Luminescence properties of mesoporous chromium(III) terephthalate and inclusion compounds of cluster complexes

K. A. Kovalenko,[a,b] D. N. Dybtsev,[a,b] S. F. Lebedkin,[c] and V. P. Fedin[a,b]★

[a]*A. V. Nikolaev Institute of Inorganic Chemistry, Siberian Branch of the Russian Academy of Sciences,*
3 prosp. Akad. Lavrent´eva, 630090 Novosibirsk, Russian Federation.
Fax: +7 (383) 330 9489. E-mail: cluster@niic.nsc.su
[b]*Novosibirsk State University,*
2 ul. Pirogova, 630090 Novosibirsk, Russian Federation
[c]*Institute of Nanotechnology, Forschungszentrum Karlsruhe,*
P.O. Box 3640, D-76021 Karlsruhe, Germany

The luminescence properties of mesoporous chromium(III) terephthalate $[Cr_3O(C_8H_4O_4)_3F(H_2O)_2]$ (MIL-101) were discovered, and the luminescence spectra were detected at temperatures from 20 to 290 K. By the interaction of MIL-101 with solutions of anionic clusters $[Mo_6Cl_{14}]^{2-}$ ($\{Mo_6\}$) and $[Re_6S_8(CN)_6]^{4-}$ ($\{Re_6\}$) new hybrid materials $\{Mo_6\}$@MIL-101 and $\{Re_6\}$@MIL-101 were synthesized, the nanoporous framework of which contains *ca*. 3.5 and 1.5 clusters per cage, respectively. The synthesized hybrid materials possess the luminescence properties different from those of the initial framework and cluster complexes.

Key words: chromium terephthalate, molybdenum clusters, rhenium clusters, coordination polymers, mesoporous structures, luminescence.

Metal-organic frameworks (coordination polymers) are regular structures consisting of metal cations linked through organic bridging ligands.[1,2] Considerable progress has recently been achieved in the synthesis of mesoporous (with the pore size values >2 nm) coordination polymers.[3—5] Studies of functional properties of these frameworks and experiments on the inclusion of large molecules or cluster complexes into mesoporous frameworks are of special interest, since they possess intrinsic functional properties, which makes it possible to create a new class of hybrid materials.[6]

The methods of preparation of unique mesoporous chromium(III) terephthalate $[Cr_3O(C_8H_4O_4)_3F(H_2O)_2]$ (MIL-101) with the zeolite-like topology of the metal-organic framework have recently been developed.[3] The fragment of the framework structure is presented in Fig. 1; two large and two small cages in the framework linked through the five- and six-membered windows are shown. One of the small nanocages (see Fig. 1) is surrounded by tetrahedra, whose apices are occupied by the μ_3-bridging oxygen atoms of the carboxylate triangular chromium complexes $Cr_3(\mu_3\text{-}O)(O_2CR)_6$, and the triangular complexes are connected at the edges of the tetrahedron through the terephthalate linkers (see inset in Fig. 1). Thick gray lines connect the centers of the adjacent tetrahedra and demonstrate the general topology of the framework corresponding to zeolite of the MTN type. This mesoporous framework (see Fig. 1) contains highly ordered nanosized cages of two types with the diameter 3.0 and 3.8 nm, which linked through the windows with van der Waals dimensions of 1.1 and 1.5 nm. Simplicity of preparation and high thermal and hydrolytic stability of the MIL-101 framework are doubtless advantages of this material over other mesoporous coordination polymers.

The synthesis of the heterogeneous catalysts based on MIL-101 by the incorporation of Keggin polyoxoanions into the framework cages has earlier[3,7] been reported. We

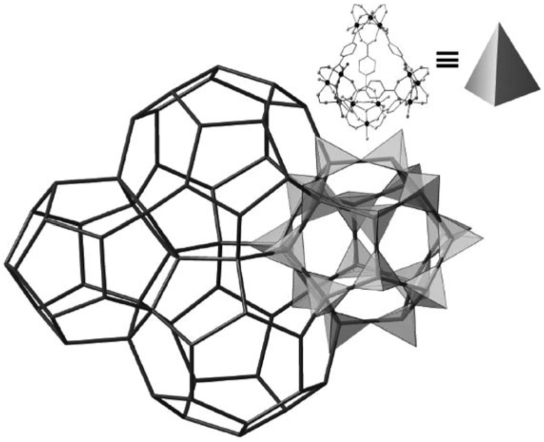

Fig. 1. Fragment of the mesoporous structure of MIL-101.

