

Reticular synthesis of HKUST-like tbo MOFs with enhanced CH₄ storage

Ioannis Spanopoulos, Constantinos Tsangarakis, Emmanuel Klontzas, Emmanuel Tylanakis, George Froudakis, Karim Adil, Youssef Belmabkhout, Mohamed Eddaoudi, and Pantelis N. Trikalitis

J. Am. Chem. Soc., **Just Accepted Manuscript** • DOI: 10.1021/jacs.5b11079 • Publication Date (Web): 22 Dec 2015

Downloaded from <http://pubs.acs.org> on December 29, 2015

Just Accepted

“Just Accepted” manuscripts have been peer-reviewed and accepted for publication. They are posted online prior to technical editing, formatting for publication and author proofing. The American Chemical Society provides “Just Accepted” as a free service to the research community to expedite the dissemination of scientific material as soon as possible after acceptance. “Just Accepted” manuscripts appear in full in PDF format accompanied by an HTML abstract. “Just Accepted” manuscripts have been fully peer reviewed, but should not be considered the official version of record. They are accessible to all readers and citable by the Digital Object Identifier (DOI®). “Just Accepted” is an optional service offered to authors. Therefore, the “Just Accepted” Web site may not include all articles that will be published in the journal. After a manuscript is technically edited and formatted, it will be removed from the “Just Accepted” Web site and published as an ASAP article. Note that technical editing may introduce minor changes to the manuscript text and/or graphics which could affect content, and all legal disclaimers and ethical guidelines that apply to the journal pertain. ACS cannot be held responsible for errors or consequences arising from the use of information contained in these “Just Accepted” manuscripts.

Reticular synthesis of HKUST-like *tbo* MOFs with enhanced CH₄ storage

Ioannis Spanopoulos[□], Constantinos Tsangarakis[□], Emmanuel Klontzas[□], Emmanuel Tylianakis[□], George Froudakis[□], Karim Adil[‡], Youssef Belmabkhout[‡], Mohamed Eddaoudi[‡] and Pantelis N. Trikalitis^{*□}

[□]Department of Chemistry, University of Crete, Voutes 71003 Heraklion, Greece; [□]Department of Materials Science and Technology, University of Crete, Voutes, 71003 Heraklion, Greece; [‡]Functional Materials Design, Discovery & Development (FMD³), Advanced Membranes & Porous Materials Center, Division of Physical Sciences and Engineering, 4700 King Abdullah University of Science and Technology (KAUST), Thuwal 23955-6900, Kingdom of Saudi Arabia.

KEYWORDS. *Supramolecular Building Layers, HKUST, tbo, Reticular chemistry, Methane storage.*

ABSTRACT: Successful implementation of reticular chemistry using a judiciously designed rigid octatopic carboxylate organic linker allowed the construction of expanded HKUST-1-like *tbo*-MOF series with intrinsic strong CH₄ adsorption sites. The Cu-analogue displayed a concomitant enhancement of the gravimetric and volumetric surface area with the highest reported CH₄ uptake among the *tbo* family, comparable to the best performing MOFs for CH₄ storage. The corresponding gravimetric (BET) and volumetric surface area of 3971 m² g⁻¹ and 2363 m² cm⁻³ represent an increase of respectively 115 % and 47 % in comparison to the corresponding values for the prototypical HKUST-1 (*tbo*-MOF-1), and 42 % and 20 % higher than *tbo*-MOF-2. High pressure methane adsorption isotherms revealed a high total gravimetric and volumetric CH₄ uptakes, reaching 372 cm³ (STP) g⁻¹ and 221 cm³ (STP) cm⁻³ respectively at 85 bar and 298 K. The corresponding working capacities between 5-80 bar were found to be 294 cm³ (STP) g⁻¹ and 175 cm³ (STP) cm⁻³ and are placed among the best performing MOFs for CH₄ storage particularly at relatively low temperature. To gain insight on the mechanism accounting for the resultant enhanced CH₄ storage capacity, molecular simulation study was performed and revealed the presence of very strong CH₄ adsorption sites near the organic linker with similar adsorption energetics as the open metal sites. The present findings supports the potential of *tbo*-MOFs based on the supramolecular building layer (SBL) approach as an ideal platform to further enhance the CH₄ storage capacity via expansion and functionalization of the quadrangular pillars.

INTRODUCTION

The utilization of fossil fuels in the energy production and the mobile transportation sector results in the emission of massive amounts of CO₂ in the atmosphere, instigating numerous health and environmental issues.¹ Thus, prompt deployment of environmental friendly fuels is of utmost importance. Natural gas, consisting of nearly 95% CH₄, is a good candidate for replacing gasoline in mobile transportation and coal in stationary power plants, since it can sustain the same energy demand with amply lessened release of CO, CO₂, NO_x, SO₂ pollutants.² Nevertheless, the deployment of methane as a typical fuel in the automotive industry has been hindered by practicalities associated to cost-effective and efficient storage of methane at concrete temperatures and pressures.³

Metal organic frameworks (MOFs) represent an exceptional class of functional solid-state materials suitable for numerous applications, due to their unique modularity, unprecedented tunability, and high degree of po-

rosity combined with diverse framework functionalities.⁴ Accordingly, MOF chemistry offers great potential to address challenging issues pertaining to CH₄ storage.^{3b, 5} As an illustration of a MOF compound with high promise for CH₄ storage, HKUST-1⁶ was reported to be the best performing material at intermediate pressures (35-65 bar), showing a total volumetric uptake of 267 cm³ (STP) cm⁻³ at 298 K and 65 bar with a corresponding working capacity (5-65 bar) of 190 cm³ (STP) cm⁻³.⁷ Although HKUST-1 exhibits remarkable performance in comparison to the best storage media, it is still far below the gravimetric and volumetric DOE target of 0.5 g/g and 264 cm³/cm³ in the range of temperatures between -40 °C to 85 °C, typical for vehicle in real operation.^{3b, 8}

Successful implementation of reticular chemistry and the molecular building block approach offer nowadays potential to ideally target MOFs with desired and appropriate structural features. For example, HKUST-1⁹ material that has an underlying *tbo*-a topology, can be further interpreted and regarded as constructed from a 2-

periodic arrays of squares, each consistent with an augmented 4,4 square lattice (**sql-a**), that are cross-linked through 4-connected pillars containing copper paddle wheels. This underlying layer, isolated through deconstruction of the crystal structure, can be targeted and constructed from judiciously selected metals and ligands. Then, rational design using pillaring strategy, also called Supermolecular Building Layer (SBL) approach,¹⁰ can be readily implemented using appropriately selected organic pillars that permit to generate the anticipated 3-periodic MOF. Based on this background and rationally, it is conceivable to reasonably target/synthesize an expanded or/and functionalized HKUST-1 like **tbo**-MOF with higher gravimetric and volumetric surface area which in turn will result in a relatively higher CH₄ uptake.

