ISSN 1070-3284, Russian Journal of Coordination Chemistry, 2022, Vol. 48, No. 8, pp. 504–509. © Pleiades Publishing, Ltd., 2022.
Russian Text © The Author(s), 2022, published in Koordinatsionnaya Khimiya, 2022, Vol. 48, No. 8, pp. 500–505.

The issue dedicated to the 70th birthday of Academician V.I. Ovcharenko

Cadmium(II)-Organic Frameworks Containing the 1,3-Bis(2-methylimidazolyl)propane Ligand

P. V. Burlak[a], **K. A. Kovalenko**[a], **D. G. Samsonenko**[a], **and V. P. Fedin**[a, *]
[a] *Nikolaev Institute of Inorganic Chemistry, Siberian Branch, Russian Academy of Sciences, Novosibirsk, Russia*
**e-mail: cluster@niic.nsc.ru*

Received December 8, 2021; revised February 3, 2022; accepted March 12, 2022

Abstract—The crystal structures of two new isoreticular metal-organic frameworks $[Cd_3(Bdc\text{-}X)_3(Bmip)_2]$ (X = Br, Bdc-Br^{2-} is 2-bromoterephthalate anion (**I**); X = NO_2, Bdc-NO_2^{2-} is 2-nitroterephthalate anion (**II**); Bmip is 1,3-bis(2-methylimidazolyl)propane) are determined by the single-crystal X-ray diffraction method. Compounds **I** and **II** contain trinuclear carboxylate building blocks $\{Cd_3(COO)_6N_4\}$ in which the cadmium atoms are coordinated by the donor nitrogen atoms of the Bmip ligands to form nonporous three-dimensional frameworks (CIF files CCDC nos. 2126695 (**I**) and 2126696 (**II**)). Compound **I** is characterized by powder X-ray diffraction, IR spectroscopy, and elemental CHN and thermogravimetric analyses. The sorption characteristics are studied and the luminescence spectra are obtained for compound **I**.

Keywords: metal-organic frameworks, cadmium complexes, 1,3-bis(2-methylimidazolyl)propane, X-ray diffraction, luminescence

DOI: 10.1134/S1070328422080024

INTRODUCTION

Metal-organic frameworks (MOF) are built of inorganic and organic building blocks/fragments, and organic polytopic ligand-linkers play the role of bridges between mononuclear metal cations or clusters/polydentate complexes. The study of MOF is one of the leading trends in the modern chemistry and materials science [1–4], since they are considered as promising materials for catalysis, storage of gases, and sensor materials and for the development of drugs with a prolonged effect, supercondensators, new conducting materials, etc. [5–15].

In spite of many interesting functional properties indicated above, in our opinion, the development of methods for the purposeful synthesis of MOF with the predicted structures and properties remains urgent. It is known that the use of sterically rigid organic ligands in the synthesis of MOF often increases the stability of the framework and makes it possible to obtain series of isoreticular compounds. Therefore, polycarboxylate ligands, in particular, terephthalic acid (H_2Bdc), are frequently used for the synthesis of MOF. On the one hand, many widely known frameworks, such as MIL-101 [16], MIL-53 [17], MOF-5 [18], UiO-66 [19], and others, are based on terephthalates. On the other hand, the use of organic ligands capable of easily changing its conformation can result in the formation of structurally nonrigid/flexible MOF [20]. These compounds can find use in selective adsorption and for the preparation of diverse smart materials, whose response is induced by the activating external action [21]. 1,3-Bis(2-methylimidazolyl)propane (Bmip) is an example of the structurally flexible ligand for the synthesis of MOF [22]. Owing to the alkyl group joining the imidazole groups, this ligand can change the conformation, bend, and stretch with the corresponding changes in the distances between the donor nitrogen atoms in the MOF from 5.6 [23] to 8.8 Å [24]. It is noteworthy that the chemistry of the MOF based on 1,3-bis(2-methylimidazolyl)propane is studied insufficiently, and 18 Bmip-based MOF are known nowadays (according to the CCDC database) [24, 25]. Such a restricted number of examples can be related, in particular, to a high conformational mobility of the flexible ligand, which impedes searching for optimum conditions of the preparation of single crystals of MOF.

