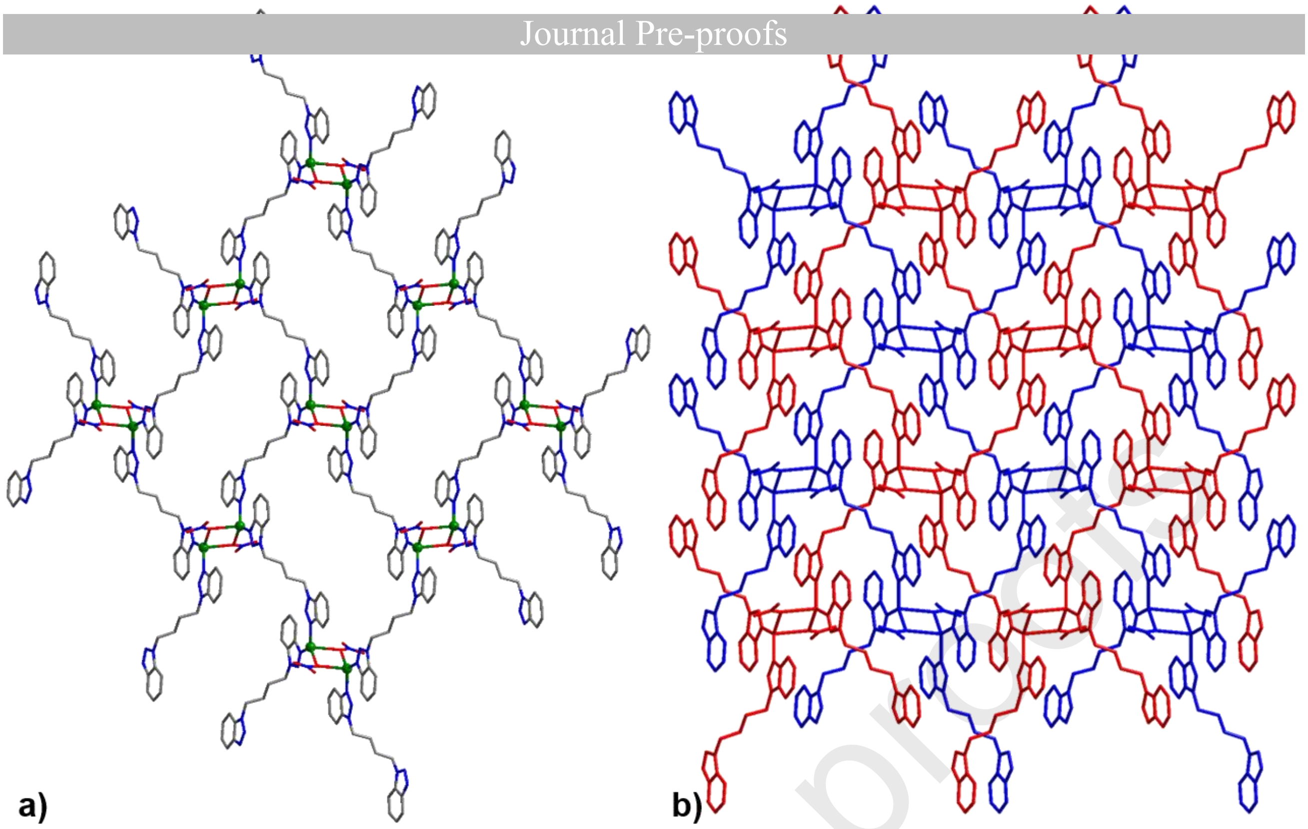


Fig. 6. Fragment of the metal-organic layer in the structure **5** (projection on *ab* plane) (a). Interweaving of metal-organic layers in the structure **5** (b). Hydrogen atoms are omitted.