Published in Russian in *Izvestiya Akademii Nauk. Seriya Khimicheskaya,* No. 4, pp. 727—730, April, 2010.

also obtained[8] the hybrid sorbent $[Re_4S_4F_{12}]^{4-}$@MIL-101 from MIL-101, which made it possible to increase the hydrogen sorption capacity.

In the present work, we report for the first time the luminescence properties of mesoporous chromium(III) terephthalate MIL-101, the synthesis and study of the characteristics of the inclusion compounds of the molybdenum and rhenium cluster complexes in the cage of the MIL-101 framework, and their luminescence properties. The octahedral anionic clusters $[Mo_6Cl_{14}]^{2-}$ ($\{Mo_6\}$)[9] and $[Re_6S_8(CN)_6]^{4-}$ ($\{Re_6\}$)[10] were chosen as guests for inclusion into the mesoporous framework MIL-101.

Results and Discussion

We have studied for the first time the luminescence properties of chromium(III) terephthalate MIL-101. The MIL-101 powder was dispersed in viscous polyfluorinated ether (ABCR) and placed between two quartz plates 1 mm thick. The luminescence spectra were recorded in the temperature range from 20 to 290 K at an angle of 30° to the exciting beam. The compound possesses very weak luminescence with a maximum at 785—790 nm at temperatures from room temperature to 200 K (Fig. 2). Nevertheless, the luminescence peak is rather narrow: the width at the half-height is 40 nm. Cooling the sample below 200 K results in a strong increase in the intensity of the luminescence maximum, which was ~100 times higher at 50 K than at 200 K. In addition to the narrow main peak, the spectra contain a distinct vibrational structure with a shoulder at 830 nm and a local maximum at 890 nm. On further cooling the sample down to 20 K the intensity of the luminescence maximum does not change. As a whole, these properties correspond to the published data[11] for numerous organic and inorganic chromium(III) compounds. The narrow-band luminescence of MIL-101 can be assigned to the transition $^2E \rightarrow {}^4A_2$ in the chromium(III) ions. At all temperatures, the excited level $^4T_2$ is higher than ^2E, most likely, because the broad-band luminescence characteristic of the transition $^4T_2 \rightarrow {}^4A_2$ is not observed (see Fig. 2).[11] The luminescence wavelength of MIL-101 is considerably higher, *i.e.*, the energy of the transition $^2E \rightarrow {}^4A_2$ is lower