In this work, we report the determination of crystal structures of two new isoreticular cadmium(II) MOF $[Cd_3(Bdc\text{-}Br)_3(Bmip)_2]$ (**I**) and $[Cd_3(Bdc\text{-}NO_2)_3(Bmip)_2]$ (**II**) simultaneously containing ligands of two types: structurally rigid 2-bromo-(Bdc-Br) and 2-nitroterephthalate (Bdc-NO_2) ligands, respectively, and structurally flexible ligand (Bmip).

EXPERIMENTAL

The purity of all reagents and solvents was not lower than reagent grade, and they were used as received. Ligand Bmip was synthesized using a modified procedure described earlier [26–28].

^1H NMR spectra were recorded on a Bruker Advance 500 spectrometer. IR spectra in a range of 4000–400 cm^{-1} were measured on a Bruker Scimitar FTS 2000 FT-IR spectrometer. Elemental analysis was carried out on a VarioMICROcube CHNS analyzer. X-ray diffraction (XRD) data were obtained on a Shimadzu XRD 7000S powder diffractometer (CuK_α radiation, $\lambda = 1.54056$ Å). Thermogravimetric analysis was carried out on a NETZSCH TG 209 F1 Iris thermoanalyzer using linear heating in a helium atmosphere with a rate of 10°/min. Solid-state luminescence spectra were detected on a Horiba Jobin Yvon Fluorolog 3 spectrometer equipped with a 450 W Xe lamp and a PM-1073 PMT detector. A Spectralon instrument with the G8 integration sphere (GMP SA) was used to determine the luminescence quantum yield. Sorption measurements were carried out on a Quantachrome Autosorb iQ automated adsorption analyzer with a CryoCooler accessory for measurements at 195 K.

XRD. Diffraction data for a single crystal of compound **I** were obtained at 100 K on the X-ray beamline of the Belok station at the Kurchatov Synchrotron Radiation Source of the National Research Center "Kurchatov Institute" (Moscow, Russia) using a Rayonix SX165 CCD two-coordinate detector ($\lambda = 0.79313$ Å, φ scan mode with an increment of 1.0°). Integration was performed, an absorption correction was applied, and unit cell parameters were determined using the XDS software [29]. Diffraction data for a single crystal of compound **II** were obtained at 150 K on an Agilent Xcalibur automated diffractometer equipped with an AtlasS2 two-coordinate detector (graphite monochromator, $\lambda(MoK_\alpha) = 0.71073$ Å, ω scan mode with an increment of 0.5°). Integration was performed, an absorption correction was applied, and unit cell parameters were determined using the CrysAlisPro software [29]. The structures were solved using the SHELXT program [30] and refined by full-matrix least squares in the anisotropic (except for hydrogen atoms) approximation using the SHELXL program [31]. The positions of the hydrogen atoms of the organic ligands were calculated geometrically and refined by the riding model. In the structures of compounds **I** and **II**, some guest molecules are strongly disordered and cannot be refined as a set of discrete positions. Therefore, the final composition was determined using the SQUEEZE/PLATON procedure [32] (59 e in 359 Å^3 for **I** and 89 e in 438 Å^3 for **II**). The crystallographic data and structure refinement details are given in Table 1.

The full tables of interatomic distances, bonds angles, coordinates of atoms, and atomic shift parameters were deposited with the Cambridge Crystallographic Data Centre (CIF files CCDC nos. 2126695 (**I**) and 2126696 (**II**); https://www.ccdc.cam.ac.uk/structures/).

