



**SYNTHESIS AND CHARACTERISATION OF NOVEL 1,2,4-TRIAZOLE
CONTAINING MANGANESE-BASED METAL ORGANIC FRAMEWORKS AS
EMERGING ELECTRODES FOR SUPERCAPATTERY DEVICE**

By

VELAN A/L RAMAN

**Thesis Submitted to the School of Graduate Studies, Universiti Putra Malaysia, in
Fulfilment of the Requirements for the Degree of Doctor of Philosophy**

March 2023

ITMA 2023 2

COPYRIGHT

All material contained within the thesis, including without limitation text, logos, icons, photographs and all other artwork, is copyright material of Universiti Putra Malaysia unless otherwise stated. Use may be made of any material contained within the thesis for non-commercial purposes from the copyright holder. Commercial use of material may only be made with the express, prior, written permission of Universiti Putra Malaysia.

Copyright © Universiti Putra Malaysia



Abstract of thesis presented to the Senate of Universiti Putra Malaysia in fulfilment of the requirement for the Doctor of Philosophy

**SYNTHESIS AND CHARACTERISATION OF NOVEL 1,2,4-TRIAZOLE
CONTAINING MANGANESE-BASED METAL-ORGANIC FRAMEWORKS AS
EMERGING ELECTRODES FOR SUPERCAPATTERY DEVICE**

By

VELAN A/L RAMAN

March 2023

Chairman : Yusran Sulaiman, PhD
Institute : Nanoscience and Nanotechnology

Electrochemical energy storage (EES) technologies including batteries and supercapacitors (SCs) are essential in addressing the need for sustainable energy issues caused by the depletion of fossil fuels. Despite extensive study and substantial progress of both SCs and batteries have been carried out, individual device performance still requires further development to fulfil current commercial expectations. Batteries have high specific energy despite having low specific power. On the other hand, SCs with low specific energy prevent them from being widely used in commercial applications. Thus, this scenario sparked a new line of inquiry, by integrating the battery and SCs into a single device known as a supercapattery. This device is predicted to have outstanding performance and a long cycle life due to the combination of capacitive and battery-grade materials. However, supercapattery technology is still developing since the current focus is on the development of high-performance novel electrode materials to design supercapattery devices. Metal-organic frameworks (MOFs) have attracted a lot of attention in the field of energy storage due to their unique properties, including large specific surface areas, adjustable pore sizes and stable porous structures. Therefore, the synthesis of novel MOFs and fabrication of them as electrode materials in supercapattery devices are essential goals in current research. Three novel Mn(II) MOFs bonded to 1,2,4-triazoles (Htrz) ligand namely UPMOF-4 ($\text{MnCl}_2 \cdot 4\text{H}_2\text{O}$ with Htrz), UPMOF-5 (anhydrous MnBr_2 with Htrz) and UPMOF-6 ($\text{Mn}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$ with Htrz) were successfully synthesised solvothermally with molar ratios of 1:2 (UPMOF-4 and UPMOF-5), 1:1.5 (UPMOF-6) at 125°C (UPMOF-4), 120°C (UPMOF-5) and 110°C (UPMOF-6). These new MOFs were characterised using powder X-ray diffraction (PXRD), thermogravimetric analysis (TGA), field emission scanning electron microscopy (FESEM), N_2 physisorption analysis and the structural determination was performed by single-crystal X-ray diffraction analysis (SCXRD). The peaks at low angles of 10° in the PXRD pattern of MOFs indicated the formation of a large unit cell of the frameworks. Thermal analysis revealed that UPMOF-4, UPMOF-5 and UPMOF-6 had high thermal stability up to 490°C, 570°C and 435°C, respectively. The N_2 adsorption-desorption measurements indicated the UPMOF-4, UPMOF-5 and UPMOF-6 had BET surface areas of

1758 m²/g, 1724 m²/g and 895 m²/g, respectively. The three novel MOFs were crystallised in a monoclinic system with different space groups, i.e. *I2/a* (UPMOF-4) and *P2₁* (UPMOF-5 and UPMOF-6). Topologically, the three-dimensional (3D) structure of UPMOF-4 owns a **pcu** network topology while UPMOF-5 and UPMOF-6 with two-dimensional (2D) structures displayed **hxl** type topology. The novel MOFs were then utilised as positive electrodes for electrochemical studies as supercapattery devices for the first time. In a three-electrode assembly in 1 M KOH, all three MOFs manifested a decent performance by showing a battery-graded nature with specific capacities of 203.1 C/g (UPMOF-4), 160.2 C/g (UPMOF-5) and 121.1 C/g (UPMOF-6). The novel MOFs were sandwiched with activated carbon (negative electrode) to fabricate supercapattery devices. UPMOF-4 showed a good specific capacity of 174.4 C/g with promising capacity retention of 90.1% even after 2500 cycles, whereas UPMOF-5 and UPMOF-6 depicted specific capacities of 132.4 C/g and 96.28 C/g with capacity retention of 88.9% and 79.9%, respectively after 2500 cycles. The density functional theory (DFT) calculation of these three MOFs revealed that UPMOF-4 has the lowest HOMO-LUMO energy gap (E_{gap}) of 0.211 eV followed by UPMOF-6 (0.777 eV) and UPMOF-5 (1.198 eV). Therefore, the good electrochemical performance of UPMOF-4 imputed to the structural stability, highly porous nature and low E_{gap} . This work indicated that all these MOFs could be emerging electrode materials for supercapattery devices.

Abstrak tesis ini dikemukakan kepada Senat Universiti Putra Malaysia sebagai memenuhi keperluan untuk ijazah Doktor Falsafah.

