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From Layered Materials to Bidimensional Metal-Organic Frameworks

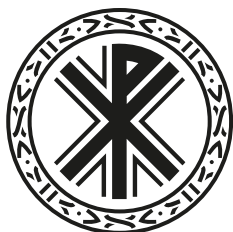
De materiales en capas a marcos metal-orgánicos bidimensionales

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ABSTRACT

Metal-organic frameworks are modular materials with a thickness of a few atomic layers. Their interest for solids and uses lies in their atomically thin-layered arrangement, surface chemical reactivity, surface/volume ratio and chemical-adsorption capacity. The study of their characteristics and features is used as a learning method. The layer-layer separation is maximal for MoS₂ owing to its layered arrangement, in which a plane of Mo atoms is sandwiched by others of S²⁻. The periodic table of the elements shows constancy in layer-layer separations for B/C/N in row 2 of the table. Design criteria and structure-property associations follow: Linear models of atom-atom separation between layers show that this increases with atomic number. Power models, especially those with two parameters, better associations. Layer-layer separation for S deviates from the models owing to MoS₂ three-strata monolayer. Miniaturization is a must for actual progress. The true control of a material or process should be done from the nanoscale. Two-dimensional nanomaterials are a way of structuring the nanoworld for this control. Monochalcogenides, dichalcogenides, etc. are easy to exfoliate. The central rule of nanoscience results: Compare cartoons with reality.

KEYWORDS: *Monolayer, Thin-layered nanostructure, Thin film, Charge transport, Host-guest chemistry.*

RESUMEN

Los marcos metal-orgánicos son materiales modulares con un espesor de unas pocas capas atómicas. Su interés para sólidos y usos reside en su organización en capas atómicamente finas, la reactividad química superficial, la relación superficie-volumen y la capacidad de adsorción química. El estudio de sus características y rasgos se usa como un método de aprendizaje. La separación capa-capa es máxima para MoS₂ debido a su orden en capas, en la cual un plano de átomos de Mo se intercala con otros de S²⁻. La tabla periódica de los elementos muestra una constancia en las separaciones capa-capa para B/C/N en la fila 2 de la tabla. Criterios de diseño y asociaciones estructura-propiedad se siguen a este hecho: Modelos lineales de separación átomo-átomo entre capas muestran que esta aumenta con el número atómico. Modelos de potencias, especialmente aquellos con dos parámetros, mejoran las asociaciones. La separación capa-capa para S se desvía de los modelos debido a la monocapa en tres estratos del MoS₂. No hay que

perderse la miniaturización para el progreso real. El verdadero control de un material o proceso se debe hacer desde la nanoescala. Los materiales bidimensionales son una manera de estructurar el nanomundo para este control. Los monocalcogenuros, dicalcogenuros, etc. son fáciles de exfoliar. Los resultados de la regla central en nanociencia: Compare los dibujos con la realidad.

PALABRAS CLAVE: *Monocapa, Nanoestructura en capa fina, Lámina delgada, Transporte de carga, Química hospedador-huésped.*

INTRODUCTION

Do you know what metal-organic (MO) frameworks (MOFs) are? Boring! We combine them with electrical conductivity and magnetism. Chemistry becomes nanochemistry while physics merges with materials science. A way of transforming matter is manufacturing nanomaterials (NMs) and nanodevices (NDs), or nanocomposites (NCs) and nanolayers. How can one reduce a material to the nanoscale or manufacture NMs and NDs? The MOFs are a class of nanoporous crystalline materials with record internal surface areas in supramolecular chemistry. How does one use MO precursors (MOPs) for growing two-dimensional (2D) MOFs? Layered-NMs questions were raised [1].

Q1. What could we do with layered structures with just the right layers?

Q2. What would the properties of materials be if we could really arrange the atoms the way we want them?

In condensed matter physics (CMP), *more is different* [2]. *The whole is more than the sum of its parts* (Aristotle). In emergent order, *The whole becomes not only more than but very different from the sum of its parts*. The emerging field of modern-physics is the study of materials-properties, as not only the sum of the properties of their parts but also as a consequence of the interaction between their constituents. Such idea is the opposite of the *reductionist* point of view of physics. Such interaction assumes the concept of *emergence*, a CMP cornerstone. Two-dimensional MOFs are a modular class of layered NMs with a thickness of a few atomic layers, typically not exceeding 50Å each one of them. What are they used for? They exhibit exceptional properties that are distinct from the bulk. Why 2D materials? Geim group informed a seminal work on the exfoliation of bulk C-graphite into C-graphene (GR) [3], which opened the field to many other 2D crystals [e.g., magnetism, superconductivity (SC)] [4]. Present research in 2D semiconductors took off thanks to GR rise, because of the need of having materials with a forbidden band to define electronic and optic-electronic (*optoelectronic*) NDs. Two-dimensional MOFs are interesting for new NMs and applications. They present uses because of their atomically thin-layered structure, large surface chemical reactivity, surface/volume ratio and capacity for chemical adsorption. Table 1 shows the classification of hybrid materials based on dimensionality [5].