Synthesis of 1,3-bis(2-methylimidazolyl)propane. A suspension of 2-methylimidazole (2-mIm) (3.28 g, 40 mmol), powdered KOH (3.36 g, 60 mmol), and DMSO (10 mL) was vigorously stirred at 80°C for 30 min. Then the reaction flask was placed in a bath with cold water, and after cooling to room temperature 1,3-dibromopropane (2.1 mL, 20 mmol) in DMSO (10 mL) was added dropwise for 30 min. The reaction mixture was stirred and refluxed overnight, water (200 mL) was added, and the resulting mixture was evaporated in vacuo on a rotary evaporator. The product was extracted from the obtained solid residue with ethyl acetate (3 × 15 mL). The removal of ethyl acetate in vacuo on a rotary evaporator gave the product as light yellow crystals. The yield was 88%. The purity of the sample was confirmed by ^1H NMR spectroscopy and elemental CHN analysis.

^1H NMR ($CDCl_3$; δ, ppm): 6.90 (d, $J = 1.3$ Hz, 2H, H4-2-mIm), 6.75 (d, $J = 1.3$ Hz, 2H, H5-2-mIm), 3.81 (t, $J = 7.1$ Hz, 4H, 2-mIm$\underline{CH_2}CH_2$), 2.26 (s, 6H, $\underline{CH_3}$-Im), 2.16 (q, $J = 7.1$ Hz, 2H, 2-mIm$\underline{CH_2}CH_2$).

For $C_{11}H_{16}N_4$			
Anal. calcd., %	C, 64.7	H, 7.9	N, 27.7
Found, %	C, 64.5	H, 7.5	N, 27.5

Synthesis of [Cd_3(Bdc-Br)$_3$(Bmip)$_2$] (I). A mixture of $Cd(NO_3)_2 \cdot 4H_2O$ (0.25 mmol, 77 mg), 2-bromoterephthalic acid H_2Bdc-Br (0.25 mmol, 62 mg), Bmip (0.25 mmol, 51 mg), DMF (13.75 mL), and ethanol (12 mL) was heated at 373 K for 24 h in a glass bottle with a screw-top. The obtained crystals were separated by decantation, washed with DMF (3 × 5 mL) and ethanol (3 × 5 mL), and dried in air. The yield was 54% (66 mg).

IR, (KBr; ν, cm^{-1}): 3502 w.br ν(O–H), 1596 m, 1544 s ν_{as}(C=O), 1504 m γ(C–C), 1480 m $\nu_s(COO^-)$, 1378 s ν_s(C=O), 1298 w, 1279 w, 1272 w, 1151 w, 1081 w, 1035 w, 999 w, 941 w, 880 w, 863 w, 841 m, 821 m, 766 s, 737 m, 665 m, 624 w, 558 w, 517 m, 466 w, 440 w, 420 w.

For $C_{46}H_{41}N_8O_{12}Br_3Cd_3$			
Anal. calcd., %	C, 37.5	H, 2.8	N, 7.6
Found, %	C, 37.6	H, 2.6	N, 7.6

Synthesis of single crystals of [Cd_3(Bdc-NO_2)$_3$(Bmip)$_2$] (II). A mixture of $Cd(NO_3)_2 \cdot 4H_2O$ (0.025 mmol, 7.7 mg), nitroterephthalic acid H_2Bdc-NO_2 (0.025 mmol, 5.3 mg), Bmip (0.025 mmol, 5.1 mg), DMF (1.2 mL), ethanol (1.2 mL), and water

Table 1. Crystallographic data and experimental and structure refinement parameters for compounds **I** and **II**