SINTESIS DAN PENCIRIAN KERANGKA LOGAM-ORGANIK BERASASKAN MANGAN YANG MENGANDUNGI 1,2,4-TRIAZOL LIGAN SEBAGAI ELEKTROD BAHARU UNTUK PERANTI SUPERKAPATERI

Oleh

VELAN A/L RAMAN

Mac 2023

Pengerusi : Yusran Sulaiman, PhD
Institut : Nanosains dan Nanoteknologi

Teknologi tenaga elektrokimia (EES) termasuk bateri dan superkapasitor(SC), adalah penting dalam menangani isu keperluan tenaga mampan yang disebabkan oleh kemerosotan bahan api fosil. Walaupun kajian meluas dan kemajuan besar kedua-dua SC dan bateri telah dijalankan, prestasi peranti individu masih memerlukan pembangunan lanjut untuk memenuhi keperluan komersil semasa.. Bateri mempunyai tenaga spesifik yang tinggi walaupun mempunyai kuasa spesifik yang rendah. Sebaliknya, SC dengan tenaga spesifik yang rendah menghalangnya daripada digunakan secara meluas dalam aplikasi komersial. Oleh itu, senario ini mencetuskan idea/penyelidikan baharu yang, mencadangkan penyatuan bateri dan SC ke dalam satu peranti yang dikenali sebagai superkapateri. Peranti ini diramalkan mempunyai prestasi yang cemerlang dan kitaran hayat yang panjang disebabkan oleh gabungan bahan kapasitif dan bahan gred bateri. Walau bagaimanapun, tumpuan yang terkini adalah pada pembangunan bahan elektrod baharu yang boleh berfungsi dengan baik dalam teknologi ini. Kerangka logam-organik (MOF) telah menarik perhatian dalam bidang penyimpanan tenaga kerana sifat uniknya seperti permukaan yang luas dan besar, saiz liang boleh dilaraskan dan struktur berliang yang stabil. Oleh itu, sintesis MOF baharu dan penggunaannya sebagai bahan elektrod dalam peranti superkapateri adalah matlamat penting dalam penyelidikan ini. Tiga novel Mn(II) MOF terikat dengan ligan 1,2,4-triazoles (Htrz) iaitu UPMOF-4 ($MnCl_2 \cdot 4H_2O$ dengan Htrz), UPMOF-5 ($MnBr_2$ dengan Htrz) dan UPMOF-6 ($Mn(NO_3)_2 \cdot 4H_2O$ dengan Htrz) berjaya disintesis secara solvoterma dengan nisbah molar 1:2 (UPMOF-4 dan UPMOF-5), 1:1.5 (UPMOF-6) pada suhu 125°C (UPMOF-4), 120°C (UPMOF-5) dan 110°C (UPMOF-6). MOF baharu ini dicirikan menggunakan analisis pembelauan sinar-X (PXRD), analisis termogravimetri (TGA), mikroskop elektron pengimbasan pancaran medan (FESEM), analisis penjerapan fizikal N_2 dan penentuan struktur dilakukan dengan analisis belauan sinar-X hablur tunggal (SCXRD). Puncak pada sudut rendah 10° dalam analisis PXRD menunjukkan pembentukan kerangka dengan sel unit besar. Analisis terma mendedahkan bahawa UPMOF-4, UPMOF-5 dan UPMOF-6 mempunyai kestabilan haba masing-masing yang tinggi sehingga 490°C, 570°C dan 435°C. Pengukuran penjerapan-penyahjerapan N_2 menunjukkan UPMOF-4, UPMOF-5 dan

UPMOF-6 mempunyai luas permukaan BET masing-masing 1758 m²/g, 1724 m²/g dan 895 m²/g. Tiga MOF baharu ini telah dihablurkan dalam sistem monoklinik dengan kumpulan ruang yang berbeza iaitu *I2/a* (UPMOF-4) dan *P2₁* (UPMOF-5 dan UPMOF-6). Struktur tiga dimensi (3D) UPMOF-4 memiliki topologi rangkaian **pcu** manakala UPMOF-5 dan UPMOF-6 dengan struktur dua dimensi (2D) memaparkan topologi jenis **hxl**. MOF baharu ini seterusnya digunakan sebagai elektrod positif untuk kajian elektrokimia sebagai peranti superkapateri buat kali pertama. Di dalam sistem tiga elektrod menggunakan 1 M KOH sebagai elektrolit, ketiga-tiga MOF menunjukkan prestasi yang baik dengan menunjukkan sifat gred bateri dengan kapasitan spesifik 203.1 C/g (UPMOF-4), 160.2 C/g (UPMOF-5) dan 121.1 C/g (UPMOF-6). MOF baharu juga diapit dengan karbon aktif (elektrod negatif) untuk menghasilkan peranti superkapateri. UPMOF-4 menunjukkan kapasitan spesifik yang baik iaitu 174.4 C/g dengan pengekal nilai kapasitan sebanyak 90.1% walaupun selepas 2500 kitaran, manakala UPMOF-5 dan UPMOF-6 mempunyai kapasitan spesifik 132.4 C/g dan 96.28 C/g dengan pengekal kapasitan masing-masing sebanyak 88.9% dan 79.9%, selepas 2500 kitaran. Pengiraan teori fungsi ketumpatan (DFT) bagi ketiga-tiga MOF ini mendedahkan bahawa UPMOF-4 mempunyai nilai jurang tenaga HOMO-LUMO (E_{gap}) terendah sebanyak 0.211 eV diikuti oleh UPMOF-6 (0.777 eV) dan UPMOF-5 (1.198 eV). Oleh itu, UPMOF-4 dengan prestasi elektrokimia yang baik ini boleh dikaitkan dengan kestabilan struktur, sifat berliang tinggi dan nilai E_{gap} rendah. Penyelidikan ini menunjukkan bahawa semua MOF ini boleh menjadi bahan elektrod baharu untuk peranti superkapateri.

ACKNOWLEDGEMENTS

In the name of God, The Most Gracious, The Most Merciful

Firstly, I would like to express my sincere gratitude to my supervisor Associate Professor Dr Yusran Sulaiman and the supervisory committee members Dr Mohamed Ibrahim Mohamed Tahir and Professor Dr Mohd Basyaruddin Abdul Rahman for their continuous support and immense knowledge of this research. I am extremely thankful to UPM and the Ministry of Higher Education Malaysia for the financial award of Skim Latihan Akademik IPTA (SLAI)/(TAM UPM 2019). Special thanks to Associate Professor Dr. Thahira Begum, who served as my former supervisor, for her invaluable time, insight, and guidance on this research.