Table 1. Classification of hybrid materials based on dimensionality

Dimensionality of organic	Dimensionality of inorganic			
	0	1	2	3
0	Molecular complexes	Hybrid inorganic chains	Hybrid inorganic layers	3D inorganic hybrids
1	Chain co-ordination polymers	Mixed inorganic-organic Layers	Mixed inorganic-organic 3D frameworks	-
2	Layered co-ordination polymers	Mixed inorganic-organic 3D frameworks	-	-
3	3D co-ordination polymers	-	-	-

In this laboratory, Coronado group reported SC-magnetism coexistence by chemical design [6]. They imagined the magnetic reversal of isolated and organized molecular-based nanoparticles (NPs), via magnetic force microscopy (MFM) [7]. They switched magnetic vortex core in a single NP [8]. To induce quantum confinement effects directly drives current interest in one-monolayer (ML)-thick 2D NMs [9]. Earlier publications described the effects of type, size and elliptical deformation on molecular polarizabilities of model single-wall carbon nanotubes (SWNTs) from atomic increments [10-13], SWNTs periodic properties and table based on the chiral vector [14,15], calculations on SWNTs solvents, co-solvents, *cyclopyranoses* [16-19] and organic-solvent dispersions [20,21], packing effect on cluster nature of SWNTs solvation features [22], information entropy analysis [23], cluster origin of SWNTs transfer phenomena [24], asymptotic analysis of coagulation-fragmentation equations of SWNT clusters [25], properties of fullerite, symmetric C-forms, similarity laws [26], fullerite crystal thermodynamic characteristics, law of corresponding states [27], cluster nature of nanohorns (SWNHs) solvent features [28], SWNTs (co-)solvent selection, *best* solvents, acids, superacids, host-guest inclusion complexes [29], C/BC₂N/BN fullerenes/SWNTs/nanocones (SWNCs)/SWNHs/buds (SWNBs)/GRs cluster solvation models in organic solvents [30-36], elementary polarizability of Sc/*fullerene*/GR aggregates, di/GR-cation interactions [37], conductive layered MOFs as a chemistry problem [38,39], conductive 2D NMs and MOFs [40]. The world of NMs was introduced as a *bottom-up* strategy in future nanotechnology. The objective of the present report is to discuss the general principles, which constitute the base for understanding conductive 2D MOFs as multifunctional NMs. Via successful examples from Mirica group, conductive 2D MOFs were discussed [41]. Back to Mendeleev's periodic table of the elements (PTE), the 2D-NMs PTE was analyzed. How does molecular science contribute to the improvement of 2D-NMs properties, facing the development of future electronic NDs? Design criteria and quantitative structure-property relationships (QSPRs) were derived: an examination was carried out on models of interlayer distance, vs. atomic number of 2D NMs, as well as deviations caused by the substructure of MLs. How could one integrate experiment, computation and theory best? Which topologies or dynamic covalent chemistry (DCC) reactions do maximize void size? Do specific chemical functionalities promote targeted applications, e. g., encapsulation of guests?



METHODS

Chemistry is not a self-contained discipline: It becomes nanochemistry while physics merges with materials science. A way of transforming matter is via manufacturing NMs and NDs, or NCs and nanolayers. How one can reduce a material to the nanoscale or manufacture nanostructures was investigated. Two-dimensional MOFs are a modular class of layered NMs with a thickness of a few atomic layers, typically not exceeding 50\AA each one of them. They are characterized by synthetic modularity. They are typically synthesized from MOPs. How one can use the precursors for the growth of some 2D MOFs was also investigated. If one considers all possible synthetic reactions, he arrives to a combinatorial range of possibilities. However, to overcome the limitation, an evolutionary algorithm (EA) was suggested, targeted upon the discovery of optimal structures and properties for molecular materials. The available methods for 2D-MOFs preparation can be subdivided into two distinct categories: *bottom-up* and *top-down* approaches. The world of NMs was introduced as a bottom-up strategy in future nanotechnology. Bottom-up methods involve building 2D NMs from the atomic scale, assembling them from atoms or molecules via, e.g., chemical vapour deposition (CVD). Finally, how one can utilize metal-organic CVD (MOCVD) for the growth of 2D MOFs was likewise investigated.

The study of 2D NMs was carried out by means of the periodic classification of their constituting chemical elements in a PTE. The elements forming 2D NMs [GR, transition metal dichalcogenides (TMDs), MoS_2 , etc.] were arranged in a PTE. A periodic classification of the properties of the chemical elements in 2D NMs was carried out via PTE. Moreover, nanotechnology adds a three-dimension (3D) to PTE: 2D NMs can present the same atoms but different structures, properties, functions and toxicities. The PTE of 2D NMs can reveal particular characteristics of its groups, periods, etc. Interesting trends can be discovered across PTE for selected groups, particularly periods.