Parameter	Value	
	I	**II**
Empirical formula	$C_{46}H_{45}N_8O_{14}Br_3Cd_3$	$C_{46}H_{45}N_{11}O_{20}Cd_3$
FW	1510.83	1409.13
Crystal system	Monoclinic	Monoclinic
Space group	*C*2/*c*	*C*2/*c*
a, Å	26.455(5)	27.6407(4)
b, Å	12.276(6)	11.82254(15)
c, Å	16.530(4)	16.7692(2)
β, deg	91.097(8)	90.1829(13)
V, Å	5367(3)	5479.87(12)
Z	4	4
F(000)	2952	2808
ρ, g cm^{-3}	1.870	1.708
μ, mm^{-1}	4.577	1.238
Crystal size, mm	0.11 × 0.10 × 0.09	0.27 × 0.24 × 0.08
Number of measured, independent, and observed ($I > 2\sigma(I)$) reflections	36064, 6069, 5926	17163, 6218, 5734
R_{int}	0.0321	0.0178
Scan range over θ, deg	2.04–30.99	1.87–28.85
Ranges of reflection indices	$-34 \le h \le 34$, $-15 \le k \le 15$, $-21 \le l \le 21$	$-36 \le h \le 32$, $-14 \le k \le 15$, $-22 \le l \le 11$
Goodness-of-fit for F^2	1.172	1.046
R factors ($I > 2\sigma(I)$)	$R_1 = 0.0440$, $wR_2 = 0.1023$	$R_1 = 0.0421$, $wR_2 = 0.1080$
R factors (for all reflections)	$R_1 = 0.0447$, $wR_2 = 0.1026$	$R_1 = 0.0454$, $wR_2 = 0.1099$
Residual electron density (max/min), e Å^{-3}	0.927/–1.040	1.693/–0.877

(0.175 mL) was heated at 373 K for 24 h in a glass bottle with a screw-top. The compositions and structures of the obtained crystals were determined by XRD. The further optimization of the synthetic procedure is needed to obtain representative amounts of an analytically pure sample.

RESULTS AND DISCUSSION

Compound [Cd_3(Bdc-Br)$_3$(Bmip)$_2$] (**I**) crystallizes in the monoclinic space group *C*2/*c*. The independent part of the structure of compound **I** contains two cadmium cations. The Cd(2) cation exists in the octahedral coordination environment of six oxygen atoms from six carboxylate groups. The Cd(2)–O distances range from 2.205(3) to 2.353(3) Å. The structure of compound **I** contains the bromoterephthalate ligands of two types. One of the ligands is localized in the partial position at the inversion center, and another ligand is arranged in the position of the general type. In both bromoterephthalates, the bromine atom is disordered over two positions (0.5/0.5 and 0.75/0.25). The coordination environment of Cd(1) contains two nitrogen atoms from two Bmip ligands and five oxygen atoms from three carboxylate groups, two of which are coordinated via the bidentate mode. The fragment of the Bmip ligand is disordered over two orientations with the relative weights 0.643(8)/0.357(8). The Cd(1)–N distances range from 2.278(4) to 2.297(6) Å, and the Cd(1)–O distances lie in a range of 2.343(3)–2.573(4) Å. The coordination number of Cd(1) can be described as 5 + 2. The Cd(2) cation and two Cd(1) cations are joined due to the bridging carboxylate groups into the trinuclear coordination fragment {Cd_3(Bmip)$_4$(μ-RCOO-κ^1,κ^1)$_2$(μ-RCOO-κ^1,κ^2)$_4$} (Fig. 1). These trinuclear fragments are connected with each other via the bridging Bdc-Br ligands to form polymeric layers parallel to the *bc* plane (Fig. 2a). The adjacent layers are linked with each other by the bridging Bmip ligands to form the three-dimensional MOF (Fig. 2b) containing

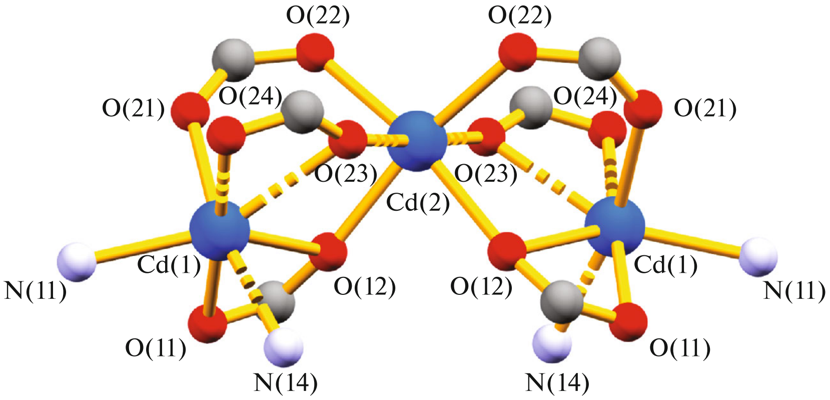

Fig. 1. Structure of the trinuclear fragment $\{Cd_3(COO)_6N_4\}$ in compound **I**.