The SBL approach has first been introduced and employed by Eddaoudi *et al.* to construct a new family of isorecticular MOFs with **tbo** topology by using quadrangular (octatopic) organic ligands instead of trigonal (tritopic) ones as in the case of HKUST-1.¹⁰ The use of quadrangular organic ligands offers the advantages to modulate porosity and functionalization of the resulting material but most importantly, it prevents self-interpenetration as it is observed in the case of MOF-388.¹¹ In this way it is possible to efficiently utilize extended organic ligands and synthesize tailor made **tbo**-MOF materials with specific pore size and volume. So far, there are only few examples of **tbo**-MOFs fabricated from quadrangular organic ligands,¹² and studied for CH₄ storage.

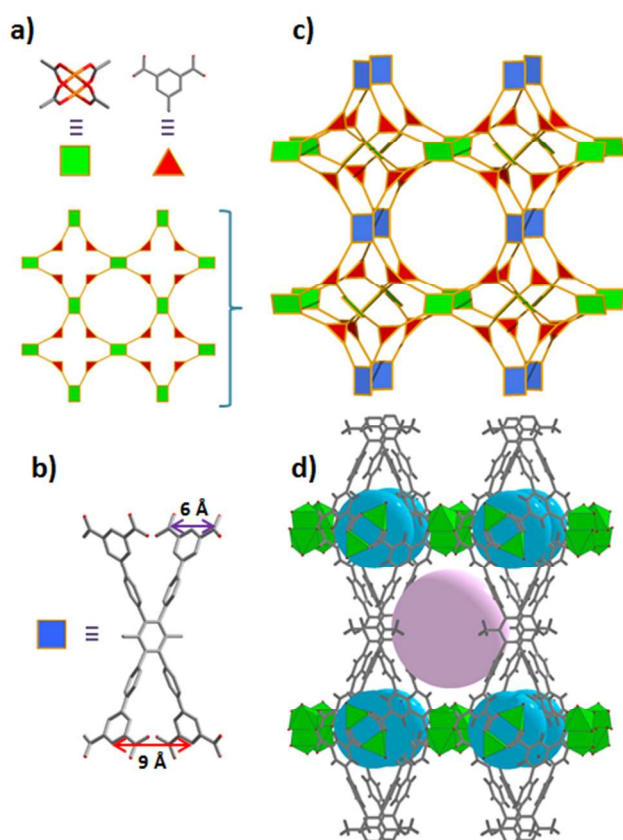


Figure 1. a) Assembly of 4-connected square-like paddle wheel and 3-connected triangle-like BTC to generate 2-periodic 4,4-connected augmented square lattice (**sql-a**). b) octatopic linker (**H₈L**) acting as

4-connected node. c) **tbo-a** topology. d) Crystal structure of Cu-**tbo**-MOF-5 showing two types of cavities.

The first attempt to fabricate high surface area HKUST-like **tbo**-MOF was achieved using tetraisophthalate ligand connected through methoxy groups to a 4-connected benzene core^{10, 13} (see scheme S2). Although the surface area and pore volume were improved, the strategy of extending the pillars without introduction of functional groups led unfortunately to a decrease in the total and working CH₄ gravimetric and volumetric uptake in the 35-65 bar range as this strategy induces the removal of dimeric paddlewheel units carrying strong CH₄ adsorption sites (see scheme S3).¹³ Therefore, maintaining adequate high CH₄ interaction sites associated with the surface area and pore volume increase is not straightforward particular in case of **tbo**-MOF platform. Accordingly, it was compelling for us to explore the use of SBL strategy to develop novel HKUST-1 like **tbo**-MOFs with extended linkers having strong CH₄ interaction sites.

To address this challenge, it is important to note that **tbo** based structure requires an isophthalate-based octatopic organic linker (four isophthalate groups) with specific geometrical constraints which limits the choice of suitable organic linkers.^{12b} To overcome these limitations, two different strategies could provide a suitable pathway to construct the targeted MOF: (i) the use of flexible octatopic linkers that has been proven to be a successful strategy¹⁰ but in turn jeopardizes the framework stability due to the increased strain energy of the ligand^{12b} (ii) the employment of highly aromatic, rigid octatopic organic pillars that can maintain/enhance the stability of the material and also increase CH₄ uptake through favorable π ...CH₄ interactions. Moreover, these interactions could be further enhanced by functionalizing the aromatic rings with methyl groups. It is evident that this strategy is highly challenging and implies the design and synthesis of new, highly aromatic *rigid* octatopic linkers suitable for the formation of expanded **tbo**-MOFs.

Indeed, we designed and synthesized the rigid octatopic organic linker 3,6-dimethyl-1,2,4,5-tetra-(biphenyl-3',5'-dicarboxylic acid)benzene (**H₈L**) shown in figure 1, which upon solvothermal reaction in presence of Co²⁺, Cu²⁺ and Zn²⁺ readily afforded the desired **tbo**-MOFs. We reasoned that the presence of two methyl groups attached to the central phenyl ring is beneficial because it will i) increase the electron density of this ring which will induce the CH₄-framework interaction enhancement at this site and in turn, will augment the total CH₄ storage capacity and ii) will reduce the relatively large size of the central structure cavity, keeping in this way the overall porosity at the micropore region.