Special thanks to Sharon Sangeetha, Nithya Rajendran and Sathish Sugumaran for their valuable friendship. This PhD journey would have been a much more difficult feat without their unwavering support and comfort. I would like to thank my research group members Nazhirah Mohd Nasri, Nurul Natasya Muhamad Khirudin, Nurul Nabihah Mohamad Ishak Nurul Farhana Ahmad Aljafree, Nur Hawa Nabilah Azman, Logeswary Fiter and Dharshini Mohanadas for their constant guidance and advice in order to accomplish this synthesis research successfully.

Lastly, I want to extend my sincere gratitude to my family for the tremendous love, support, and hope they have shown me. This thesis would not have been conceivable without such hope. I'm grateful to you all for the strength you gave me.

This thesis was submitted to the Senate of Universiti Putra Malaysia and has been accepted as fulfilment of the requirement for the degree of Doctor of Philosophy. The members of the Supervisory Committee were as follows:

Yusran bin Sulaiman, PhD

Associate Professor, ChM
Faculty of Science
Universiti Putra Malaysia
(Chairman)

Mohamed Ibrahim bin Mohamed Tahir, PhD

Senior lecturer
Faculty of Science
Universiti Putra Malaysia
(Member)

Mohd Basyaruddin bin Abdul Rahman, PhD

Professor, ChM
Faculty of Science
Universiti Putra Malaysia
(Member)

ZALILAH MOHD SHARIFF, PhD

Professor and Dean
School of Graduate Studies
Universiti Putra Malaysia

Date: 11 May 2023

Declaration by the Graduate Student

I hereby confirm that:

- this thesis is my original work;
- quotations, illustrations and citations have been duly referenced;
- this thesis has not been submitted previously or concurrently for any other degree at any other institutions;
- intellectual property from the thesis and copyright of thesis are fully-owned by Universiti Putra Malaysia, as according to the Universiti Putra Malaysia (Research) Rules 2012;
- written permission must be obtained from supervisor and the office of Deputy Vice-Chancellor (Research and Innovation) before thesis is published (in the form of written, printed or in electronic form) including books, journals, modules, proceedings, popular writings, seminar papers, manuscripts, posters, reports, lecture notes, learning modules or any other materials as stated in the Universiti Putra Malaysia (Research) Rules 2012;
- there is no plagiarism or data falsification/fabrication in the thesis, and scholarly integrity is upheld as according to the Universiti Putra Malaysia (Graduate Studies) Rules 2003 (Revision 2012-2013) and the Universiti Putra Malaysia (Research) Rules 2012. The thesis has undergone plagiarism detection software.

Signature: _____ Date: _____

Name and Matric No: Velan A/L Raman

Declaration by Members of the Supervisory Committee

This is to confirm that:

- the research conducted and the writing of this thesis was under our supervision;
- supervision responsibilities as stated in the Universiti Putra Malaysia (Graduate Studies) Rules 2003 (Revision 2012-2013) are adhered to.

Signature: _____

Name of
Chairman of
Supervisory
Committee:

Yusran bin Sulaiman

Signature: _____

Name of
Member of
Supervisory
Committee:

Mohamed Ibrahim bin Mohamed Tahir

Signature: _____

Name of
Member of
Supervisory
Committee:

Mohd Basyaruddin bin Abdul Rahman

TABLE OF CONTENT

	Page
ABSTRACT	i
ABSTRAK	iii
ACKNOWLEDGEMENTS	v
APPROVAL	vi
DECLARATION	ix
LIST OF FIGURES	xiii
LIST OF TABLES	xvii
LIST OF ABBREVIATIONS	xviii
CHAPTER	
1 INTRODUCTION	
1.1 Background of research	1
1.2 Problem statement	4
1.3 Research objectives	5
1.4 Research scopes	6
1.5 Research hypothesis	7
1.6 Organisation of thesis	7
2 LITERATURE REVIEW	
2.1 Design and synthesis of metal-organic frameworks(MOFs)	8
2.1.1 Metal with vacant sites	9
2.1.2 Organic linkers as building blocks	10
2.1.3 Conventional synthesis	12
2.2 Crucial aspects in synthesis of MOFs	13
2.2.1 Rigidity, flexibility and thermal stability of framework	14
2.2.2 Influence of experimental parameters on MOF synthesis	15
2.3 Chemistry of 1,2,4-triazole	20
2.3.1 Coordination and structural features of 1,2,4-triazole	21
2.3.2 Metal-1,2-4-triazole derivative frameworks	23
2.4 Utilisation of MOFs in supercapacitors (SCs) and supercapattery applications	31
2.4.1 Fundamentals of electrochemical energy storage devices.	32
2.4.2 Manganese MOFs as supercapacitor electrode	35
2.4.3 Supercapattery as a renowned energy storage	38
3 METHODOLOGY	
3.1 Introduction	42
3.2 Chemicals and reagents	42
3.3 Reaction conditions for synthesis of manganese MOFs	42
3.3.1 Table of reaction conditions for three manganese-	43

	organic frameworks (Mn-MOFs)	
3.4	Optimum conditions for the synthesis of Mn-MOFs	48
3.4.1	Synthesis of UPMOF-4	48
3.4.2	Synthesis of UPMOF-5	48
3.4.3	Synthesis of UPMOF-6	48
3.5	Characterisation of Mn-MOFs	
3.5.1	Single Crystal X-Ray Diffraction (SCXRD)	49
3.5.2	Topological Analysis	49
3.5.3	Powder X-Ray Diffraction (PXRD)	50
3.5.4	Thermogravimetric Analysis (TGA)	50
3.5.5	Field Emission Scanning Electron Microscopy (FESEM)	51
3.5.6	N ₂ -Physisorption Analysis	51
3.4.7	X-ray Photoelectron Spectroscopy (XPS)	52
3.4.8	Density Functional theory (DFT)	52
3.6	Preparation of Mn-MOFs as electrodes for supercapattery studies	
3.6.1	Three-electrode configuration	53
3.6.2	Two-electrode supercapattery device assembly	54
3.6.3	Electrochemical characterisations	54
4	RESULTS AND DISCUSSION	
4.1	Facile synthesis and characterisations of novel Mn-1,2,4-triazole framework (UPMOF-4) as an emerging electrode material for supercapattery device	
4.1.1	Structural description of UPMOF-4	55
4.1.2	PXRD patterns and TGA analysis of UPMOF-4	56
4.1.3	Morphology and N ₂ sorption studies of UPMOF-4	59
4.1.4	XPS analysis of UPMOF-4	61
4.1.5	Electrochemical studies in a three-electrode configuration	64
4.1.6	Supercapattery device assembly using UPMOF-4 as positive electrode	67
4.1.7	Conclusion	70
4.2	1,2,4-triazole (Htrz) functionalised manganese-organic framework (UPMOF-5) as a battery-type electrode for supercapattery	
4.2.1	Structural description of UPMOF-5	71
4.2.2	PXRD patterns and thermal analysis of UPMOF-5	72
4.2.3	Morphology and N ₂ sorption studies of UPMOF-5	74
4.2.4	XPS analysis of UPMOF-5	76
4.2.5	Electrochemical studies in a three-electrode system	78
4.2.6	Supercapattery device assembly using UPMOF-5 as	81