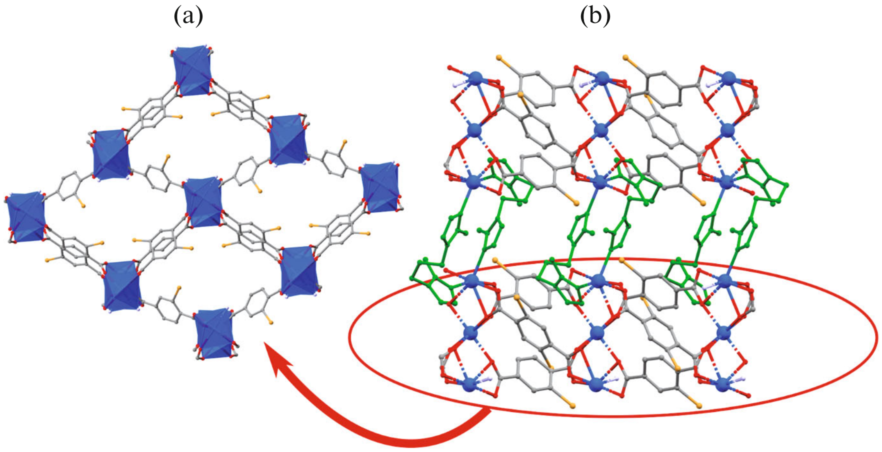

Fig. 2. (a) Structure of $[Cd_3(Bdc\text{-}Br)_3(Bmip)_2]$: the dimeric layer built of the trinuclear cadmium clusters and Bdc-Br^{2-} ligands; and (b) 3D structure: the dimeric layers joined by the Bmip ligands.

only small isolated cavities (6% of the unit cell volume as calculated using the Mercury program).

Compound $[Cd_3(Bdc\text{-}NO_2)_3(Bmip)_2]$ (**II**) is isostructural to compound **I**. The differences are as follows. The structure of compound **II** contains 2-nitroterephthalatae instead of 2-bromoterephthalate. The nitro group is disordered only at one of two Bdc-NO_2^{2-} ligands, which is localized in the partial position at the inversion center. The structure of compound **II** exhibits no disordering of the neutral Bmip ligand. The Cd(2)–O distances lie in a range of 2.177(3)–2.347(3) Å. The Cd(1)–O distances lie in a range of 2.332(3)–2.675(3) Å, and the Cd(1)–N distances are 2.273(3) and 2.287(4) Å. The structure of compound **II** is dense as that of compound **I**, and the free space volume calculated using the Mercury program is only 4%.

Compound **I** was characterized by XRD, IR spectroscopy, and thermogravimetric and elemental analyses. The powder pattern of compound **I** completely corresponds to that calculated from the single-crystal XRD data (Fig. 3). According to the thermal analysis data, compound **I** is highly thermally stable. Its heating to 300°C does not change the weight of the sample (Fig. 4).