It was investigated what 2D MOFs are used for and how molecular science contributes to improving the properties of 2D NMs, facing the development of future electronic NDs. Conductive 2D MOFs present entirely different properties, which can be modulated and accessed via modular synthesis, from a broad number of structurally distinct molecular building units. Some design criteria and QSPRs were derived: we analyzed a series of linear and power models of interatomic distance between layers, vs. atomic number of 2D NMs, and deviations caused by the substructure of MLs.

RESULTS

Table 2 gives some representative 2D NMs with their interatomic distance between every layer: C-graphite, black P (P-black), TMD MoS_2 , BN-*h* and an MOF. All interlayer distances are lesser than $3.5 \ll 50\text{\AA}$. A steadiness results in this distance for C-graphite, P-black, BN-*h* and MOF. However, this distance is the greatest for MoS_2 because of its layered structure, in which a plane of Mo atoms is sandwiched by other planes of S^{2-} ions. These three strata form an ML of MoS_2 .



Table 2. Representation of two-dimensional materials with interatomic distance between every layer

Representative two-dimensional material	Interatomic distance between every layer [Å]
C-graphite	3.33
P-black	3.34
MoS ₂	3.49
BN- <i>h</i>	3.33
Metal-organic framework	3.32

The PTE of some 2D NMs (*cf.* Fig. 1) shows elements [B-N, P, S, Mo] with oxidation states (OSs) 6, 3, 5, -3, etc. The constancy in Table 1 in interlayer distances is shown in B, C and N atoms (BN-*h* and C-graphite) in period 2 of PTE.

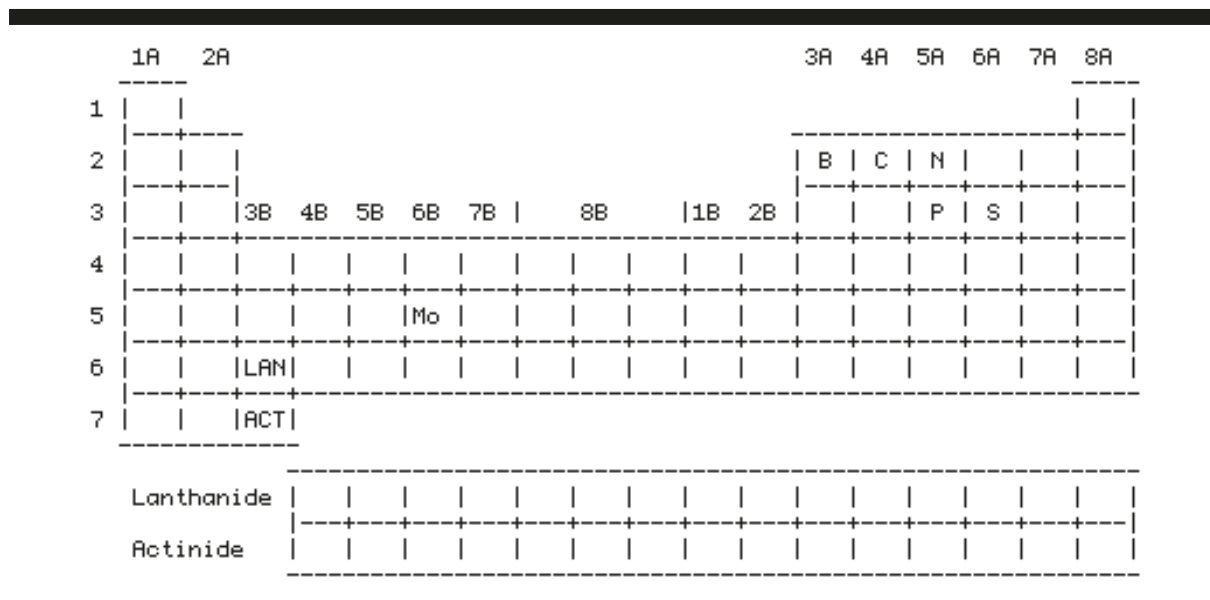


Figure 1. Periodic table of the elements of some two-dimensional nanomaterials.

Some QSPRs were derived: A linear fit of interlayer distances vs. atomic number *Z* of 2D NMs (*cf.* Fig. 2) turns out to be:

$$d = (3.32 \pm 0.04) + (0.00454 \pm 0.00183)Z, N = 6 \quad r = 0.778 \quad s = 0.057 \quad F = 6.2 \tag{1}$$

and shows that this distance rises with *Z*. However, the distance for S (*Z* = 16, MoS₂) deviates from the fit because of the three-strata ML of MoS₂. The slope decays four-fold if only group-V elements (N and P) are included in the following trend line:

$$d = 3.32 + 0.001250Z \tag{2}$$



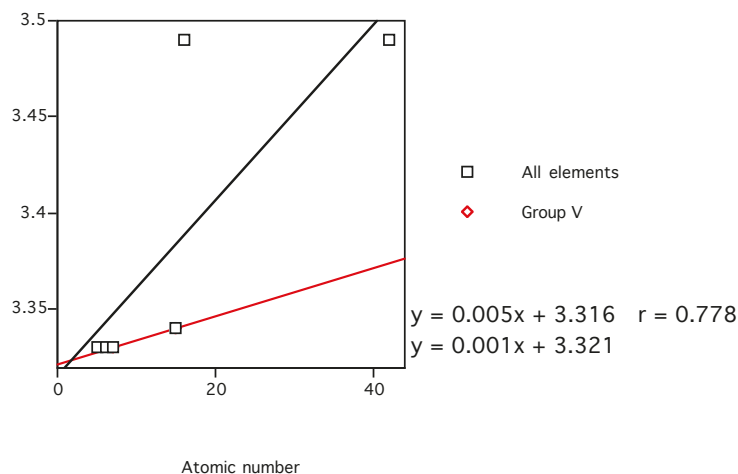


Figure 2. Interatomic distances between every layer vs. atomic number of some two-dimensional nanomaterials.

The good results obtained with both linear fits suggest trying power fits. A three-parameter power fit of interlayer distances vs. Z (*cf.* Fig. 3) improves the model:

$$d = 0.1693 + 3.02Z^{0.0257}, \quad N = 6 \quad r = 0.819 \quad s = 0.047 \quad (3)$$

Again, this distance for S (MoS_2) diverges from the fit because of the three-strata ML of MoS_2 .

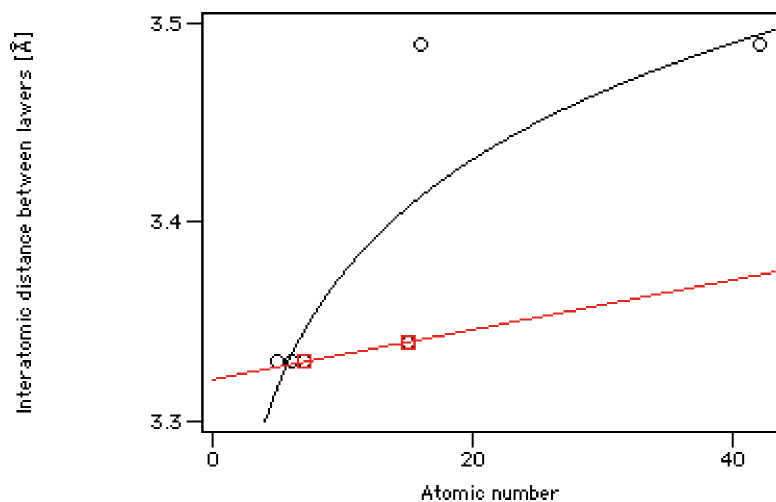


Figure 3. Power fit with three parameters of interlayer distances vs. Z of 2D NMs. Circles: All elements. Squares: Group V.



However, the independent term 0.1693 in Eq. (3) is too small and close to zero, which suggests trying a fit with only two parameters. A two-parameter power fit of the distances vs. Z (*cf.* Fig. 4) improves the correlation:

$$d = (3.19 \pm 1.02)Z^{(0.0244 \pm 0.0085)}, N = 6 \quad r = 0.820 \quad s = 0.015 \quad F = 8.2 \quad (4)$$

Once more, this distance for S (MoS_2) strays from the fit because of the three-strata ML of MoS_2 .

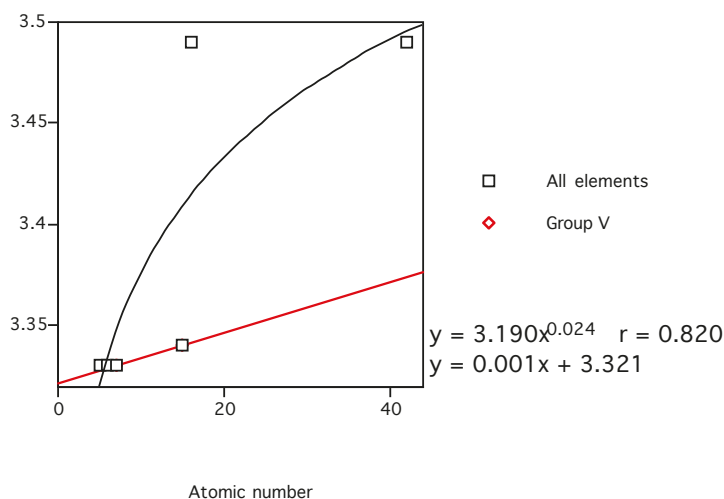


Figure 4. Power fit with two parameters of interlayer distances vs. Z of some two-dimensional nanomaterials.

Table 3 reports three possible modes of charge transport (CT) in 2D MOFs: hopping CT, through-space CT and through-bond CT.