Here we show that while the Co-**tbo**-MOF-5 and Zn-**tbo**-MOF-5 MOFs were found unstable upon solvent removal, due to the resultant incompatible coordination geometry of the metal center, the Cu-**tbo**-MOF-5 showed excellent structural stability and methane sorption capabilities. Notably, in comparison with HKUST-1, the present expanded Cu-**tbo**-MOF-5 analogue displays a 115%

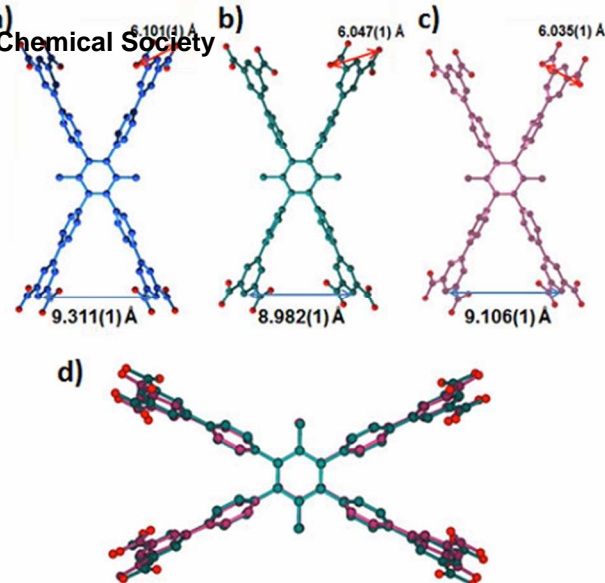
and 47 % increase in the gravimetric and volumetric surface area, respectively.¹⁴ Detailed CH₄ adsorption measurements revealed that Cu-**tbo**-MOF-5 exhibits very high gravimetric and volumetric storage capacities reaching 372 cm³ (STP) g⁻¹ (0.266 g g⁻¹) and 221 cm³ (STP) cm³ respectively, at 85 bar and 298 K. The gravimetric working capacity between 5-80 bar at 298 K is 294 cm³ (STP) g⁻¹ (0.217 g g⁻¹). This value surpasses two of the currently best performing MOFs for CH₄ storage, HKUST-1⁷ (0.162 g g⁻¹) and MOF-519⁶ (0.172 g g⁻¹) and places Cu-**tbo**-MOF-5 among the best performing MOFs for CH₄ storage. Quantum chemistry calculations and Monte Carlo simulations confirmed the experimental results and shed light on CH₄-framework interactions that helped to better understand the observed CH₄ adsorption mechanism.

RESULTS AND DISCUSSION

The design of new, large and rigid quadrangular isophthalate-based organic linkers for the construction of expanded **tbo**-MOFs necessitates to define the appropriate geometrical attribute to readily pillar the 2-periodic layers. The in-deep analysis of the structure reveals that the distance between the neighboring isophthalate groups of the organic moieties, indicated in figure 1b by the red arrow, is of prime importance for the fabrication of the targeted MOF. Indeed, as the distance between the carboxylates belonging to an isophthalic moiety is almost fixed, ~6 Å, the required distance between two neighboring isophthalates has to be of ~9 Å to accommodate the distance between two paddle-wheels from the 2-periodic layers. The use of such an organic linker with the adequate distance and consequently with the appropriate conformation will allow the generation of the desired **tbo**-MOF with no conformational change of the ligand and will *in-fine* result in relatively more stable structure.^{12b} The successful synthesis of the designed ligand, as shown in figure 2, allowed us to fabricate the desired **tbo**-MOFs. Indeed, solvothermal reaction between **H₈L** and Co(NO₃)₂·6H₂O, Cu(NO₃)₂·3H₂O or Zn(NO₃)₂·6H₂O readily afforded the construction of the corresponding MOFs with the expected **tbo** topology. These MOFs are denoted here as Co-**tbo**-MOF-5, Cu-**tbo**-MOF-5 and Zn-**tbo**-MOF-5 respectively. Powder X-ray diffraction analysis (PXRD) indicated that the three MOFs are isostructural compounds (see figure S7).

Figure 2. a) The structure of **H₈L** linker a) as predicted by DFT, b) in Cu-**tbo**-MOF-5 and c) in Zn-**tbo**-MOF-5. d) Overlay of the DFT-predicted structure of the ligand and that found in Cu-**tbo**-MOF-5, showing that there is only a small change in the dihedral angle of the isophthalate groups, when **L⁸⁻** is incorporated into the **tbo** framework.

Initially, single crystals were isolated only in the case of Zn-**tbo**-MOF-5 (colorless plates, see figure S5) while Co-**tbo**-MOF-5 and Cu-**tbo**-MOF-5 were isolated in a microcrystalline form. Remarkably, green plate-like single crystals of Cu-**tbo**-MOF-5 were obtained in a high quality through a facile, single-crystal-to-single-crystal topotactic and quantitative exchange of Zn²⁺ by Cu²⁺ (see SI). The quantitative replacement of Zn²⁺ by Cu²⁺ was confirmed by EDS (see figure S6). The structure of Zn-**tbo**-MOF-5 and Cu-**tbo**-MOF-5 was determined by single



crystal X-ray diffraction experiments (see Table S1 and S2). The purity of these materials have been confirmed by comparison between the experimental and calculated PXRD patterns (see figure S7). Given that both **tbo** MOFs are isostructural, the structure of Cu-**tbo**-MOF-5 will be presented in more detail below.

Cu-**tbo**-MOF-5 crystallizes in the orthorhombic system, space group *Fmmm* with large unit cell parameters, $a = 25.616(2)$ Å, $b = 28.157(3)$ Å and $c = 40.549(4)$ Å resulting in a unit cell volume of $29247(5)$ Å³. The corresponding volume of Zn-**tbo**-MOF-5 was found slightly bigger, reaching $29811(10)$ Å³, as expected due to the slightly longer Zn-O bond length. As expected from the **tbo**-type structure, the framework consists of dimeric paddlewheel [M₂(O₂C)₄, M = Cu²⁺ and Zn²⁺] units in which the metal cations exhibit a square pyramidal MO₅ geometry (see figure 1). These 4-connected paddlewheels are linked to each other's through isophthalic moieties of the ligand, resulting in a neutral 3-periodic framework with microporous cavities of different sizes (see figure 1). Precisely, the larger cavity of approximately 16 Å in length along the *c*-axis is located between the layers (see orange sphere in figure 1) which has two different widths along the *a*-axis due to the different arrangement of the central phenyl ring carrying the two methyl groups, pointing alternatively inside and outside of the cavity. A smaller cavity of approximately 11 Å exists within the layers (see green sphere in figure 1).¹⁵ The size of these cavities was further confirmed experimentally by accurate microporous analysis in the case of Cu-**tbo**-MOF-5 using Ar at 87 K. The total solvent accessible free volume for Cu-**tbo**-MOF-5 was found to be 73 %, using the PLATON software.¹⁶