Another MOF of the similar composition $[Cd_3(Bdc)_3(Bmip)_2]$ (**III**) [33], which was synthesized using unsubstituted terephthalic acid (H_2Bdc), was described [33]. Compounds **I**–**III** are isoreticular, crystallize in the monoclinic space group *C*2/*c*, are based on the similar in structure trinuclear inorganic building blocks, and have the same topology of the three-dimensional frameworks. However, the unit cell volumes differ strongly (5367(3) $Å^3$ for **I**, 5479.87(12) $Å^3$ for **II**, and 6220.0(9) $Å^3$ for **III**). Unlike compounds **I** and **II**, the framework of compound **III** is permanently porous, and the volume accessible for the inclusion of guest molecules is 32.4%. A comparison of the structures shows that in compounds **I** and **II** the distance between the donor nitrogen atoms of the flexible 1,3-bis(2-methylimidazolyl)propane ligand is 6.924 and 6.837 Å, respectively, versus 7.363 Å in com-

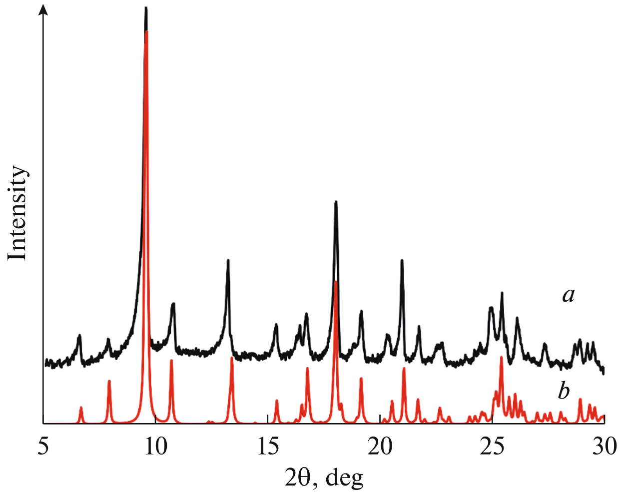

Fig. 3. XRD patterns of $[Cd_3(Bdc\text{-}Br)_3(Bmip)_2]$: (*a*) experimental and (*b*) calculated from the single-crystal XRD data.

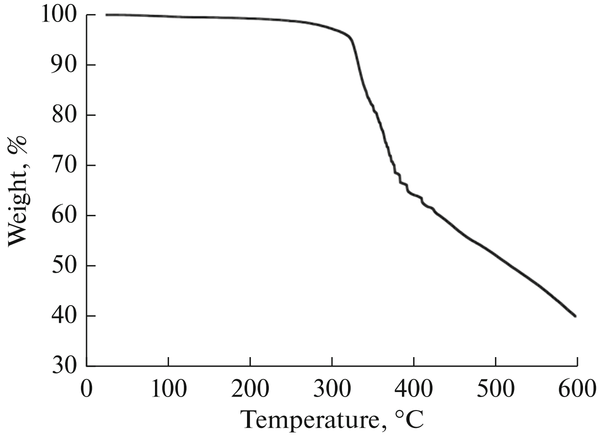

Fig. 4. Thermogravimetric curve for $[Cd_3(Bdc\text{-}Br)_3(Bmip)_2]$.

pound **III**. Such strong differences in the ligand structure caused by its conformational mobility lead to considerable changes in the sorption properties: the framework of compound **III** sorbs an appreciable amount of carbon dioxide, whereas the isotherms of low-temperature adsorption of carbon dioxide at 195 K for compound **I** show an almost zero capacity.

The photophysical properties were studied for compound **I**. The excitation spectrum of complex **I** contain two broad bands (Fig. 5). Based on the published data, we can assign the observed excitation maxima to the absorption of 2-bromoterephthalate (325 nm) and 1,3-bis(2-methylimidazolyl)propane (375 nm). The photoluminescence spectra were recorded at two different excitation wavelengths. In both cases, the sample emits blue radiation with a broad emission band at 440 nm with an excitation wavelength at 325 nm and a maximum at 450 nm at an excitation wavelength of 375 nm. The Cd(II) complexes with the electronic configuration d^{10} are not redox-active, and no metal-to-ligand (MLCT) or ligand-to-metal (LMCT) charge-transfer mechanisms are observed for these compounds. In our case, ligand-centered luminescence occurs, and the observed emission can be attributed to the intraligand transitions $\pi^* \rightarrow \pi$ and/or $\pi^* \rightarrow n$ in the organic ligands. The quantum yield for compound **I** was 19% at $\lambda_{em} = 375$ nm. A rather high quantum yield can be the result of a higher mechanical stability (rigidity) of the nonporous framework of compound **I**. In fact, the dense structure prevents possible vibrations of the organic linkers and the whole framework thus decreasing the probability of photoexcited electron state relaxation via consecutive vibrational states.