	positive electrode	
4.2.7	Conclusion	84
4.3	Synthesis and characterisation of manganese-1,2,4-triazole framework (UPMOF-6) as a battery-type electrode for supercapattery	
4.3.1	Structural description of UPMOF-6	84
4.3.2	PXRD patterns and thermal analysis of UPMOF-6	86
4.3.3	Morphology and N ₂ sorption studies of UPMOF-6	88
4.3.4	XPS analysis of UPMOF-6	90
4.3.5	Electrochemical studies in a three-electrode system	92
4.3.6	Supercapattery device assembly using UPMOF-6 as positive electrode	94
4.3.7	Conclusion	97
4.4	Comparison of electrochemical performances of UPMOF-4, UPMOF-5 and UPMOF-6 with the aid of DFT calculation and BET surface area	
4.4.1	DFT analysis of UPMOF-4, UPMOF-5 and UPMOF-6	97
4.4.2	Factors that influence the electrochemical performance of UPMOF-4, UPMOF-5 and UPMOF-6	99
5	CONCLUSIONS AND FUTURE RECOMMENDATIONS	101
	REFERENCES	103
	APPENDICES	115
	BIODATA OF STUDENT	118
	LIST OF PUBLICATIONS	119

LIST OF FIGURES

Figure		Page
1.1	Synthesis and factors affecting the formation of MOFs	1
1.2	N-donor heterocyclic azole linkers	3
1.3	The tautomers of 1,2,3-triazole and 1,2,4-triazole	4
2.1	Overview of synthetic routes/end products in the synthesis of MOFs	8
2.2	Schematic diagram of hexagonal/pentagonal window MIL-101	10
2.3	The covalent bond formation between metal clusters and linkers	11
2.4	Examples of organic linkers used in the synthesis of MOFs	12
2.5	Preparation of MOF thin film with polyaniline	13
2.6	Sonochemical synthesis of the catenation isomers PCN-6 and PCN-6' upon adjusting the ultrasonic power level	14
2.7	Crucial factors that influence the formation of MOFs	16
2.8	Coordination of Cd(II) metal centre with biphenyl tricarboxylic acid in the different solvents: (1) DMF, (2) DMA and (3) DEF	17
2.9	Twofold parallel interpenetration in 2D MOF	18
2.10	Two Tm-succinates obtained under different temperatures	19
2.11	Structural formulas of azoles	21
2.12	Coordination modes of 1,2,4-triazole (A) Protonated 1,2,4-triazole (B) Deprotonated 1,2,4-triazole	23
2.13	(A) ORTEP view of Mn(II) triazolate framework 1 (B) polyhedral representation in the plane <i>bc</i>	25
2.14	ORTEP view of Mn(II) triazolate framework 4	26
2.15	(A) Trinuclear triangular building block constructing the framework of $[\text{Cu}_3(\mu_3\text{-OH})(\text{Htrz})_3(\text{OH})_2(\text{H}_2\text{O})_4]_n \cdot 4.5n(\text{H}_2\text{O})$ (5); (B) representation of the crystal packing of $[\text{Cu}_3(\mu_3\text{-OH})(\text{Htrz})_3(\text{OH})_2(\text{H}_2\text{O})_4]_n \cdot 4.5n(\text{H}_2\text{O})$ emphasizing the 1D channels along the crystallographic <i>a</i> axis	27
2.16	The crystal structure of ${}^3_\infty[\text{Yb}(\text{Tz})_3]$	28
2.17	(A) View of coordination environment of copper atom, (B) view of 1-D inorganic $[\text{Cu}_3\text{Br}_3]_n$	30

2.18	HOMO-LUMO energy level of as-synthesised CTF, CICTF and FCTF	31
2.19	Typical CV plot of battery and supercapacitor	32
2.20	The characteristic GCD plots of a supercapacitor (left) and a battery (right), based on which the specific capacitance/capacity, energy density, and power density calculated	33
2.21	Criteria for distinguishing between pseudocapacitive and battery materials	34
2.22	High-magnification SEM images of Mn-LMOF	36
2.23	3D supramolecular framework of Mn-LMOF	37
2.24	Schematic diagram of (A) ELDC, (B) pseudocapacitor, and (C) battery-grade materials	39
2.25	Schematic illustration of the fabrication process of M-MOFs	40
2.26	Schematic representation of assembled supercapattery device	41
4.1	(a) UPMOF-4 is synthesized through the reaction of manganese chloride with 1,2,4-triazole in DMA. (b) ORTEP representation (50% probability) of the asymmetric unit of UPMOF-4. (c), (d) Ball and stick, and polyhedral representation of the two types of SBUs. (e), (f), Representation of the UPMOF-4 framework, view along the <i>x</i> , and <i>y</i> -axis, respectively. Colour code: Mn (purple); O(red); Cl(green); N(blue); and C(black)	56
4.2	Simulated and as-synthesised PXRD patterns of UPMOF-4	57
4.3	TGA-DTG curves of UPMOF-4	59
4.4	(a) 3000 times (b) 10,000 times magnification FESEM images of UPMOF-4	60
4.5	Nitrogen sorption isotherm of UPMOF-4 collected at 77K	61
4.6	(a) Survey spectrum of UPMOF-4. (b,c,d,e and f) spectra of C 1s, O 1s, N 1s, Mn 2p and Cl 2p of UPMOF-4	63
4.7	(a) CV plots of UPMOF-4 at scan rates of 1-50 mV/s. (b) Log current versus Log scan rate plot. (c) Anodic and cathodic peaks versus the scan rate	65
4.8	(a) GCD plots of UPMOF-4 at different current densities. (b) Specific capacity versus current density plot. (c) EIS plot of UPMOF-4 at the frequency of 0.1-100kHz	67
4.9	(a) Comparison of the CV curves of AC and battery-grade materials. (b) CV curves of the supercapattery device in 1.4 V.	68