Proper activation of the Cu-**tbo**-MOF-5 was successfully achieved by applying a straightforward activation procedure using volatile solvents such as acetone and CH₂Cl₂ to exchange the DMF molecules followed by drying under vacuum and heating at 60° C overnight (see SI). In contrast, all attempts to properly activate Co-**tbo**-MOF-5 and Zn-**tbo**-MOF-5 using available methodologies such as supercritical CO₂ drying failed and leading to a systematic structural collapse. The origin of such phenomena can be directly correlated to the unstable distorted square planar MO₄ geometry (M= Co²⁺, Zn²⁺) resulted

from the paddle-wheels de-solvation under activation process. Accordingly, upon activation, the coordinated solvent molecules located at the apical positions of the paddle-wheels are removed resulting in four coordinated metal centers. The formation of stable paddle-wheel units SBUs necessitates that metal centers adopt a square planar geometry. Although for Cu^{2+} the 4-connected square planar environment is a stable geometry with carboxylate-based ligands, it is not the case for Co^{2+} and Zn^{2+} cations which both prefer/adopt the more stable tetrahedral geometry.^{12f} The later destroys the dimeric paddle-wheels leading to the collapse of the framework.^{12c}

Argon adsorption isotherm recorded at 87 K confirmed the permanent porosity of Cu-**tbo**-MOF-5 showing a fully reversible type-I isotherm, characteristic of a microporous material, see figure 3. The BET (Langmuir) surface area, calculated in the pressure range 0.007-0.01 p/p₀, was found to be 3971 m² g⁻¹ (4123 m² g⁻¹), which is more than double (115 %) compared to the prototypical **tbo** MOF, HKUST-1 (BET area, 1850 m² g⁻¹)⁷ and 37% higher than **tbo**-MOF-2.^{10, 13} Taking into account the crystallographic density of Cu-**tbo**-MOF-5 ($\rho = 0.595 \text{ g cm}^{-3}$), the calculated volumetric BET area is 2363 m² cm⁻³ which is significantly higher (47 %) compared to the corresponding value of HKUST-1 ($\rho = 0.868 \text{ g cm}^{-3}$, 1606 m² cm⁻³). The calculated geometric surface area using the nonorthoSA software¹⁷ (probe diameter 3.4 Å) is 3850 m² g⁻¹ which is very close to the experimental BET value and confirms that Cu-**tbo**-MOF-5 framework retains its

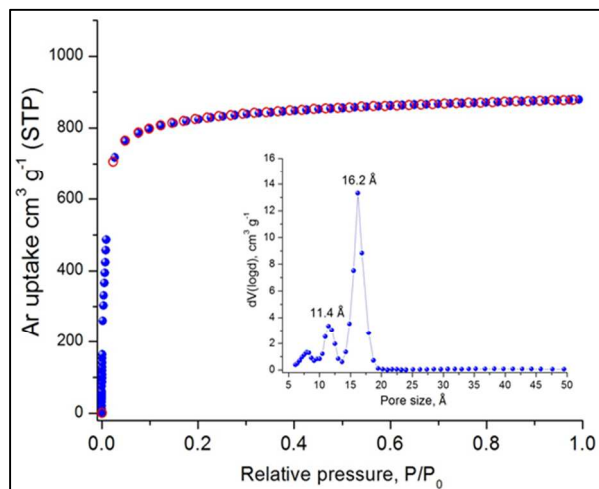


Figure 3. Argon sorption isotherm at 87 K for Cu-**tbo**-MOF-5 and the corresponding pore size distribution curve calculated by NLDFT.

structural integrity upon pore system activation. This is also supported by the total pore volume calculated from the Ar adsorption isotherm at 0.992 p/p₀ that it is found to be 1.12 cm³ g⁻¹, which is in close agreement with the crystallographic value of 1.22 cm³ g⁻¹. In addition to gas-sorption results, the structural integrity of activated Cu-**tbo**-MOF-5 was also confirmed by PXRD measurements (see figure S8). The pore size distribution was calculated using Non-Local Density Functional Theory (NLDFT) after a successful fitting of the Ar adsorption isotherm data using a suitable NLDFT kernel (see figure S11). Accordingly, the corresponding curve (see inset in figure 3) shows two distinct

peaks centered at 16.2 Å and 11.4 Å, in full agreement with the crystallographic analysis. Thermogravimetric analysis (TGA) and variable temperature X-ray powder diffraction (VT-PXRD) measurements demonstrate that Cu-**tbo**-MOF-5 is stable up to 250 °C (see figures S26 and S27).

The high gravimetric and volumetric surface area, due to the large pore volume in the micropore region, in combination with the high degree of aromaticity, the methyl groups at the central ring and the presence of unsaturated Cu^{2+} sites, make Cu-**tbo**-MOF-5 a very promising material for gas storage. Accordingly, extensive CH_4 sorption measurements at different temperatures and pressures were performed in order to evaluate the Cu-**tbo**-MOF-5 in terms of key CH_4 properties including the saturation uptake, total uptake, working capacity and isosteric heat of adsorption. CH_4 adsorption measurements recorded at its boiling point (112 K) and up to 1 bar showed a fully reversible type-I isotherm, with a high saturation uptake of 691 cm³ (STP) g⁻¹, (404 cm³ (STP) cm⁻³), see Figure S12. The total pore volume calculated at 0.99 p/p₀ using CH_4 as a probe molecule is 1.17 cm³ g⁻¹ and is in an excellent agreement with both the experimental value obtained from Ar adsorption (1.2 cm³ g⁻¹) at 87 K and the calculated from the crystal structure (1.22 cm³ g⁻¹), indicating that the pore space in Cu-**tbo**-MOF-5 is fully accessible by CH_4 molecules. From the CH_4 adsorption isotherms recorded at 273 K, 283 K and 298 K, the calculated isosteric heat of adsorption at zero coverage, Q_{st}^0 , using a virial type equation was estimated to be 20.4 kJ mol⁻¹ and remained nearly constant as function of the surface coverage (see figure S15). Interestingly, this value is higher compared to HKUST-1 (17 kJ mol⁻¹) and among the highest reported for MOFs (see Table S1).^{5a} For example, Ni-MOF-74 with very high density of open metal sites showed a Q_{st}^0 value