Thus, the family of isoreticular metal-organic frameworks of the cadmium(II) polymers is based on two types of ligands: structurally rigid terephthalates

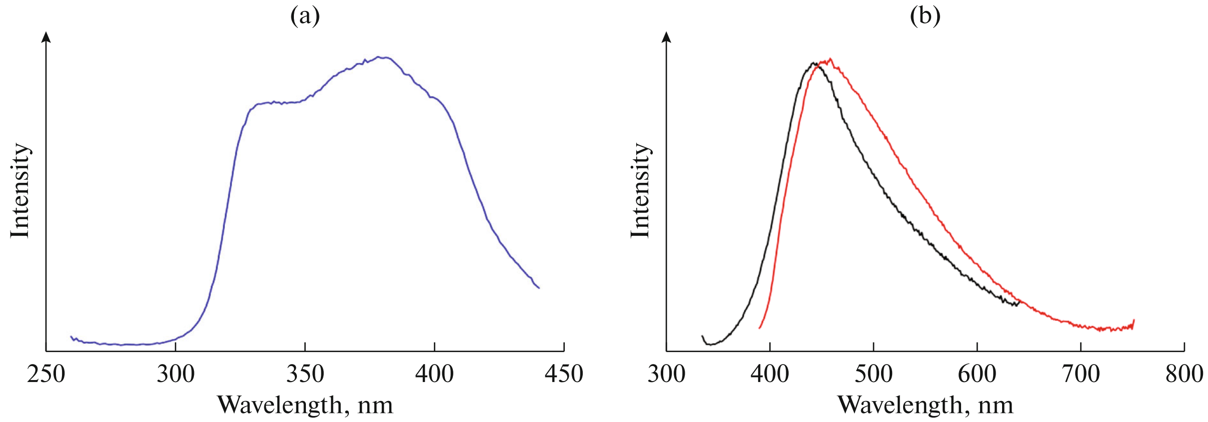

Fig. 5. (a) Solid-state excitation spectra at 450 nm and (b) solid-state emission spectra at $\lambda_{exc} = 325$ nm (black) and 375 nm (red).

and structurally flexible 1,3-bis(2-methylimidazolyl)propane. The introduction of the substituents into the terephthalate ligand was shown to afford nonporous frameworks due to changing the conformation of the flexible ligand.

FUNDING

This work was supported by the Russian Foundation for Basic Research, project no. 20-33-90207. The analytical characterization of the synthesized compounds was supported by the Ministry of Science and Higher Education of the Russian Federation, project no. 121031700321-3.

CONFLICT OF INTEREST

The authors declare that they have no conflicts of interest.