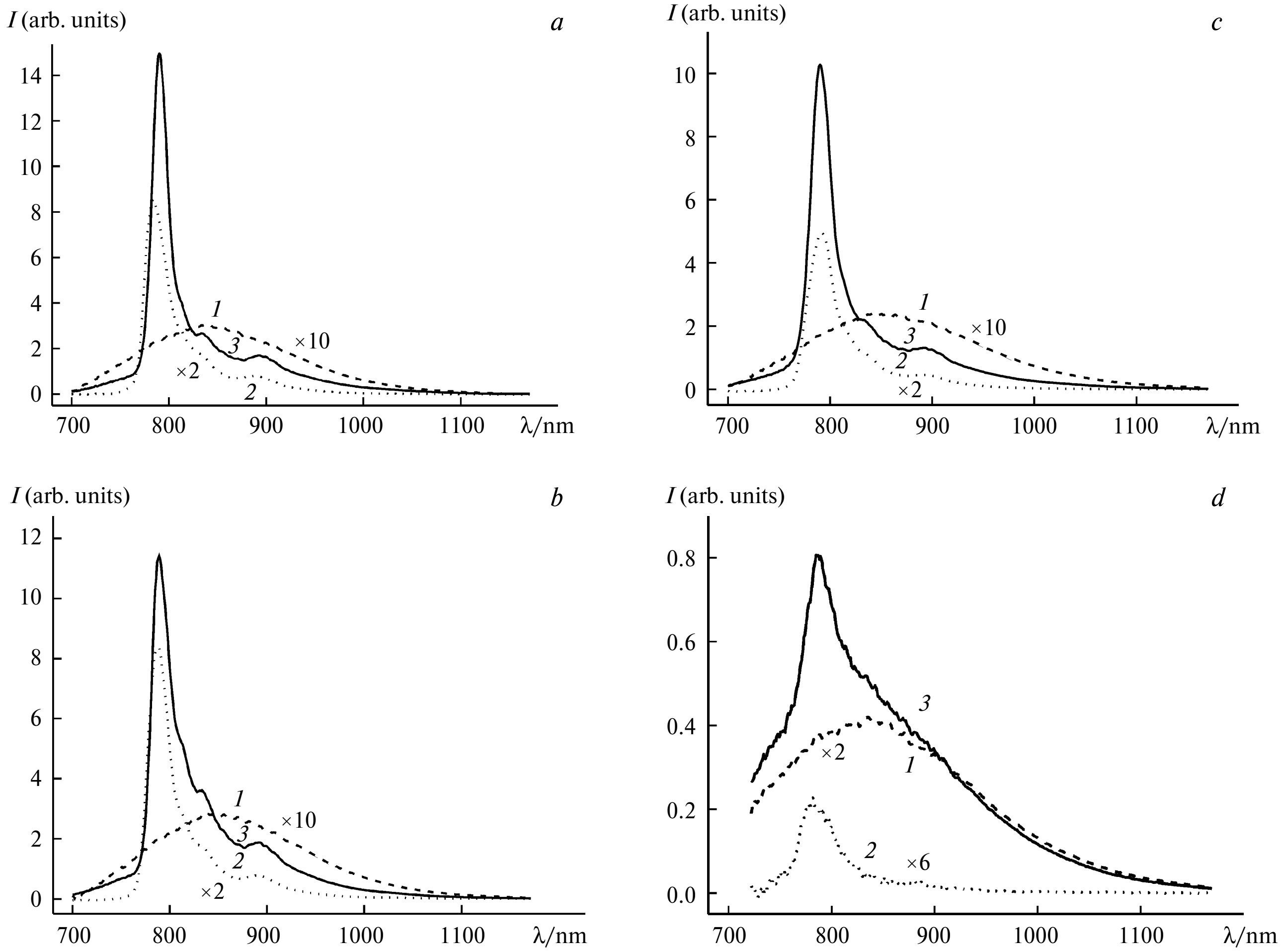

Fig. 2. Comparison of the photoluminescence spectra of $\{Mo_6\}$ (*1*), MIL-101 (*2*), and hybrid material $\{Mo_6\}$@MIL-101 (*3*) at 20 (*a*), 50 (*b*), 100 (*c*), and 200 K (*d*). The excitation wavelength is 350 nm.

than that typical of the luminescence of Cr^{III} in the inorganic matrices (~694 nm). This effect can be due to the electronic interaction in the metal-organic framework of MIL-101, which results in the partial delocalization of an excited electron in chromium ions.[11] Note that the luminescence excitation spectrum of MIL-101 (approximately corresponding to the absorption spectrum) is almost temperature-independent (Fig. 3, *a*).

In the present work, we studied the luminescence properties of the hybrid materials containing the luminescent clusters in the luminescent framework. It is well known[9,10] that the cluster complexes $\{Mo_6\}$ and $\{Re_6\}$ possess luminescence properties. The van der Waals size of the anions does not exceed 1 nm, which allows their easy penetration into the mesoporous framework. The MIL-101 matrix has a positive charge, due to which ionic interactions occur between the guest and matrix, which makes it possible to prepare these compounds by ion exchange.