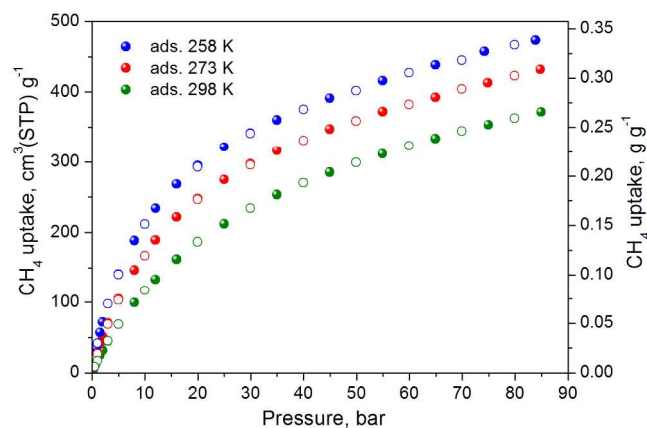


Figure 4. Total gravimetric CH_4 adsorption (closed symbols) and desorption (open symbols) isotherms of Cu-**tbo** at the indicated temperatures.

of 21.4 kJ mol⁻¹. As we described in detail below, accurate theoretical calculations revealed that in Cu-**tbo**-MOF-5, in addition to the open Cu^{2+} sites, there are three (3) distinct sites with interaction strength equal to that of open Cu^{2+} sites (~20 kJ mol⁻¹) and reasoning the observed high Q_{st}^0 value.

High pressure CH₄ measurements at different temperatures, shown in figure 4, revealed that Cu-**tbo**-MOF-5 exhibited one of the highest gravimetric uptakes for MOFs, reaching 372 cm³ (STP) g⁻¹ (0.266 g g⁻¹) at 85 bar and 298 K. The corresponding values at 273 K and 258 K are 432 cm³ (STP) g⁻¹ (0.309 g g⁻¹) and 473 cm³ (STP) g⁻¹ (0.338 g g⁻¹), respectively. The later is 67.7 % of the current gravimetric DOE target, 700 cm³ (STP) g⁻¹ (0.5 g g⁻¹). The gravimetric working capacity between 5-80 bar at 298 K is 294 cm³ (STP) g⁻¹ (0.217 g g⁻¹) which surpasses two of the best performing MOFs for CH₄ storage, HKUST-1 and MOF-519 showing 227 cm³ (STP) g⁻¹ (0.162 g g⁻¹) and 241 cm³ (STP) g⁻¹ (0.172 g g⁻¹)⁶ respectively, under the same conditions (see figure 5a and Tables S1, S2). It is also higher compared to other high expanded **tbo**-MOFs like **tbo**-MOF-2, as shown in figure S24 (253 cm³ g⁻¹ vs 225 cm³ g⁻¹ at 35 bar and 298 K).¹³ Using the crystal density of Cu-**tbo**-MOF-5 (0.595 g cm⁻³), the calculated total volumetric uptake at 85 bar and 298 K, 273 K and 258 K is 221 cm³ (STP) cm⁻³, 257 cm³ (STP) cm⁻³ and 282 cm³ (STP) cm⁻³ respectively. The corresponding volumetric working capacities between 5-80 bar are 175 cm³ (STP) cm⁻³, 189 cm³ (STP) cm⁻³ and 194 cm³ (STP) cm⁻³. These values compare well with the best performing MOFs as shown in figure 5b (see also table S2).^{7, 18} Interestingly, although Cu-**tbo**-MOF-5 has a significantly higher volumetric surface area compared to the prototypical **tbo** MOF, HKUST-1, the later showed a higher volumetric working capacity, 200 cm³ (STP) cm⁻³ between 5-80 bar at 298 K that is mainly attributed to the considerably higher (~46%) crystal density of HKUST-1 (0.868 g cm⁻³).

A detailed comparison of CH₄ storage properties in terms of working capacities between HKUST-1 and Cu-**tbo**-MOF-5 revealed important findings. In fact, Cu-**tbo**-MOF-5 shows higher gravimetric working capacity between 5-65 bar (more relevant to real applications than the 5-35 bar range due to the upper limit achievable with inexpensive two-stage compressors) by 22.7% at 298K while in the range 5-80 bar the corresponding increase is 29.6%. The volumetric working capacity shows a decrease of 16.8% in the range 5-65 bar but a much lower decrease, 12.5%, in the range 5-80 bar, both at 298K. Because a temperature decrease has a similar effect in

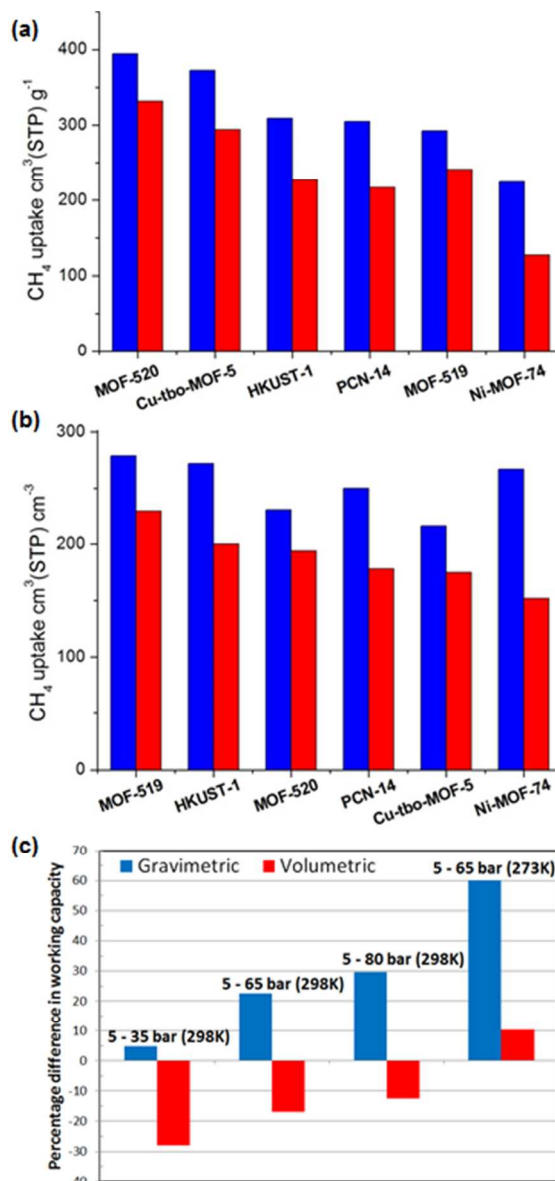


Figure 5. Comparison of a) gravimetric and b) volumetric CH₄ total uptake (blue) at 80 bar/298 K and the corresponding working capacities (red) between 5-80 bar/298 K, of Cu-**tbo**-MOF-5 with some top performing MOFs. (c) Percentage difference in gravimetric (blue) and volumetric (red) working capacities between Cu-**tbo**-MOF-5 and HKUST-1 at the indicated pressure ranges and temperatures.