Table 3. Possible modes of charge transport (CT) in two-dimensional metal-organic frameworks

Mode of CT	Scheme	Examples
Hopping	$D-e^- \rightarrow A-e^- \rightarrow D-e^- \rightarrow A$	$M_2(\text{DEBDC})$ MOF ($M = \text{Mn}^{2+}, \text{Fe}^{2+}$; $E = \text{O}, \text{S}$) Fe-MOF-74
Through space	$e^- \rightarrow \bullet \rightarrow e^- \rightarrow \bullet \rightarrow e^- \rightarrow \bullet \rightarrow e^- \rightarrow \bullet \rightarrow e^-$	TFF-based MOF ^a Anthraquinone disulphonate-based MOF
Through bond	$e^- \text{---} e^- \text{---} e^-$ $D-A-D-A$	$\text{Cu}[\text{Cu}(\text{pdt})_2]$ MOF ^b

^a TFF: tetrathiafulvalene.

^b pdt: 2,3-pyrazinedithiolate.



Table 4 compares band transport to hopping transport.

Table 4. Comparison between band transport and hopping transport

Parameter	Band transport (ballistic transport)	Hopping transport
Examples	Crystalline semiconductors	Disordered solids, polycrystalline and amorphous semiconductors
Underlying mechanism	Delocalized molecular wavefunctions over the entire volume	Transition between localized sites via tunnelling (electrons) or overcoming potential barriers (ions)
Inter-site distance	Bond length (less than 1nm)	Typically more than 1nm
Mean free path	Larger than the inter-site distance	Inter-site distance
Mobility	Typically larger than $1\text{cm}^2\cdot\text{V}^{-1}\text{s}^{-1}$; independent of electric field; decays with rising temperature	Typically smaller than $0.01\text{cm}^2\cdot\text{V}^{-1}\text{s}^{-1}$; depends on electric field; rises with rising temperature

Table 5 reproduces the functional and differential forms of electronic transport mechanisms [42].

Table 5. Electronic transport mechanisms

Transport mechanism	Effect of electric field	Functional form	Differential form
Fowler-Nordheim tunnelling (field emission) ^a		$I = A_{\text{eff}} \frac{e^3 m}{8\pi h m \phi_B} E^2 \exp\left(-\frac{8\pi\sqrt{2m}}{3he} \frac{\phi_B^{3/2}}{E}\right)$	$\frac{d \ln I}{dV} = \frac{1}{V} + \frac{8\pi}{3he} \sqrt{2m} \frac{\phi_B^{3/2}}{V^2}$
Thermionic emission ^b	Lowers barrier height	$I = A_{\text{eff}} A^* T^2 \exp\left[-\frac{e}{k_B T} \left(\phi_B - \sqrt{\frac{eE}{4\pi\epsilon_0\epsilon_r}}\right)\right]$	$\frac{d \ln I}{dV} = \frac{e}{4k_B T} \left(\frac{e}{\pi\epsilon_0\epsilon_r}\right)^{1/2} V^{-1/2}$
Arrhenius equation ^c		$I = e\mu n E \exp\left(-\frac{E_a}{k_B T}\right)$	$\frac{d \ln I}{dE} = \frac{1}{E}$
Poole-Frenkel hopping	Assists thermal ionization of trapped charges	$I = e\mu n E \exp\left[-\frac{e}{k_B T} \left(\phi_B - \sqrt{\frac{eE}{4\pi\epsilon_0\epsilon_r}}\right)\right]$	$\frac{d \ln I}{dE} = \frac{1}{E} + \frac{e}{4k_B T} \left(\frac{e}{\pi\epsilon_0\epsilon_r}\right)^{1/2} E^{-1/2}$
Thermally-assisted tunnelling ^d		$I = \frac{V}{2\pi} \left(\frac{k_B T t}{2\pi}\right)^{1/2} \exp\left[-\frac{\phi}{k_B T} + \frac{V^2 \Theta}{24(k_B T)^3}\right]$	$\frac{d \ln I}{dV} = \frac{1}{V} + \frac{V\Theta}{12(k_B T)^3}$

^a I is the measured current, V is the applied voltage, A_{eff} is the effective contact area, h is Planck's constant, ϕ_B is the barrier height, E is the applied electric field, m is the effective mass.

^b A^* is Richardson's constant, T is the temperature, k_B is Boltzmann's constant, ϵ_0 and ϵ_r are the vacuum and the relative permittivity, respectively.

^c E_a is the activation energy.

^d $t = t(y)$ is an elliptical function; Θ is a function of t , the applied field and the barrier height.



Table 6 collects five core organic ligand building blocks for the construction of 2D MOFs. Notice that the core organic ligand building block benzene [hexathiobenzene (HXB)], with metal Cu^{II} and heteroatom S, forms an MOF topology with non-porous continuous sheets.