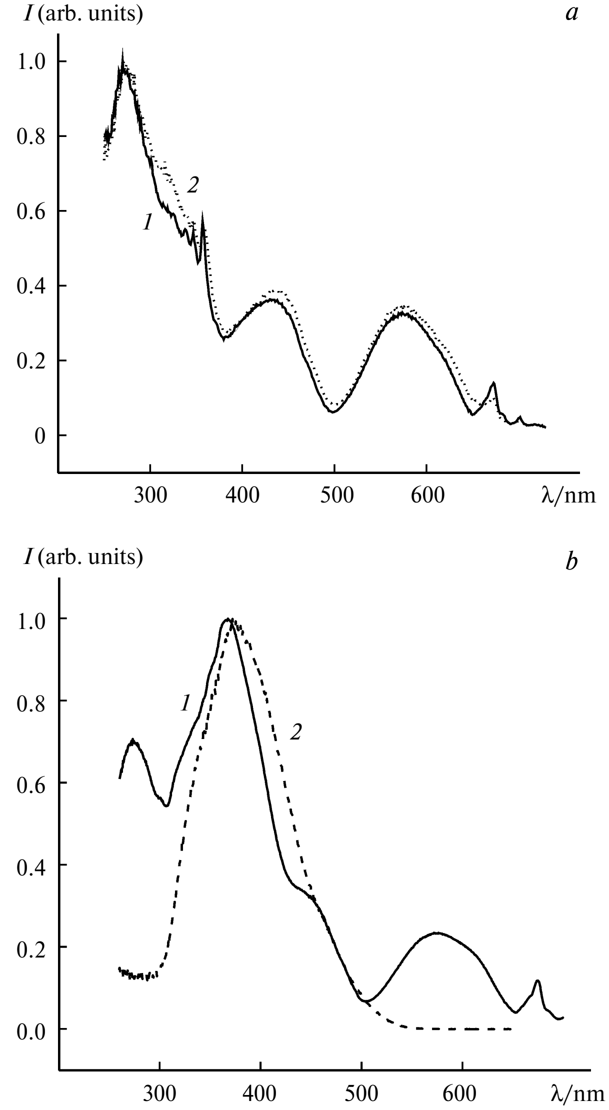

Fig. 3. Luminescence excitation spectra of MIL-101 (*a*) and hybrid material $\{Mo_6\}$@MIL-101 (*b*) at 20 (*1*) and 290 K (*2*). The excitation wavelength is 800 nm.

The hybrid material $\{Mo_6\}$@MIL-101 was synthesized by stirring a suspension of $(Et_4N)_2[Mo_6Cl_{14}]$ and MIL-101 in DMF for 4 h at 80 °C. The hybrid material $\{Re_6\}$@MIL-101 was prepared by stirring a suspension of $(Bu_4N)_4[Re_6S_8(CN)_6]$ and MIL-101 in acetonitrile for 6 h at room temperature. According to the X-ray diffraction data, the inclusion of clusters does not result in distortions in the metal-organic framework, because the positions of reflections for the initial MIL-101 and synthesized hybrid materials in the most characteristic region of low angles almost coincide. In addition, the position of the vibrational bands of the carboxyl group of the terephthalate $\nu_a(COO) = 1622\ cm^{-1}$ and $\nu_s(COO) = 1401\ cm^{-1}$ ($\Delta = 221\ cm^{-1}$) is retained in the IR spectra, which corresponds to the bridging coordination mode of the terephthalate to the Cr_3O clusters. According to the elemental analysis (ICP-AES), the Cr/Re ratio in the samples is 3.4, while the Cr/Mo ratio is 1.6. The unit cell of MIL-101 contains 816 Cr atoms, 16 small (3.0 nm) cages and eight large (3.8 nm) cavities. With allowance for this fact, the number of the $\{Mo_6\}$ and $\{Re_6\}$ clusters in the MIL-101 framework is, on the average, 3.5 and 1.5, respectively, per a large or small cage. Thus, the new hybrid luminescent materials, in which the cluster complexes are located in the cages of the luminescent mesoporous metal-organic framework, were synthesized.