REFERENCES

1. Furukawa, H., Cordova, K.E., O'Keeffe, M., et al., *Science*, 2013, vol. 341, no. 6149, p. 1230444.
2. Zhou, H.-C. and Kitagawa, S., *Chem. Soc. Rev.*, 2014, vol. 43, p. 5415.
3. Czaja, A.U., Trukhan, N., and Müller, U., *Chem. Soc. Rev.*, 2009, vol. 38, no. 5, p. 1284.
4. Cui, Y., Li, B., He, H., et al., *Acc. Chem. Res.*, 2016, vol. 49, no. 3, p. 483.
5. Corma, A., Garcia, H., and Xamena, F.X.L., *Chem. Rev.*, 2010, vol. 110, no. 8, p. 4606.
6. Wang, A., Li, J., and Zhang, T., *Nature Rev. Chem.*, 2018, vol. 2, p. 65.
7. Suh, M.P., Park, H.J., Prasad, T.K., et al., *Chem. Rev.*, 2012, vol. 112, no. 2, p. 782.
8. Sumida, K., Rogow, D.L., Mason, J.A., et al., *Chem. Rev.*, 2012, vol. 112, no. 2, p. 724.
9. He, Y., Zhou, W., Qian, G., et al., *Chem. Soc. Rev.*, 2014, vol. 43, no. 16, p. 5657.
10. Tsivadze, A.Y., Aksyutin, O.E., Ishkov, A., et al., *Russ. Chem. Rev.*, 2019, vol. 88, no. 9, p. 925.
11. Kreno, L.E., Leong, K., Farha, O.K., et al., *Chem. Rev.*, 2012, vol. 112, no. 2, p. 1105.
12. Ponomareva, V.G., Kovalenko, K.A., Chupakhin, A.P., et al., *J. Am. Chem. Soc.*, 2012, vol. 134, no. 38, p. 15640.
13. Lim, D.-W. and Kitagawa, H., *Chem. Soc. Rev.*, 2021, vol. 50, no. 11, p. 6349.
14. Yan, J., Wang, Q., Wei, T., et al., *Adv. Energy Mater.*, 2014, vol. 4, p. 1300816.
15. Horcajada, P., Gref, R., Baati, T., et al., *Chem. Rev.*, 2012, vol. 112, no. 2, p. 1232.
16. Férey, G., Mellot-Draznieks, C., Serre, C., et al., *Science*, 2005, vol. 309, no. 5743, p. 2040.
17. Serre, C., Millange, F., Thouvenot, C., et al., *Nature*, 2002, vol. 124, no. 45, p. 13519.
18. Li, H., Eddaoudi, M., O'Keeffe, M., et al., *Nature*, 1999, vol. 402, p. 276.
19. Cavka, J., Jakobsen, S., Olsbuy, U., et al., *J. Am. Chem. Soc.*, 2008, vol. 130, no. 42, p. 13850.
20. Schneemann, A., Bon, V., Schwedler, I., et al., *Chem. Soc. Rev.*, 2014, vol. 43, no. 16, p. 6062.
21. Xu, L., Liu, B., Zheng, F.K., et al., *J. Solid State Chem.*, 2005, vol. 178, no. 11, p. 3396.
22. Hao, H.J., Liu, F., Su, H., et al., *CrystEngComm*, 2012, vol. 14, no. 20, p. 6726.
23. Altaf, M., Mansha, M., Sohail, M., et al., *New J. Chem.*, 2017, vol. 41, no. 8, p. 2980.
24. Wang, J., Lu, L., He, J., et al., *J. Mol. Struct.*, 2019, vol. 1182, no. 2, p. 79.
25. Xue, L.P., Li, Z.H., Maet, L.F., et al., *CrystEngComm*, 2015, vol. 17, no. 33, p. 6441.
26. Barsukova, M.O., Sapchenko, S.A., Kovalenko, K.A., et al., *New J. Chem.*, 2018, vol. 42, no. 8, p. 6408.
27. Barsukova, M.O., Samsonenko, D.G., Goncharova, T.V., et al., *Russ. Chem. Bull.*, 2016, vol. 65, p. 2914.
28. Barsukova, M., Goncharova, T., Samsonenko, D., et al., *Crystals*, 2016, vol. 10, p. 132.
29. *CrysAlisPro 1.171.38.46. Rigaku Oxford Diffraction*. The Woodlands (TX, USA), 2015.
30. Sheldrick, G.M., *Acta Crystallogr., Sect. A: Found. Adv.*, 2015, vol. 71, p. 3.
31. Sheldrick, G.M., *Acta Crystallogr., Sect. C: Struct. Chem.*, 2015, vol. 71, p. 3.
32. Spek, A.L., *Acta Crystallogr., Sect. C: Struct. Chem.*, 2015, vol. 71, no. 1, p. 9.
33. Shi, J.-T., Yue, K., Liu, B., et al., *CrystEngComm*, 2014, vol. 16, no. 15, p. 3097.

Translated by E. Yablonskaya