The colorless square prismatic crystals of $[Ag(L_6)(NO_3)]_\infty$ (**6**) were formed in the reaction mixture of $AgNO_3$ and $\mathbf{L_6}$ in acetonitrile. The asymmetric unit of **6** consists of a silver(I) cation in a distorted triangular environment of two N atoms of two $\mathbf{L_6}$ ligands and one O atom of the nitrate anion (Fig. S6). The Ag–O distance is 2.333(2) Å, the Ag–N distances are 2.266(2) and 2.330(2) Å. The angles between the atoms in the Ag coordination environment are 100.0°, 105.1° and 154.9° emphasizing notable distortions. There are also two additional weak Ag···N interactions from each plane of the coordination triangle between the Ag(I) cation and nitrogen atoms in position 2 of benzotriazole rings. We consider such interactions to be predominantly ionic since the corresponding interatomic distances ($Ag\cdots N_{12}$ = 2.614 Å and $Ag\cdots N_{15}$ = 2.800 Å) are far longer than the normal coordination interaction. In addition, the deviations of angles between the actual N···Ag vectors and the directions of imaginary lone electron pairs on the corresponding nitrogen atoms are too significant (*ca*. 29° for $Ag\cdots N_{12}$ and 38° for $Ag\cdots N_{15}$) for the conventional coordination bonds. Nevertheless, taking into account both coordination and ionic interactions the coordination environment around the Ag(I) cations could also be described as distorted triangular bipyramidal with coordination number CN = 3+2. In the crystal structure of **6** the silver cations are connected with each other via the Ag–N bonds built with the nitrogen atoms in neighboring positions of the first benzotriazole fragment of the $\mathbf{L_6}$ ligand to form a polymeric chain. The chains are interconnected via the Ag–N bonds built with the nitrogen atom of the second benzotriazole ring to form a metal-organic layer parallel to *bc* plane (Fig. 7). The layers alternate along [100] direction to form two-layered crystal packing. The TG curve demonstrates no weight loss till ~250 °C (see Supplementary materials), which testifies to the absence of guest molecules.

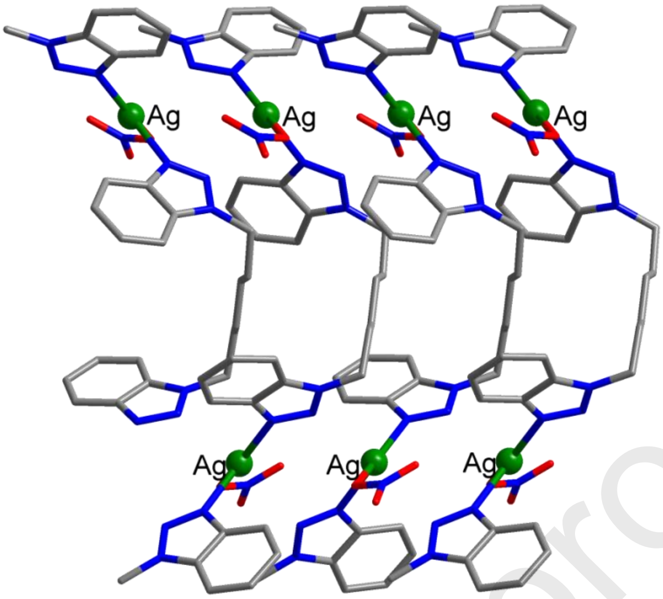


Fig. 7. Fragment of the polymeric layer in the structure **6** (projection on *bc* plane). Hydrogen atoms are omitted. Ag(I) cations are shown with green balls.

When the $AgNO_3$:**L₆** ratio in acetonitrile solution was more than 2, colorless plate crystals of compound **7** were formed. Compound **7** has a layered structure similar to compound **6** (Fig. 8), and it has the same chemical composition. The difference is in the coordination mode of a nitrate anion and orientation of monodentate coordinated benzotriazole fragments of the **L₆** ligand. The nitrate anion acts as a bridging ligand connecting two silver cations with one oxygen atom. The Ag–O distances are 2.485(2) and 2.776(2) Å. Thus, silver(I) cation has distorted trigonal bipyramidal coordination environment, in which two axial positions are occupied by O atoms of two nitrate anions, and three equatorial positions are occupied by N atoms of three **L₆** ligands (Fig. S7). The Ag–N distances are 2.252(3), 2.344(2), and 2.596(3) Å. In the structure of **7**, metal-organic layers are parallel to *ac* plane, and they alternate along *b* axis. The TG curve demonstrates no weight loss till ~230 °C (see Supplementary materials), which testifies to the absence of guest molecules.