The luminescence spectra of $\{Mo_6\}$@MIL-101 and $\{Re_6\}$@MIL-101 were obtained under the conditions similar to those for the initial MIL-101 matrix. The luminescence spectra of the clusters have rather broad peak at ~100 nm with a maximum at 840 nm for the $\{Mo_6\}$ cluster and 720 nm for the $\{Re_6\}$ cluster. The luminescence spectra of the $\{Mo_6\}$ cluster depends very weakly on temperature: on cooling the sample from room temperature to 20 K, the intensity increases only by 1.5 times (see Fig. 2). On cooling from room temperature to 20 K, the luminescence spectrum of the $\{Re_6\}$ cluster undergoes considerable changes: the radiation maximum is shifted to the long-wavelength region and at 20 K the maximum lies at 830 nm, and the intensity increases ~4 times. At room temperature the luminescence intensity of the cluster complexes is higher than that for MIL-101. On cooling below 200 K, the luminescence of MIL-101 is much more intense than that for the cluster complexes. Therefore, the luminescence spectrum of the hybrid materials can be presented, in the first approximation, as the sum of the luminescence spectra of the framework and cluster complex (see Fig. 2), where the luminescence of the framework (MIL-101) predominates on cooling below 200 K. At the same time, luminescence of hybrid materials have some specific features. For instance, an increase in the luminescence for the hybrid materials shifts when the sample is cooled from room temperature (for the "free" matrix it is 200 K) and persists down to 20 K (for the "free" matrix the intensity increase terminates when 50 K is reached). In the temperature range studied, the luminescence intensity of the hybrid materials exceeds the luminescence intensity of the initial matrix several times (see Fig. 2). At ~20 K the luminescence of the hybrid materials is ~4 times more intense than the photoluminescence of MIL-101 (estimated for the samples with the equal layer thicknesses, *i.e.*, with approximately the same absorption of the exciting light). In addition, for the hybrid materials, the luminescence peak of Cr^{III} is shifted to the long-wavelength region by 4—5 nm. Noticeable difference are also observed when the luminescence excitation spectra of the "free" matrix and hybrid materials are compared. In the latter case, the excitation spectrum strongly changes on cooling, whereas the excitation spectra of MIL-101 and individual cluster complexes are weakly temperature-dependent (see Fig. 3).

Thus, in the present work the luminescence properties of mesoporous chromium(III) terephthalate were discovered and the hybrid inclusion materials $\{Mo_6\}$ and $\{Re_6\}$ in MIL-101 with the luminescence properties different from the properties of the free framework and cluster complexes were obtained and characterized. It can be assumed that the appreciable influence of the inclusion compounds on the photoluminescence of MIL-101 is general. Since the porous materials are promising for gas separation and storage, it is especially interesting to study further the influence of gas sorption on the photoluminescence of MIL-101.

Experimental

Mesoporous chromium terephthalate MIL-101 and the clusters were synthesized according to procedures described previously.[3,9,10] X-ray diffraction analysis of polycrystalline samples was carried out on a Philips APD1700 diffractometer using Cu-Kα radiation (λ = 1.54060 and 1.54439 Å). IR spectra in the range 4000—400 cm^{-1} were recorded on a SCIMITAR FTS 2000 FTIR spectrometer in KBr pellets. Photoluminescence measurements were carried out on a Spex Fluorolog-3 spectrometer equipped with a xenon lamp (450 W), double monochromators for excitation and emission, and Hamamatsu R928 (for the wavelength range ~300—850 nm) and R5508 (~700—1400 nm) thermoelectrically cooled photomultipliers as detectors. Elemental analysis was carried out by atomic emission spectrometry with inductively coupled plasma on an iCAP 6000 instrument.

Synthesis of $\{Mo_6\}$@MIL-101. Cluster $(Et_4N)_2[Mo_6Cl_{14}]$ (200 mg) was dissolved in DMF (0.5 mL), MIL-101 (100 mg) was added, and the suspension formed was stirred for 4 h at 80 °C. The precipitate was filtered off, washed with acetonitrile (2×0.5 mL) on the filter, and dried in air for 1 day at 65 °C. The yield was 120 mg. IR, ν/cm^{-1}: 3398 m, 2931 w, 1668 s, 1622 s, 1555 s, 1506 s, 1434 s, 1401 s, 1300 w, 1255 w, 1162 w, 1100 w, 1018 w, 887 w, 830 w, 748 m, 663 m, 587 s, 470 w, 390 m.