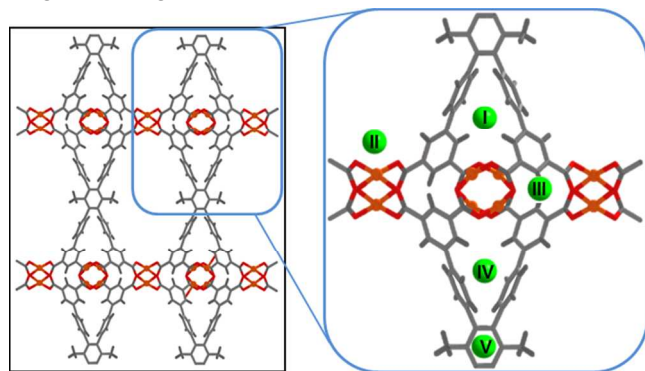
CH₄ uptake as the increase in pressure, it is relevant to compare the corresponding CH₄ working capacities between the two solids at a lower temperature. Remarkably, at 273K the volumetric working capacity in the range 5-65 bar is *increased* by 10.3 % (the percentage different between 298K and 273K is 27.1%) while the gravimetric working capacity shows an impressive increase of 60.1%. These results are shown in figure 5c.

A very rare behavior is noticed in Cu-**tbo**-MOF-5. Indeed, the increase of both gravimetric and volumetric working capacity is observed as the temperature is decreasing, which is the opposite for HKUST-1 and other high performance MOFs including UTSA-76 and NU-111. This kind of dependence of the working capacity suggests that a combination of pressure and temperature swing could be an effective method for methane storage and release.¹⁹ For example, using Cu-**tbo**-MOF-5, an adsorption at 258 K at 65 bar followed by

1 a desorption at 5 bar and 298K, will result in a volumetric
2 working capacity of $220 \text{ cm}^3(\text{STP}) \text{ cm}^{-3}$ which is 83% of the
3 DOE target ($264 \text{ cm}^3 \text{ cm}^{-3}$), if the packing loss is ignored.

4 The above results could originate from the synergistic
5 effect between pore volume (this correlates with surface
6 area) and CH_4 -framework interactions. Accordingly, due to
7 higher pore volume and moderate CH_4 -framework interactions
8 in Cu-**tbo**-MOF-5, the uptake is smaller in the low pressure
9 region (5 bar range) compared to the high pressure range (see
10 figure 4), leading in this way to higher working capacities. The
11 opposite is true for HKUST-1 where pore confinement due to
12 smaller pore volume results in increased CH_4 uptake at lower
13 pressures and saturation close to 65 bar (see figure S24).

14 Computational methods were employed with the
15 aim to identify the CH_4 adsorption sites in Cu-**tbo**-MOF-5
16 and in particular, to better understand the effect of the
17 various structural features of the extended **tbo**-type
18 framework on the observed CH_4 storage properties. Ac-
19 cordingly, Quantum chemistry calculations and Monte
20 Carlo simulations with the Grand Canonical ensemble
21 (GCMC) were performed in order to investigate the ener-
22 getics of the CH_4 adsorption and to simulate adsorption
23 isotherms at different conditions. Interestingly, the calcu-
24 lations showed that Cu-**tbo**-MOF-5 possesses four (4)
25 highly energetic CH_4 adsorption sites of equal strength
26 ($\sim 20 \text{ kJ mol}^{-1}$), indicated as I, II, III, and IV in figure 6 and
27 one more, V, with relatively lower interaction energy (15 kJ mol^{-1}).
28 More specifically, in addition to the open Cu^{2+}
29 sites (II), usually being energetically the highest interac-
30 tion sites in MOFs, there are three more, I, III and IV, of
31 equal strength, located at the positions shown in figure 6.
32 As expected from the **tbo** topology, I, II and III are the
33 most energetic ones, similarly to HKUST-1.²⁰ However, it
34 is interesting to highlight that sites IV and V are also
35 found to be highly energetic because of the particular
36 structure of the ligand. The high adsorption strength of
37 the IV site is attributed to the local geometry of the small
38 v-shaped pocket of the ligand and the subsequent in-
39 creased dispersion interactions of the CH_4 molecule
40 (π -H-C interactions) with the opposite aromatic rings
41 (see figure 6). A less energetic, but important in terms of
42 its strength ($\sim 15 \text{ kJ mol}^{-1}$), is site V at the top of the central
43 phenyl ring of the ligand carrying the two methyl groups.
44 The calculations showed that the origin of the amplified
45 strength of this site, as compared to the other phenyl
46 rings of the ligand ($\sim 10 \text{ kJ mol}^{-1}$), is the electron



47 **Figure 6.** The five major CH_4 adsorption sites in Cu-**tbo**-MOF-5. The
48 sites I-IV have the same interaction strength of $\sim 20 \text{ kJ mol}^{-1}$ while the
49
50
51
52
53
54
55
56
57

58 site V has 15 kJ mol^{-1} . Site I is located at the window entrance of the
59 octahedral cage, site II at the axial position of the Cu^{2+} paddlewheel,
60 site III between the carboxylate groups inside the cage, site IV at the
v-shaped pocket formed by the neighboring arms of the ligand and site
V at the top of the central phenyl ring of the ligand carrying the two
methyl groups.

donating nature of the two methyl groups. In addition,
due the orientation of the organic ligand, these groups are
pointing inside the large cavity of the structure, creating
in this way a window of $\sim 8 \text{ \AA}$ which favors $\text{CH}_4 \cdots \text{CH}_4$ and
 CH_4 -framework interactions.²¹ This is supported by the
calculations which showed that with the loading augmen-
tation, an additional increase of $\sim 2 \text{ kJ mol}^{-1}$ to the average
adsorption strength is observed, apparently due to favor-
able $\text{CH}_4 \cdots \text{CH}_4$ interactions. These results are in full
agreement with the experimental Q_{st} values and also ex-
plain the slight increase of Q_{st} as a function of surface
coverage at low pressures (between 0-1 bar) (see figure
S15). GCMC simulations slightly overestimate (8 %) the
total gravimetric CH_4 uptake at high pressures (see figure
S32) which notably correlates very well with the differ-
ence between the observed ($1.12 \text{ cm}^3 \text{ g}^{-1}$) and calculated
total pore volume ($1.22 \text{ cm}^3 \text{ g}^{-1}$) of Cu-**tbo**-MOF-5.