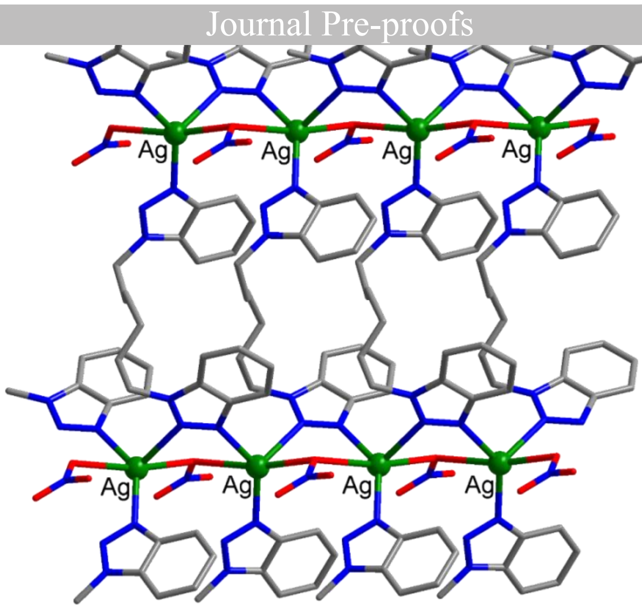


Fig. 8. Fragment of the polymeric layer in the structure **7**, projection on the *ac* plane. Hydrogen atoms are omitted.

IR spectra of the ligands and coordination compounds

The IR spectra for ligand isomers show the aromatic C-H stretching vibrations in the region of 3055-3070 cm^{-1}, the aliphatic C-H stretching vibrations are found in 2961-2866 cm^{-1} region. Bands of 1,2,3-benzotriazole ring stretching vibrations characteristic for 1-substituted derivatives [45] can be found near 1616 and 1590 cm^{-1} in the spectra of compounds **L_3-L_6** and **L_3'-L_6'**. The corresponding bands for 2-substituted triazole rings were detected near 1564 cm^{-1} in the spectra of compounds **L_3''-L_6''**. Bands of in-plane ring stretching vibrations of 1-substituted benzotriazole rings were detected near 1496 cm-1 in the spectra of compounds **L_3-L_6** and **L_3'-L_6'**, while these bands are absent in the spectra of 2-substituted benzotriazole derivatives **L_3''-L_6''**. Bands of out-of plane ring vibrations and CH deformations [45] were detected at about 796 cm^{-1} for 1-substituted derivatives and near 844 cm^{-1} for 2-substituted compounds.

The IR spectra of the complexes **1**-**7** some of the bands associated with benzotriazole vibrations are shifted towards higher frequencies as a result of the coordination. The IR spectra of the complexes also feature characteristic bands of nitrate ion vibrations near 1385 and 1285 cm^{-1} [46].

Luminescent properties of the coordination polymers

The solid-state photoluminescence properties of the phase-pure compounds **1**, **2** and **6** were investigated and compared with those of the ligands **L_3** and **L_6** (Figs. 9, 10). Typically, aromatic heterocyclic systems with lone electron pairs on the nitrogen atoms feature two emission peaks in the luminescence spectra, corresponding to the relaxation from ππ* or nπ* excited states [47,48]. The excitation spectra of the ligand **L_3** (λ_{em} = 380 nm) contains one peak at λ = 330 nm obviously related to the transitions within the π electron system of the benzotriazole moiety. The emission spectra (λ_{ex} = 330 of the photoexcited electron relaxation on the π* orbital. The main emission peak at shorter wavelengths should be attributed to the π*→π electron transition as a dominating pathway. Simultaneously, the non-irradiative n→π transfer takes place enabling the alternative photoemission pathway through π*→n electron transition, apparently observed as the weak shoulder at longer wavelengths. The excitation spectra (λ_{em} = 400 nm) of Cd(II) coordination compounds **1** and **2** feature one peak at 329–332 nm, very similar to that of the ligand **L$_3$**. The emission spectra (λ_{ex} = 330 nm) of the complexes **1** and **2** also contain two components. The blue line (λ = 392 nm for **1** and λ = 398 nm for **2**) should be assigned to the relaxation of the ππ* excited state. The bathochromic shift, compared to the spectra of the ligand **L$_3$**, results from the coordination interaction with cadmium cations. Indeed, the strongest shift is observed for the compound **2**, having only coordinated benzotriazole moieties, while for **1**, having both coordinated and non-coordinated benzotriazolyl groups this shift is less pronounced.