Synthesis of $\{Re_6\}$@MIL-101. Cluster $(Bu_4N)_4[Re_6S_8(CN)_6]$ (350 mg) was dissolved in MeCN (0.5 mL), MIL-101 (100 mg) was added, and the suspension formed was stirred for 6 h at ~20 °C. The precipitate was filtered off, washed with acetone (2×0.5 mL) on the filter, and dried in air for 1 day at 65 °C. The yield was 120 mg. IR, ν/cm^{-1}: 3402 m, 2960 m, 2874 m, 2116 m, 1622 s, 1531 s, 1506 s, 1485 w, 1401 s, 1159 w, 1106 w, 1064 w, 1017 w, 886 w, 829 w, 749 m, 653 w, 584 m, 471 w, 394 w.

Study of luminescence properties. Powdered samples for the study of the photoluminescence properties were dispersed in viscous fluorinated ether (ABCR), placed between two thin quartz plates, and fixed on the cold top of an optical cryostat with feedback (Leybold), operating in the temperature range from 14 to 293 K. Photoluminescence was detected at an angle of ~30° relative to the exciting beam. All emission spectra were corrected to the wavelength-dependent response from the spectrometer and detector.

This work was financially supported by the Russian Foundation for Basic Research (Project Nos 07-03-00436 and 08-03-12007).

References

1. S. Kitagawa, R. Kitaura, S.-I. Noro, *Angew. Chem., Int. Ed.*, 2004, **116**, 2334.
2. C. Janiak, *Dalton Trans.*, 2003, 2781.
3. G. Férey, C. Mellot-Draznieks, C. Serre, F. Millange, J. Dutour, S. Surblé, I. Margiolaki, *Science*, 2005, **309**, 2040.
4. G. Férey, C. Serre, C. Mellot-Draznieks, F. Millange, S. Surblé, J. Dutour, I. Margiolaki, *Angew. Chem.*, 2004, **116**, 6456.
5. Y. K. Park, S. B. Choi, H. Kim, K. Kim, B.-H. Won, K. Choi, J.-S. Choi, W.-S. Ahn, N. Won, S. Kim, D. H. Jung, S.-H. Choi, G.-H. Kim, S.-S. Cha, Y. H. Jhon, J. K. Yang, J. Kim, *Angew. Chem., Int. Ed.*, 2007, **43**, 8230.
6. G. Férey, *Chem. Soc. Rev.*, 2008, **37**, 191.
7. N. V. Maksimchuk, M. N. Timofeeva, M. S. Melgunov, A. N. Shmakov, Y. A. Chesalov, D. N. Dybtsev, V. P. Fedin, O. A. Kholdeeva, *J. Catal.*, 2008, **257**, 315; N. V. Maksimchuk, K. A. Kovalenko, S. S. Arzumanov, Y. A. Chesalov, M. S. Melgunov, A. G. Stepanov, V. P. Fedin, O. A. Kholdeeva, *Inorg. Chem.*, 2010, **49**, 2920.
8. D. N. Dybtsev, K. A. Kovalenko, Yu. V. Mironov, V. P. Fedin, G. Férey, N. A. Yakovleva, E. A. Berdonosova, S. N. Klyamkin, E. V. Kogan, *Izv. Akad. Nauk*, *Ser. Khim.*, 2009, 1576 [*Russ. Chem. Bull., Int. Ed.*, 2009, **58**, 1623].
9. A. W. Maverick, H. B. Gray, *J. Am. Chem. Soc.*, 1981, **103**, 1299.
10. T. G. Gray, C. M. Rudzinski, E. E. Meyer, R. H. Holm, D. G. Nocera, *J. Am. Chem. Soc.*, 2003, **125**, 4755.
11. L. S. Forster, *Coord. Chem. Rev.*, 2004, **248**, 261.

Received February 4, 2009;
in revised form October 2, 2009