In addition to CH_4 , H_2 and CO_2 sorption mea-
surements were performed in the low pressure region (0-1
bar) at various temperatures. Accordingly, H_2 adsorption
at 77 K revealed an impressive uptake of $261 \text{ cm}^3 (\text{STP}) \text{ g}^{-1}$
(2.3 wt %) at 1 bar with a Q_{st} of 6.3 kJ mol^{-1} (see figure S21
and S19). A very high CO_2 uptake was also found, reaching
at 273 K, 298 K and 1 bar, $149 \text{ cm}^3 (\text{STP}) \text{ g}^{-1}$ (6.6 mmol g^{-1})
and $80 \text{ cm}^3 (\text{STP}) \text{ g}^{-1}$ (3.6 mmol g^{-1}), respectively (see figure
S17). The corresponding Q_{st} at zero coverage, determined
for the isotherms recorded at 273 K, 283 K and 298 K, is
estimated to be 24.5 kJ mol^{-1} and found to be constant as
function of the surface coverage, indicating the presence
of uniform CO_2 -framework interactions in Cu-**tbo**-MOF-5
(see figure S18). Using the IAST model, the calculated
 CO_2/CH_4 selectivity at 273 K and 298 K for a 5/95 molar
mixture is 5.1 and 4.2, respectively (see figure S20).

CONCLUSIONS

In conclusion, we have demonstrated how reticu-
lar chemistry and more specifically the Supermolecular
Building Layer (SBL) approach can allow the synthesis of
a new series of **tbo**-MOFs with significantly enhanced
gravimetric and volumetric surface area, compared to the
prototype **tbo** MOF, HKUST-1. The design of an original
expanded, highly aromatic and rigid organic linkers with
intrinsic strong CH_4 adsorption sites, allowed the isola-
tion of a new very stable porous MOF, namely Cu-**tbo**-
MOF-5 that shows very high gravimetric and volumetric
BET surface area, reaching $3971 \text{ m}^2 (\text{STP}) \text{ g}^{-1}$ and 2363 m^2
 cm^{-3} , respectively. Extensive gas adsorption measure-
ments, at various temperatures and pressures, revealed
that Cu-**tbo**-MOF-5 is currently among the best perform-
ing MOFs for CH_4 storage, showing a gravimetric total
uptake of $372 \text{ cm}^3 (\text{STP}) \text{ g}^{-1}$ at 85 bar and 298 K, which is
higher than that in HKUST-1 and MOF-519, and also an
impressive volumetric total capacity of $221 \text{ cm}^3 (\text{STP}) \text{ cm}^{-3}$,

under the same conditions (working capacity between 5–80 bar, 175 cm³ cm⁻³). Theoretical calculations of the CH₄ adsorption in Cu-tbo-MOF-5, revealed the presence of multiple strong adsorption sites of equal strength with the open Cu²⁺ sites (~20 kJ mol⁻¹), which concurs with the experimentally determined isosteric heat of adsorption. The increased strength of these sites originates from both the particular structural features of the ligand and the tbo-MOF structural features, tbo topology. These significant results provide new directions for the design and construction of novel tbo-MOFs with further improved CH₄ storage properties, namely with enhanced volumetric total and working capacities while maintaining a high density of strong interaction sites.

ASSOCIATED CONTENT

Supporting Information

Experimental details, powder XRD, NMR, TGA, gas-sorption isotherms and related calculations. This material is available free of charge via the Internet at <http://pubs.acs.org>.

AUTHOR INFORMATION

Corresponding Author

* ptrikal@uoc.gr

ACKNOWLEDGMENT

The authors thank Diamond Light Source for access to beamline I19 (MT10189) that contributed to the results presented here and in particular for the determination of Cu-tbo-MOF-5 structure and also D. Allan and H. Nowell for their assistance during the measurements. We also thank HZB for the allocation of synchrotron radiation beamtime, used to solve the Zn-tbo-MOF-5 structure. This research has been co-financed by the European Union (European Social Fund – ESF) and Greek national funds through the Operational Program "Education and Lifelong Learning" of the National Strategic Reference Framework (NSRF) – Research Funding Program: ARISTEIA II – 4862.