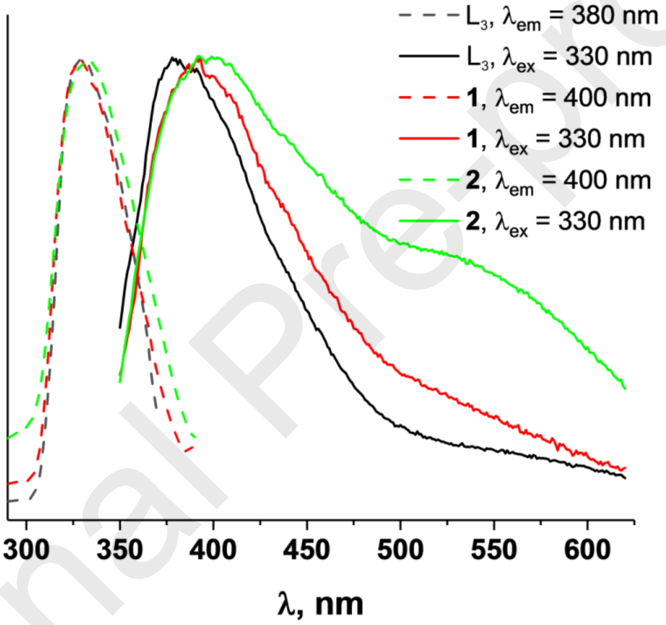


Fig. 9. Solid-state luminescence spectra of compounds **1**, **2** and **L$_3$**.

A very similar benzotriazole-centered luminescence behavior and relations between the spectra were observed for the silver coordination polymer **6** and the corresponding ligand **L$_6$** (Fig. 10). The excitation spectra of the ligand **L$_6$** and compound **6** recorded with λ_{em} = 400 nm look very similar and demonstrate one band with the peak maximum at λ = 343 nm (for **L$_6$**) or λ = 352 nm (for **6**). The excitation of the samples at λ_{ex} = 350 nm reveals two bands in the emission spectra, corresponding to the π*→π and the π*→n electron transitions. The positions of the maxima are 392 and *ca*. 540 (shoulder) nm in case of **L$_6$**, 402 and 548 nm in case of **6** for the blue and red components of the spectra, respectively. Slight bathochromic shift (Δλ = +10 nm) of the blue emission line of **6**, compared with the ligand **L$_6$** is explained by the coordination interaction of the benzotriazole groups with silver(I) cations. The existence of rather strong π*→n luminescence in the coordination compound **6** support the absence of the co ns. Otherwise, the involvement of the corresponding non-bonding lone electron pair in the donor-acceptor interactions would eliminate such transition. The excitation spectra of the ligand **L$_6$** and compound **6** recorded with λ_{em} = 550 nm contain two maxima for each compound: λ = 364 and 438 nm for **L$_6$** as well as λ = 355 and 431 nm for **6**. The peak at $\lambda \approx 360$ nm must be attributed to the higher energy $\pi \rightarrow \pi^*$ transition while the peak at $\lambda \approx 435$ nm should correspond to the excitation of lower energy $n \rightarrow \pi^*$ electron transition. Consequently, the luminescence spectra of both **L$_6$** and **6**, excited at lower energy (λ_{ex} = 440 nm) reveal only one peak positioned at λ = 529 nm for **L$_6$** and λ = 525 nm for **6**, corresponding to the $\pi^* \rightarrow n$ relaxation. The measured quantum yield for this transition is *ca*. 3% for both **L$_6$** and **6**.

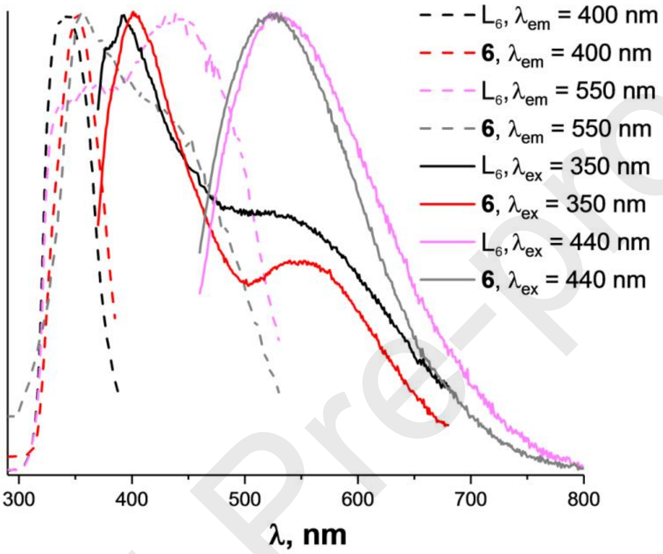


Fig. 10. Solid-state luminescence spectra of **6** and **L$_6$**.