	(c) <i>b</i> -value fitting of the data points at various potential windows	
4.10	(a) GCD plots of supercapattery device at various current densities. (b) Specific energy and specific power are calculated from GCD plots. (c) EIS measurement of supercapattery device at 0.01-100 kHz. (d) The cycle stability of assembled device at 50 mV/s	70
4.11	(a) Reaction of manganese bromide and 1,2,4-triazole affords the 2D UPMOF-5. (b) ORTEP representation (50% probability) of the asymmetric unit of UPMOF-5, (c) Representation with a perpendicular view of one of the layers UPMOF-5. (d) Perspective representation of the layer stacking viewed from <i>b</i> -axis. The H atoms have been omitted for clarity. Colour code: Mn (pale blue); O (red); Br (brown); N (blue); C (black)	72
4.12	Simulated and as-synthesised PXRD patterns of UPMOF-5	73
4.13	TGA-DTG curves of UPMOF-5	74
4.14	(a) 5000x, (b) 10,000x magnification FESEM images of UPMOF-5	75
4.15	N ₂ sorption isotherm of UPMOF-5 collected at 77K	76
4.16	(a) Survey spectrum of UPMOF-5. (b,c,d,e and f) spectra of C 1s, N 1s, O 1s, Mn 2p and Br 3d of UPMOF-5	77
4.17	(a) CV plots of UPMOF-5 at scan rates of 1-50 mV/s. (b) Log current versus Log scan rate plot. (c) Anodic and cathodic peaks versus the square root of scan rate	79
4.18	(a) GCD plots of UPMOF-5 at different current densities. (b) Specific capacity versus current density plot. (c) EIS plot of UPMOF-5 at the frequency of 0.1-100kHz	81
4.19	(a) CV curves of AC and battery-grade material (UPMOF-5) at a scan rate of 5 mV/s. (b) CV curves of the supercapattery device in 1.4 V. (c) <i>b</i> -value fitting of the data points at various potential windows	82
4.20	(a) GCD plots of supercapattery device at various current densities. (b) Specific energy and Specific power are calculated from GCD plots. (c) EIS measurement of supercapattery device at 0.01-100 kHz. (d) The cycle stability of assembled device at 50 mV/s.	83
4.21	(a) Reaction of manganese nitrate and 1,2,4-triazole with ORTEP representation (50% probability) of the asymmetric unit of UPMOF-6, (b) Representation with a perpendicular	85

view of one of the layers UPMOF-6. (c) Perspective representation of the layer stacking viewed from *b*-axis. (d) Topological representation of UPMOF-5 and UPMOF-6. The H atoms have been omitted for clarity. Colour code: Mn (pale blue); O (red); Br (brown); N (blue); C (black).

4.22	Simulated and as-synthesised PXRD patterns of UPMOF-6	86
4.23	TGA-DTG curves of UPMOF-6	88
4.24	(a) 50 times, (b) 100 times magnification FESEM images of UPMOF-6. (c) Indistinct image of UPMOF-6 at 500 times magnification	89
4.25	N ₂ sorption isotherm of UPMOF-6 collected at 77K	90
4.26	(a) Survey spectrum of UPMOF-6. (b,c,d and e) spectra of C 1s, O 1s, N 1s and Mn 2p of UPMOF-6	91
4.27	(a) CV plots of UPMOF-6 at scan rates of 1-50 mV/s. (b) Log current versus Log scan rate plot. (c) Anodic and cathodic peaks versus the scan rate	93
4.28	(a) GCD plots of UPMOF-6 at different current densities. (b) Specific capacity versus current density plot. (c) EIS plot of UPMOF-6 at the frequency of 0.1-100kHz	94
4.29	(a) CV curves of AC and battery-grade material (UPMOF-6) at a scan rate of 5 mV/s. (b) CV curves of the supercapattery device in 1.3 V. (c) <i>b</i> -value fitting of the data points at various potential windows	95
4.30	(a) GCD plots of supercapattery device at various current densities. (b) Specific energy and Specific power are calculated from GCD plots. (c) EIS measurement of supercapattery device at 0.01-100 kHz. (d) The cycle stability of assembled device at 50 mV/s	96
4.31	HOMO and LUMO levels of novel UPMOF-4, UPMOF-5 and UPMOF-6 at Gaussian B3LYP/6-31G(d) level	99

LIST OF TABLES

Table		Page
2.1	Coordination diversity of the guanazole linker in the presence of anions	29
3.1	Reaction conditions of UPMOF-4, UPMOF-5 and UPMOF-6	43-47
4.1	Indexed PXRD pattern of UPMOF-4	58
4.2	Comparison of specific capacities of various MOFs in supercapattery device	66
4.3	Indexed PXRD pattern of UPMOF-5	73
4.4	Comparison of specific capacities of various MOFs in a three-electrode configuration	80
4.5	Indexed PXRD pattern of UPMOF-6	87
4.6	Summary of electrochemical data in accordance to BET surface area and HOMO-LUMO energy gap	100