Table 6. Core organic ligand building blocks for constructing two-dimensional MOFs varying in pore size and shape

Core organic ligand building block	MOF topology	Pore size [nm]
Benzoquinone (dwbq) ^a	Non-planar 2D MOFs	1.5
Benzene (HXB) ^b (M = Ni^{II} , Cu^{II} , Pd^{II} ; X = S, NH)	Sheets with hexagonal pores	1.2
Benzene (HXB) ^b (M = Cu^{II} ; X = S)	Non-porous continuous sheets	-
Triphenylene (HXTP) ^c	MOFs with hexagonal pore apertures	2.0
Phthalocyanine (Pc)	Square pore shapes	1.8

^a dwbq: 2,5-dihydroxy-1,4-benzoquinone.

^b HXB: hexaiminobenzene or hexathiobenzene.

^c HXTP: hexaiminotriphenylene or hexathiotriphenylene.

Table 7 lists three triphenylene-based organic ligands with three cross-linking heteroatoms (O, S and NH). Notice that heteroatom O with organic ligand hexahydroxytriphenylene (HHTP), and metal Ni^{II} or Co^{II} forms an interpolated stacking mode with a different ABAB pattern.

Table 7. Three triphenylene-based organic ligands with interchanged O-NH-S heteroatom

Heteroatom	Organic ligand	Metal	Stacking mode	Pattern
O	HHTP ^a	Cu^{II}	Slipped parallel	AAAA
		Ni^{II} or Co^{II}	Interpolated	ABAB
NH	HITP ^b	Ni^{II} or Cu^{II}	Slipped parallel	AAAA
S	HTTP ^c	Co^{II} , Ni^{II} or Cu^{II}	Eclipsed	AAAA
		Pt^{II}	Staggered	AAAA

^a HHTP: hexahydroxytriphenylene.

^b HITP: hexaiminotriphenylene.

^c HTTP: hexathiotriphenylene.

The progress in the field of conductive 2D MOFs was reviewed with applications [e.g., chemical sensing, field-effect transistors (FETs), energy conversion, energy storage and catalysis]. Table 8 presents post-synthetic modification techniques for prefabricated MOFs.

Table 8. Post-synthetic modification techniques for prefabricated metal-organic frameworks

Post-synthetic modification technique
Ligand exchange
Metal exchange
Stratified synthesis



Table 9 indicates four general methods of integrating conductive 2D MOFs into NDs.

Table 9. General methods of integrating conductive two-dimensional metal-organic frameworks into nanodevices

Method	Description
Drop casting	Bulk MOF is suspended in a solvent and subsequently deposited on to the substrate of interest to create a coating of MOF
Mechanical abrasion	Compression of bulk MOF powder into a pellet in the form of a pencil to enable drawing MOF patterns on substrates
Templated growth	It synthesizes MOFs directly on the substrate to form conformal contact
Layer-by-layer assembly	It carefully controls the growth of MOFs by exposing the substrate to a solution of metal node and organic linker sequentially

Table 10 shows 16 applications of 2D MOFs (11 of traditional and five of conductive 2D MOFs).

Table 10. Applications of traditional and conductive two-dimensional metal-organic frameworks

Area of applicability
Traditional two-dimensional metal-organic frameworks
Hydrogen (H ₂) storage
Catalysis
Biological imaging and sensing
Drug delivery systems
Methane (CH ₄) storage
Semiconductors
Bio-mimetic mineralization
Carbon dioxide (CO ₂) capture
Desalination/ion separation
Water vapour capture
Ferroelectrics and multiferroics
Conductive two-dimensional metal-organic frameworks
Electrically transduced chemical sensing
MOF-based electronics
Energy conversion: H ₂ and O ₂ evolution
Energy storage
Electrochemically controlled capture and release

ANALYSIS

The statistical analysis was carried out via multiple linear regression (MLR), using Microsoft Office 2018 Excel, MacCurveFit vs. 1.5.2 and CA-Cricket Graph III vs. 1.5.2. In the analysis of variance (ANOVA), the Fisher's least significant difference was taken at $p < 0.05$.



The calculated statistics are the number of data points, n , the correlation coefficient r , the standard deviation s and the Fisher's ratio F . The correlation coefficient r was used for the role of the calibration function of the regression equations, jointly with the standard deviation s . The least-squares regression was used to determine the predictability of the equations, which were contrasted and authenticated considering the correlation coefficient r . The procedure supplies a technique for choosing the most excellent collection of indices.

The quality of the models in Eqs. (3) and (4) is good, based on the value of the correlation coefficient r that results greater than 0.8. In addition, following least-squares regression, every standard error of the coefficients of the regression Eqs. (1) and (4) is satisfactory, because it is always smaller than the corresponding value in both equations. All of this suggests that Eq. (4) is the preferred model for the interatomic distance between every layer vs. the atomic number Z .