Antibacterial and antifungal activity

Silver coordination polymers are known to demonstrate bactericidal effects even in heterogeneous conditions, associated with the migration of silver ions or its molecular complexes into the medium [49–54] The antimicrobial efficiency of **L$_4$**, **L$_6$** and [Ag(**L$_6$**)(NO$_3$)]$_\infty$ (**6**) was evaluated *in vitro* by their minimal inhibitory concentrations (MIC, µg/ml). The compounds were tested against such opportunistic microorganisms as *Staphylococcus albus*, *Escherichia coli*, *Pseudomonas aeruginosa*, *Klebsiella pneumonia* bacteria and *Candida albicans* yeast. Individual tested ligands demonstrate weak bacteriostatic effect, although it is higher than for the unsubstituted benzotriazole (BtaH) (Table 2).

The benzotriazole complex with silver nitrate [Ag(BtaH)NO$_3$] [55] does not inhibit any test culture used probably due to the strong coordination between the ligand and the metal ion. It should be noted that the coordination polymer **6** demonstrates a species-specific antibacterial effect during at least 3 days, which is probably due to a slow release of silver ions from the polymer layer, indicating its potential applicability as an additive to polymeric antibacterial films.

Table 2. Antibacterial activity of compounds tested.

Test culture	MIC, μg/ml			Bactericidal effect, 200 μg/ml			
	L$_4$	**L$_6$**	BtaH	[Ag(BtaH)NO$_3$]	Compound **6**		
					1 day	2 days	3 days
St. albus	1024	1024	1024+	–	+	+	+
E. coli	1024	1024+	1024+	–	–	–	–
Ps. aeruginosa	1024	1024	1024+	–	+	+	+
Kl. pneumoniae	1024	512	1024+	–	+	+	+
C. albicans	512	n.d.	1024+	–	–	–	–

«1024+» - MIC could not be reached, «+» - bacteria are inhibited totally.

Conclusion

In summary, a convenient method for the preparation and isomer separation of bis(benzotriazolyl)alkanes was proposed. Three new coordination compounds with cadmium nitrate and four coordination polymers with silver nitrate were prepared and structurally characterized. In case of cadmium(II) ions solvent-dependent effect of dimensionality of the coordination compound was observed. In all cases, bis(benzotriazole-1-yl)alkanes acted as bridging ligands and nitrogen atoms in position 3 of the heterocycle acted as donor atoms. Both cadmium(II) and silver(I) coordination polymers demonstrated two-band emission spectra, associated with $\pi^* \rightarrow \pi$ and $\pi^* \rightarrow n$ transitions. Coordination polymer of silver nitrate with 1,6-bis(benzo-1,2,3-tirazol-1-yl)hexane demonstrated a stable bactericidal effect even after 72 hours of exposure to culture medium.

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Appendix A. Supplementary data

CCDC 1952607-1952613 contain the supplementary crystallographic data for compounds **1**-**7**. These data can be obtained free of charge via http://www.ccdc.cam.ac.uk/conts/retrieving.html, or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: (+44) 1223-336-033; or e-mail: deposit@ccdc.cam.ac.uk.

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Synopsis

New coordination compounds of cadmium(II) and silver(I) with bis(1,2,3-benzotriazol-1-yl)alkanes were prepared and structurally characterized. 1,3-Bis(benzo-1,2,3-triazol-1-yl)propane formed both discrete complexes and 1D coordination polymers with cadmium(II) ions. Longer ligands 1,4-bis(benzo-1,2,3-triazol-1-yl)butane and 1,6-bis(benzo-1,2,3-triazol-1-yl)hexane formed 2D coordination polymers with silver(I) ions. Luminescent properties and antibacterial activity of the prepared coordination compounds were evaluated.