LIST OF ABBREVIATIONS

AC	Activated carbon
4,4-bpy	4,4-bipyridine
B3LYP	Becke's three-parameter hybrid functional using LYP correlation functional
BDC	1,4-benzenedicarboxylic acid
BET	Brunauer-Emmett-Teller
BPDC	Biphenyl-4,4'-dicarboxylic acid
BPT	Biphenyl tricarboxylic acid
BTC	1,3,5-benzenetricarboxylic acid
BTZE	1, 2-bis (tetrazol-1-yl) ethane
CCDC	Cambridge Crystallographic Data Centre
CIF	Crystal information file
CTFs	Triazine-based organic frameworks
CTPY	4-carboxy-4, 2', 6', 4''-terpyridine
CU(INA)	MOF derived from copper acetate with isonicotinic acid
CV	Cyclic voltammetry
DEF	<i>N,N'</i> -diethylformamide
DMA	<i>N,N'</i> -dimethylacetamide
DMF	<i>N,N'</i> -dimethylformamide
DFT	Density functional theory
EES	Electrochemical energy storage
EDLCs	Electrical double-layer capacitors
E_{gap}	Energy gap
EIS	Electrochemical impedance spectroscopy
ESR	Equivalent series resistance
FESEM	Field emission scanning microscopy
FMO	Frontier molecular orbital
GCD	Galvanostatic charging/discharging

H ₂ tfbdc	2,3,5,6-tetrafluoroterephthalic acid
HKUST-1	Hong Kong University of Science and Technology, MOF made of copper nitrate and 1,3,5-benzenetricarboxylic acid
Hdatrz	Guanazole (3,5-diamino-1,2,4-triazole)
HOMO	Highest occupied molecular orbital
Htrz	1,2,4-triazole
Hxl net	Hexagonal network topology
IRMOF	Isorecticular metal-organic frameworks
LUMO	Lowest unoccupied molecular orbital
MIL-53	MOF derived from scandium and oxygen (ScO ₆) nodes with BDC
MIL-68	MOF derived from ferum nitrate and benzene 1,4-dicarboxylic acid
MIL-101	MOF made from chromium nitrate and 1,4-benzenedicarboxylic acid
MIL-88B-NH ₂	MOF containing chromium ion and amino-1,4-benzenedicarboxylic acid
Mn-LMOF	Layered manganese-organic framework
Mn-MOFs	Manganese-organic frameworks
MOFs	Metal-organic frameworks
MOF-5	MOF made from Zinc nitrate and 1,4-benzenedicarboxylic acid
MOF-74	MOF made from magnesium nitrate and 2,5-dihydroxyterephthalic
MTBS	Methyl tributyl ammonium methyl sulfate
NMP	N-methyl-2-pyrrolidone
OCP	Open circuit potential
PCU net	Primitive cubic topology network
PCs	Pseudocapacitors
PCN-6	MOF containing zinc nitrate and 4,4-biphenyldicarboxylic acid
PXRD	Powder X-ray Diffraction
PTFE	Polytetrafluoroethylene
SCXRD	Single crystal X-ray diffraction
SC	Supercapacitors
SCN	Thiocyanate ions
TGA	Thermogravimetric analysis

TIPA	Tris(4imidazolyphenyl)amine
XPS	X-ray photoelectron spectroscopy
ZIF-8	Zeolitic Imidazolate Framework-8; MOF made from zinc nitrate and imidazole
Zn-BTC	MOF derived from zinc acetate and 1,3,5-benzenetricarbocyclic acid



CHAPTER 1

INTRODUCTION

1.1 Research Background

Metal-organic frameworks (MOFs) are a rapidly emerging unique type of crystalline porous materials in reticular chemistry that describe the linking of molecular building blocks by strong bonds to develop extended crystalline structures (Yaghi, 2019). In relation to this, MOFs or porous coordination polymers are self-assembled from the inorganic metal cluster and organic bridging ligands via strong covalent bonds (**Figure 1.1**).

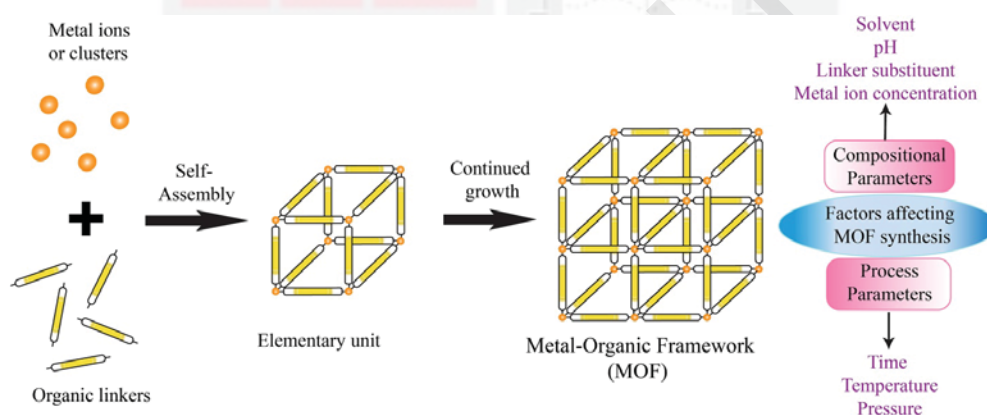


Figure 1.1: Synthesis and factors affecting the formation of MOFs (Sharanyakanth and Radhakrishnan, 2020).

The structures of MOFs are also influenced by several factors related to synthetic and process parameters (**Figure 1.1**), including changes in pH, temperature, choice of solvent, metal ion and organic linker (Sharanyakanth and Radhakrishnan, 2020). MOFs are typically synthesised in mild settings using either a standard approach (above room temperature) or a non-conventional method (below or at room temperature). Microwave, electrochemical, mechanochemical, ultrasonic, and high-throughput syntheses are some of the additional methods used to make MOFs.

In MOF chemistry, the functionality of ligands plays a key role in order to access a broad range of promising applications in which the newly synthesised MOFs can provide a platform to integrate various chemical functionalities in many useful applications (Chen and Wu, 2018). A predominant feature of MOFs is that their framework structure, pore environment, and functionality can be finely controlled by the choice of metal and organic

linkers. In particular, organic linkers are the essential units of coordination polymers regardless of their synthetic routes or strategies.

The flexibility and versatility of organic ligands have also been recognised as the key value of coordination polymers. In this context, the N-donor linkers namely azoles, five-membered aromatic nitrogen heterocycles are increasingly used to design and synthesise new families of coordination polymers (Zhang *et al.* (2012). Generally, these ligands including imidazole, pyrazole, triazole and tetrazole (**Figure 1.2**) are promising because easy to be synthesised, mostly soluble in common organic solvents and readily bind to 3d-metals (Bai *et al.*, 2011). Among these, the most-versatile azole ligands are triazoles, (Bai *et al.*, 2011) the aromatic heterocyclic five-membered ring with three nitrogen atoms that exhibit in symmetric and asymmetric structures namely 1,2,4-triazole and 1,2,3-triazole.