DISCUSSION

Nanotechnology is a term used to describe precise control of the structure of matter. Four levels are defined, which describe the production of progressively more capable atomically precise (AP, and partially AP) nanosystems [43]. Level 1 includes chemical synthesis, NMs synthesis, nanolithography and biotechnology; level 2 includes AP macromolecular self-assembly and AP mechanical manipulation; level 3 includes biomimetic or machine-based productive nanosystems; level 4 includes high-throughput AP manufacturing. The 2D MOFs are typically synthesized from MOPs. Considering all possible reactions, one reaches a combinatorial range of results. However, an EA was suggested, targeted upon the discovery of optimal structures and properties for molecular materials. What could we do with layered structures with just the right layers ([1] *cf.* Fig. 5)? The *reductionist* hypothesis may still be a topic of controversy among philosophers but, among the vast majority of active scientists, it is accepted without question. In CMP, *more is different* [2]. *The whole is more than the sum of its parts* (Aristotle). In emergent order, *The whole becomes not only more than but very different from the sum of its parts* [2]. The emerging field of modern physics is the study of NMs properties, as not only the sum of the features of their parts but also a consequence of the interaction between their constituents. Such idea is the opposite of the *reductionist* point of view of physics. Such interaction assumes the concept of *emergence*, a cornerstone of CMP. A false corollary of reductionism is that if everything obeys the same fundamental laws, then the only scientists who are studying anything really fundamental are those who are working on those laws. The main fallacy in this kind of thinking is that the *reductionist* hypothesis does not, by any means, imply a *constructionist* one: The ability to reduce everything to simple fundamental laws does not imply the ability to start from those laws, and reconstruct the universe.



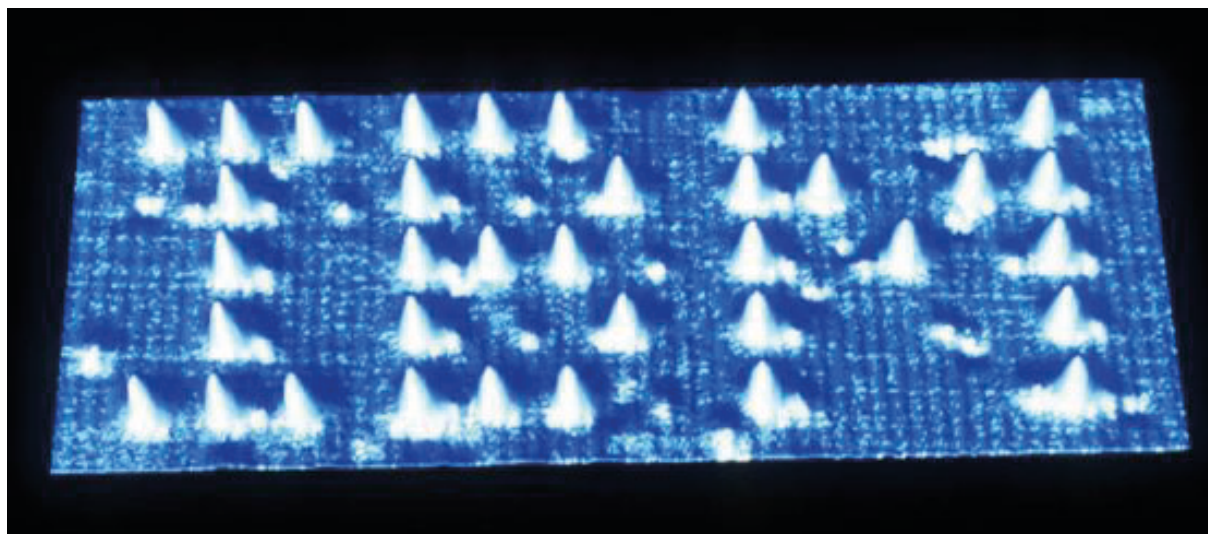


Figure 5. International Business Machines (IBM) logo spelled out using Xe atoms:
The image represents electronic density.

Chemistry becomes nanochemistry while physics merges with materials science. A way of transforming matter is manufacturing NMs and NDs, or NCs and nanolayers. Present research in 2D semiconductors took off thanks to the rise of GR, because of the necessity of having materials with a forbidden band to define electronic and optoelectronic NDs. The 2D MOFs are a modular class of layered NMs. They exhibit exceptional properties different from the bulk. The study of their structural, electronic and optical properties was used as a learning method. All interlayer distances resulted lesser than $3.5 \ll 50 \text{ \AA}$. They were the greatest for TMD MoS_2 because of its layered structure, in which a plane of Mo atoms is sandwiched by other planes of S^{2-} ions. The three strata form an ML of MoS_2 . Every Mo atom exists at the centre of a *trigonal prismatic co-ordination sphere*, and is covalently bonded to six S^{2-} ions. The 2D-NMs PTE was analyzed: A steadiness resulted in interlayer distances for B, C and N atoms in period 2 of PTE. It was investigated how molecular science contributes to improving the properties of 2D NMs, facing the development of future electronic NDs. Some design criteria and QSPRs were derived: A series of linear fits of interatomic distance between layers, vs. atomic number Z of some 2D NMs, showed that this distance rose with Z . Non-linear power models, especially those with two parameters, improved the fits. In all correlations, this distance for S (MoS_2) deviated because of the three-stratum ML of MoS_2 . It was investigated how to best integrate *experiment, computation and theory*.