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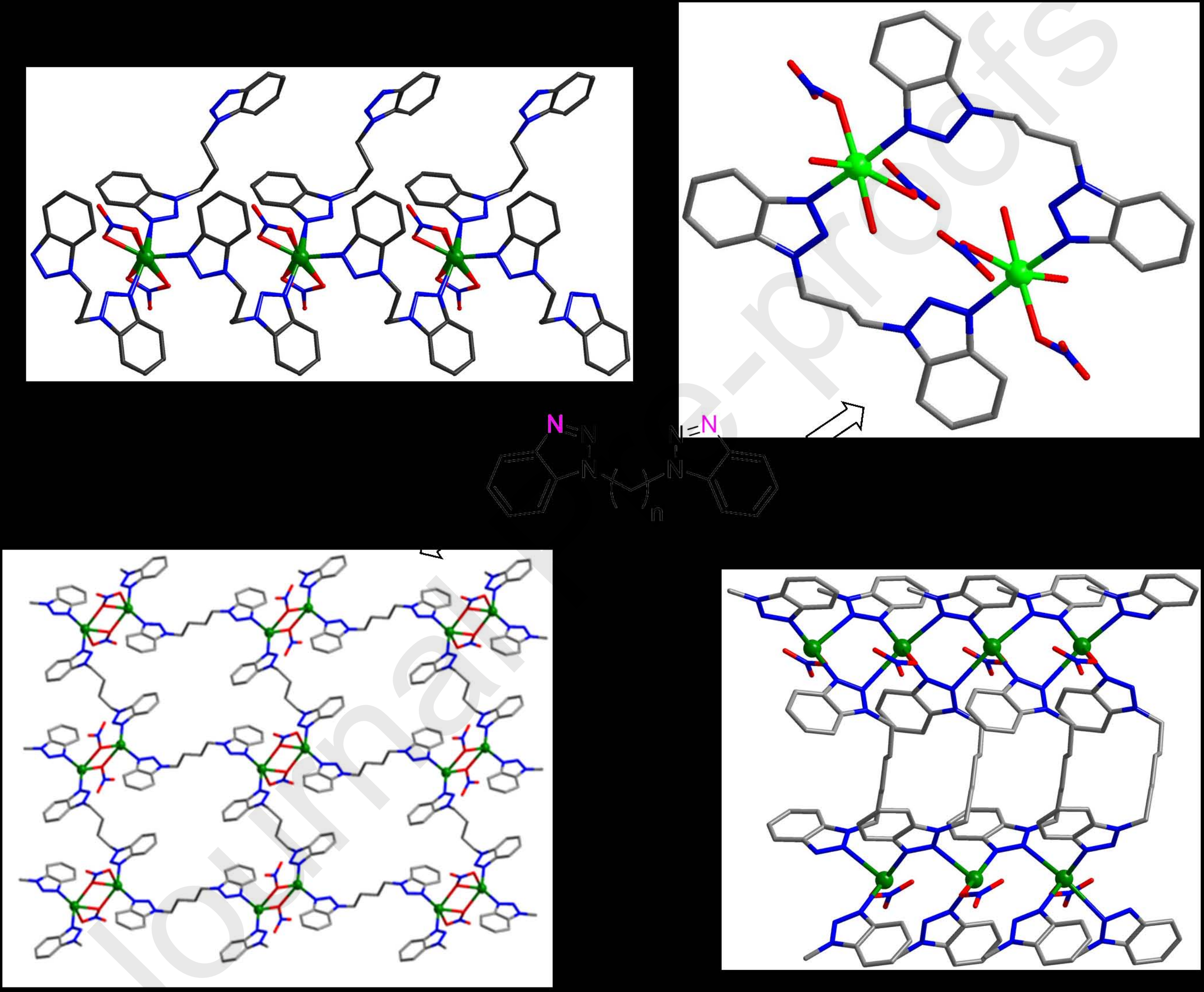
Roman D. Marchenko: Methodology, Investigation, Writing- Original draft preparation A**nna A. Lysova**: Investigation, Writing- Original draft preparation **Denis G. Samsonenko**: Investigation, Visualization **Danil N. Dybtsev**: Methodology, Writing- Reviewing and Editing **Andrei S. Potapov**: Conceptualization, Writing- Reviewing and Editing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