Figure 1.2: N-donor heterocyclic azole linkers.

The triazole ring is a useful organic heterocyclic molecule made up of two carbon atoms and three nitrogen atoms in a diunsaturated five-membered ring structure. The relative positions of the three nitrogen atoms differ between two sets of isomers. Each of them has two tautomers (**Figure 1.3**) that differed by which hydrogen bonded to the nitrogen (Nasri *et al.*, 2021). This linker has been comprehensively studied due to the multiple binding capacities that allow for more-rigid coordination much like metal carboxylate cluster chemistry (Bai *et al.*, 2011). In coordination chemistry, the derivatives of 1,2,4-triazoles are extensively studied (Aromí *et al.*, 2011). Thus, the synthesis of metal-1,2,4-triazole frameworks has attracted great attention over the last few years due to the possibility of obtaining a wide variety of aesthetically appealing MOF structures that could also be of great interest in porous materials fields for some applications (Gangu *et al.*, 2016).

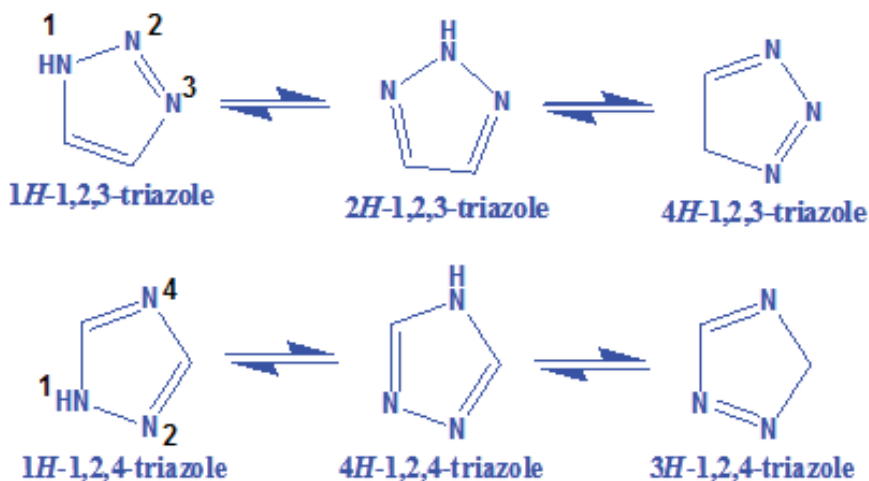


Figure 1.3: The tautomers of 1,2,3-triazole and 1,2,4-triazole (Nasri *et al.*, 2021).

Electrochemical energy storage (EES) technologies are mostly categorised as batteries and supercapacitors (SCs) and are based on electrochemical processes or electrostatic interactions to store energy. Despite extensive studies and substantial advances in the development of both technologies (SCs and batteries), the performance of individual devices continues to fall short of commercial expectations (Gu and Yushin, 2014, Numan *et al.*, 2021). Therefore, SCs and batteries are merged to assemble the device that can give high specific energy and high specific power, respectively. A two-terminal device known as a "supercapattery" can be created by joining a capacitive electrode and a battery electrode (Chen, 2016). Supercapattery is predicted to have a long cycle life and remarkable energy storage performance due to the combination of capacitive and battery-grade materials (Numan *et al.*, 2021). On the other hand, MOFs have extended frameworks, with potential porosity, and display high specific surface areas. Due to their features, MOFs are receiving great attention to be used as electrodes in energy storage devices, (Li *et al.*, 2019b, Mohanadas *et al.*, 2021) and a few successful works using MOFs in the assembly of supercapattery devices have been recently reported.

In view of this, the investigation of the metal-1,2,4-triazole framework in the field of electrochemistry is quite recent but expanding. Although few reports have mentioned triazoles are electrochemically inactive (Fischer *et al.*, 2020) but incorporating them with electro-active metal may enhance the electrochemical properties (Norková *et al.*, 2011). Moreover, it is well known that modulating the structure of linkers will crucially enhance the charge transfer inside of the framework (Behera *et al.*, 2009) and fabricating the MOFs with conductive properties will immensely improve electron conduction, due to most of the MOFs with insulating character (Allendorf *et al.*, 2011, Behera *et al.*, 2009, Jahan *et al.*, 2010, Zhang *et al.*, 2019) limit them from being used as electrode materials or electrocatalysts. Thus, this research focused on the synthesis of novel Mn-MOFs by incorporating 1,2,4 triazole as a linker to examine their electrochemical performance.

1.2 Problem Statement

The depletion of natural fossil fuels intensifies the search for renewable and sustainable energy conversion and storage technologies. The figures for the use of fossil fuels to meet human requirements are at an all-time high, combined with environmental concerns; therefore, reliance on fossil fuels is predicted to fall in the following years. As a result, scientists working on renewable energy resources are eager to develop a new approach to reduce our reliance on fossil fuels while yet meeting the demands of the modern world. There are two primary rivals, supercapacitors and batteries that require special attention from researchers in order to alleviate the worrying situation (Faisal *et al.*, 2021). SC also known as ultracapacitors have high specific power, fast charge-discharge long service life compared to batteries including environmental protection (Zhi *et al.*, 2013). The supercapacitors are mainly divided into electrical double-layer capacitors (EDLCs) and pseudocapacitors (PCs) depending on their operating mechanism in energy storage (Zhang *et al.*, 2021).

In comparison to other energy storage technologies, batteries have an unusually high specific energy which qualifies them for commercial application in a variety of electronic devices (Faisal *et al.*, 2021). However, because of the battery's poor specific power hindered its usage in high-speed electronic devices. SCs, unlike batteries, are recognised for their high specific power, which allows them to be used in rapid-response systems. However, there is a problem with this technology's poor specific energy (Yuan *et al.*, 2012). Recently, a new approach has been developed to overcome the limitations of both systems. This new technology is developed by combining the advantages of both technologies into a single device, which is referred to as a supercapattery (Iqbal *et al.*, 2020a). The supercapattery is a combination of an SC and a battery that can be used in a variety of electrical devices. The two energy storage techniques that occur in supercapattery are dependent on the electrode material utilised. Mostly, carbonaceous materials are employed as electrodes in EDLC-type SCs and store charges in the electrolyte via the surface of the electrode material to produce an electrical double-layer structure and no chemical reaction takes place during charging and discharging (Jiang and Liu, 2019).