REFERENCES

- (a) Markewitz, P.; Kuckshinrichs, W.; Leitner, W.; Linssen, J.; Zapp, P.; Bongartz, R.; Schreiber, A.; Muller, T. E., *Energy Environ. Sci.* **2012**, *5* (6), 7281-7305; (b) Liu, C.; Li, F.; Ma, L. P.; Cheng, H. M., *Adv. Mater.* **2010**, *22* (8), E28-+; (c) D'Alessandro, D. M.; Smit, B.; Long, J. R., *Angew. Chem. Int. Ed.* **2010**, *49* (35), 6058-6082; (d) Li, S.-L.; Xu, Q., *Energy Environ. Sci.* **2013**, *6* (6), 1656-1683.
- Lozano-Castello, D.; Alcaniz-Monge, J.; de la Casa-Lillo, M. A.; Cazorla-Amoros, D.; Linares-Solano, A., *Fuel* **2002**, *81* (14), 1777-1803.
- (a) Beckner, M.; Dailly, A., *Applied Energy* **2015**, *149*, 69-74; (b) Mason, J. A.; Veenstra, M.; Long, J. R., *Chem. Sci.* **2014**, *5* (1), 32-51.
- (a) Yaghi, O. M.; O'Keeffe, M.; Ockwig, N. W.; Chae, H. K.; Eddaoudi, M.; Kim, J., *Nature* **2003**, *423* (6941), 705-714; (b) Furukawa, H.; Cordova, K. E.; O'Keeffe, M.; Yaghi, O. M., *Science* **2013**, *341* (6149), 974; (c) Almeida Paz, F. A.; Klinowski, J.; Vilela, S. M. F.; Tome, J. P. C.; Cavaleiro, J. A. S.; Rocha, J., *Chem. Soc. Rev.* **2012**, *41* (3), 1088-1110; (d) Assen, A. H.; Belmabkhout, Y.; Adil, K.; Bhatt, P. M.; Xue, D.-X.; Jiang, H.; Eddaoudi, M., *Angew. Chem. Int. Ed.* **2015**, *54*, 14353-14358; (e) Xue, D.-X.; Belmabkhout, Y.; Shekha, O.; Jiang, H.; Adil, K.; Cairns, A. J.; Eddaoudi, M., *J. Am. Chem. Soc.* **2015**, *137*, 5034; (f) Lu, W.; Wei, Z.; Gu, Z.-Y.; Liu, T.-F.; Park, J.; Park, J.; Tian, J.; Zhang, M.; Zhang, Q.; Gentle, T., III; Bosch, M.; Zhou, H.-C., *Chem. Soc. Rev.* **2014**, *43* (16), 5561-5593; (g) Guillerme, V.; Kim, D.; Eubank, J. F.; Luebke, R.; Liu, X.; Adil, K.; Lah, M. S.; Eddaoudi, M., *Chem. Soc. Rev.* **2014**, *43*, 6141.
- (a) He, Y.; Zhou, W.; Qian, G.; Chen, B., *Chem. Soc. Rev.* **2014**, *43* (16), 5657-5678; (b) Elizabeth Casco, M.; Martinez-Escandell, M.; Gadea-Ramos, E.; Kaneko, K.; Silvestre-Albero, J.; Rodriguez-Reinoso, F., *Chem. Mater.* **2015**, *27* (3), 959-964; (c) Alezi, D.; Belmabkhout, Y.; Suetin, M.; Bhatt, P. M.; Weselinski, L. J.; Solovyeva, V.; Adil, K.; Spanopoulos, I.; Trikalitis, P. N.; Emwas, A.-H.; Eddaoudi, M., *J. Am. Chem. Soc.* **2015**, *137* (41), 13308-13318.
- Gandara, F.; Furukawa, H.; Lee, S.; Yaghi, O. M., *J. Am. Chem. Soc.* **2014**, *136* (14), 5271-5274.
- Peng, Y.; Krungleviciute, V.; Eryazici, I.; Hupp, J. T.; Farha, O. K.; Yildirim, T., *J. Am. Chem. Soc.* **2013**, *135* (32), 11887-11894.
- Methane Opportunities for Vehicular Energy, Advanced Research Project Agency – Energy, U.S. Dept. of Energy, Funding Opportunity no. DE-FOA-0000672 **2012**.
- O'Keeffe, M.; Peskov, M. A.; Ramsden, S. J.; Yaghi, O. M., *Acc. Chem. Res.* **2008**, *41* (12), 1782-1789.
- Eubank, J. F.; Mouttaki, H.; Cairns, A. J.; Belmabkhout, Y.; Wojtas, L.; Luebke, R.; Alkordi, M.; Eddaoudi, M., *J. Am. Chem. Soc.* **2011**, *133* (36), 14204-14207.
- Furukawa, H.; Go, Y. B.; Ko, N.; Park, Y. K.; Uribe-Romo, F. J.; Kim, J.; O'Keeffe, M.; Yaghi, O. M., *Inorg. Chem.* **2011**, *50* (18), 9147-9152.
- (a) Lu, W.; Yuan, D.; Makal, T. A.; Li, J.-R.; Zhou, H.-C., *Angew. Chem. Int. Ed.* **2012**, *51* (7), 1580-1584; (b) Shustova, N. B.; Cozzolino, A. F.; Dinca, M., *J. Am. Chem. Soc.* **2012**, *134* (48), 19596-19599; (c) Wei, Z.; Lu, W.; Jiang, H.-L.; Zhou, H.-C., *Inorg. Chem.* **2013**, *52* (3), 1164-1166; (d) Yang, X.-L.; Xie, M.-H.; Zou, C.; He, Y.; Chen, B.; O'Keeffe, M.; Wu, C.-D., *J. Am. Chem. Soc.* **2012**, *134* (25), 10638-10645; (e) Yang, X.-L.; Zou, C.; He, Y.; Zhao, M.; Chen, B.; Xiang, S.; O'Keeffe, M.; Wu, C.-D., *Chem. Eur. J.* **2014**, *20* (5), 1447-1452.
- Belmabkhout, Y.; Mouttaki, H.; Eubank, J. F.; Guillerme, V.; Eddaoudi, M., *RSC Adv.* **2014**, *4* (109), 63855-63859.
- Chui, S. S. Y.; Lo, S. M. F.; Charmant, J. P. H.; Orpen, A. G.; Williams, I. D., *Science* **1999**, *283* (5405), 1148-1150.
- A detailed and representative description of the different cavities formed in tbo-type MOFs is provided in reference #7.
- Spek, A. L., *Acta Crystallogr. Sect. D.* **2009**, *65*, 148-155.
- Dueren, T.; Millange, F.; Ferey, G.; Walton, K. S.; Snurr, R. Q., *J. Phys. Chem. C* **2007**, *111* (42), 15350-15356.
- Gutov, O. V.; Bury, W.; Gomez-Gualdrón, D. A.; Krungleviciute, V.; Fairen-Jimenez, D.; Mondloch, J. E.; Sarjeant, A. A.; Al-Juaid, S. S.; Snurr, R. Q.; Hupp, J. T.; Yildirim, T.; Farha, O. K., *Chem. Eur. J.* **2014**, *20* (39), 12389-12393.
- (a) Sun, B.; Kayal, S.; Chakraborty A., *Energy* **2014**, *76*, 419-427. (b) Kayal, S.; Sun, B.; Chakraborty, A., *Energy*, **2015**, *91*, 772-781.
- Wu, H.; Simmons, J. M.; Liu, Y.; Brown, C. M.; Wang, X.-S.; Ma, S.; Peterson, V. K.; Southon, P. D.; Kepert, C. J.; Zhou, H.-C.; Yildirim, T.; Zhou, W., *Chem. Eur. J.* **2010**, *16* (17), 5205-5214.
- Wilmer, C. E.; Leaf, M.; Lee, C. Y.; Farha, O. K.; Hauser, B. G.; Hupp, J. T.; Snurr, R. Q., *Nat. Chem.* **2012**, *4* (2), 83-89.

TOC