The MOFs usually present permanent porosity. Their chemically addressable structures, combined with their ability to store large quantities of small molecules within their pores, led to applications in gas storage, heterogeneous catalysis, sensing, drug delivery, etc. Co-ordination modulation, the addition of monomeric modulators to synthetic mixtures, can tune particle size from nanometres to centimetres, by capping of crystallites (decreasing) or co-ordinative competition with ligands (increasing). Research in 2D NMs predicts a revolution in the world of electronics. Powerful NDs development is



conceived in chemistry and physics laboratories throughout the world, for which the study of molecular interactions is a tool. Chalcogen NCs are analyte pre-concentration, imaging and detection tools from environmental to proteomic studies. Progress existed in conducting 2D MOFs with applications spanning chemical sensing, FETs, energy conversion, energy storage and catalysis. With greater understanding and control over QSPR, conducting 2D MOFs presents the potential to make a lasting impact as broadly useful multifunctional NMs. They are interesting for NMs and applications. They present uses because of their atomically thin-layered structure and ease of exfoliation, large surface chemical reactivity, high surface/volume ratio and large capacity for chemical adsorption. The changes of the electrical and optical properties were studied in conductive 2D MOFs, on using them as one or a few atomic MLs, and their applications in photodetector and photonic NDs. The NMs could be ideal companions of GR for a future electronic and optoelectronic nanotechnology, based on NMs with a thickness of a few atomic layers, typically not exceeding 50 Å each one of them. Nanotechnology describes precise control of the structure of matter. The *bona fide* control and monitorization of a material or process should be done from the nanostructured world. The 2D NMs, e. g., MOFs, are a way of structuring the nanoworld for this control and monitorization. Monochalcogenides (e. g., InSe and GaSe), dichalcogenides (e. g., MoS₂ and MoSe₂) and other layered materials (e. g., BN-*h*, phosphorene and metal halide perovskite) are easy to exfoliate. However, metal halide perovskites are unstable to humidity and light, and most contain toxic Pb. The central rule of nanoscience results: Compare cartoons with reality.

CONCLUSION

From the present results and discussion, the following conclusions can be drawn.

1. Miniaturization is a must for actual progress. Nature is not classical. The physical properties of nanomaterials differ significantly from those of conventional ones, because of large surface-to-volume ratios and quantum effects. When one gets to the nanoworld, one has a lot of new things that would happen and that completely represent new opportunities for design.

2. The whole becomes not only more than but different from the sum of its parts. Chemistry is not a self-contained discipline: It becomes nanochemistry, while physics merges with materials science. A way of transforming matter is manufacturing nanomaterials and nanodevices, or nanocomposites and nanolayers.

3. Two-dimensional metal-organic frameworks are a modular class of layered materials, with exceptional properties different from the bulk. Due to the work on exfoliation of C-graphite into C-graphene, materials were obtained and characterized as thin-layered nanostructures, typically not exceeding 50 Å per layer. The study of their structural, electronic and optical properties was used as a learning method.

4. The periodic table of the elements, for some two-dimensional materials, showed interesting trends spotted across the table for selected periods: A steadiness resulted in interlayer distances for B, C and N atoms in period 2 of the table. Future work on the rest of chemical elements in Mendeleev's periodic table is needed. Science is seen from outside as *experimental* but another *theoretical* science exists, and *classification* is a part of this theoretical science.



5. Quantitative structure-property relationships were derived: A series of linear models of interatomic distance between layers, vs. atomic number of some two-dimensional materials, showed that this distance rises with atomic number. Non-linear power fits, especially one with two parameters, improved the models. In all regressions, the interlayer distance for S (MoS_2) deviated from the fit because of the three-stratum monolayer of MoS_2 .

6. The analysis of the core organic ligand building blocks for the construction of two-dimensional metal-organic frameworks showed that the core organic ligand building block benzene (hexathiobenzene), with metal Cu^{II} and heteroatom S, forms a metal-organic framework topology with non-porous continuous sheets.

7. The examination of the triphenylene-based organic ligands, with three cross-linking heteroatoms (O, S and NH), showed that heteroatom O with organic ligand hexahydroxytriphenylene, and metal Ni^{II} or Co^{II} forms an interpolated stacking mode with a different ABAB pattern.

8. Two-dimensional metal-organic frameworks are interesting for materials and applications. They present uses because of their atomically thin-layered structure, large surface chemical reactivity, high surface/volume ratio and large capacity for chemical adsorption. Results may bring chemical and physical properties into the *flatland* for their future use in sensors, membranes, etc.

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