In battery-grade materials, the energy is collected at the active surfaces of electrodes, where reversible, rapid redox reactions occur, and the electrode materials are made up of conducting polymers and a wide range of transition metal complexes. The supercapattery, which combines two storage methods in one device, is created by using one electrode from each technology.(Faisal *et al.*, 2021, Iqbal *et al.*, 2020a). Supercapattery has attracted a lot of interest due to its special abilities to produce high specific power from the supercapacitor side and high specific energy from the counterpart. This technology has a specific power and specific energy than batteries, a longer cycle life, and is more stable. (Faisal *et al.*, 2021).

Generally, MOFs, metal oxides and conductive polymers are suitable materials for electrodes because of their exclusive redox-active (Calbo *et al.*, 2019) properties and available oxidation state (Athouël *et al.*, 2008). These interesting features lead us to favourably choose Mn as the metal centre for this synthesis work. In essence, the position of Mn as a transition metal in the periodic table with five unpaired electrons leads to the

most oxidation states including the highest oxidation state +7 in the whole periodic table (Muñoz-Páez, 1994). This novel property of Mn makes it significantly redox-active which could achieve superior electrochemical performance, especially in faradic redox reactions of electrochemical energy storage devices. For instance, manganese oxide-based electrode materials have been intensely studied on their electrochemical performance due to Mn has of the most noteworthy number of different oxides, most of which have unique tunnel structures that empowers bulk redox reactions (Hu *et al.*, 2018). Interestingly, the five stable oxidation states of Mn provide plenty of chances for redox reactions including the ion exchange between the manganese oxide and electrolytes (Wang *et al.*, 2012). According to the standard calculation method (Mathieu Toupin, 2004), the manganese oxide (MnO₂) showed a high theoretical capacitance of 1370 F/g within a wider potential window of 1 V (Zhi *et al.*, 2013). These evidently support that manganese-based electrodes are promising in electrochemical applications namely in supercapacitors.

Thus, attracted by these extraordinary features of manganese and 1,2,4-triazole. Herein, we report the synthesis of novel Mn-1,2,4-triazole frameworks, crystal structures and their electrochemical behaviour in conventional three-electrode configuration and supercapattery device assembly. To the best of our knowledge, this will be the first Mn-MOFs derived from 1,2,4-triazole tested for electrochemical studies namely supercapattery.

1.3 Research Objectives

The overall goals of this research are to synthesise and structurally characterise new manganese-based metal-organic frameworks (MOFs) with 1,2,4-triazole linker and study their supercapattery performance. The following are the research's specific objectives:

1. To synthesise and characterise new Mn-MOFs containing 1,2,4-triazole linker using physicochemical, computational analysis and spectroscopic techniques namely, single crystal X-ray Diffraction (SCXRD) analysis, powder X-ray diffraction (PXRD) analysis, thermogravimetric analysis (TGA) field emission scanning electron microscopy (FESEM), X-ray photoelectron spectroscopy (XPS) and N₂ physisorption analysis.
2. To evaluate the electrochemical performance of new Mn-MOFs in three-electrode configuration and supercapattery device assembly.
3. To compare the electrochemical performance of newly synthesised Mn-MOFs with the aid of density functional theory (DFT) calculations and BET surface area.

1.4 Research Scopes

The scope of this study is divided into several sections; the first section focuses on the synthesis of new Mn-MOFs with 1,2,4-triazole linkers. Numerous parameters were investigated to optimise the synthesis conditions and obtain the high-quality crystals.. These parameters included the metal-ligand molar ratio, the reaction temperature, the duration of the reaction, and the type and volume of the reaction solvents. The compounds were then characterised using powder X-ray diffraction (PXRD) to determine the crystal lattice.

Thermogravimetric analysis (TGA) was used to determine the compound's thermal stability, while field emission scanning electron microscopy (FESEM) was used to study the morphology of the synthesised MOFs. Finally, the Mn-MOFs' surface area and pore volume were determined using N₂ physisorption analysis.

The second section is concerned with the elucidation and structural investigation of the new Mn-MOFs. One such non-destructive analytical technique, known as single crystal X-ray diffraction (SCXRD), was used to obtain detailed information on crystalline substances' internal lattice, including unit cell dimensions and lengths of bonds, bond angles and the details of site-ordering in each crystal. The single crystal refinement data generated by X-ray analysis was interpreted and solved using OLEX2 crystallographic software to obtain the crystal structure. The hydrogen atoms were refined using independent and constrained refinement techniques. Due to their disordered distribution in the structures' voids, it was impossible to refine the lattice solvent molecules; therefore, the electron density at the voids was subtracted from the reflection data using the SQUEEZE procedure, which was implemented in the PLATON software package. Then, to examine the structural characteristics of the newly synthesised Mn-MOFs concerning their network structure (net) topology the TOPOS 4.0 Professional Software were used. Identifying the bridging nodes between ligands and metals was necessary to determine the simplified net topology, which would provide a better understanding of the structural features of the complicated structures. The MOFs were then utilised as electrodes to study their electrochemical behaviour in a conventional three-electrode configuration. Finally, the novel Mn-MOFs were assembled into supercapattery devices to evaluate their supercapattery performance. There were several limitations on this research particularly to obtain good quality crystals for the Mn-MOFs which are suitable for SCXRD analysis, sometimes it was influenced by the humidity of environment which limits the formation of crystals.

1.5 Research hypothesis

A few hypotheses have been made:

1. The conventional solvothermal route can minimise solubility problems of organic linkers namely 1,2,4-triazole and is able to generate larger Mn-MOF crystals which are suitable for SCXRD analysis.
2. Incorporating anions such as F⁻, Cl⁻, Br⁻, I⁻, NO₃⁻ and SO₄²⁻ during the synthesis of Mn-MOFs can provide an interesting architecture of frameworks and anticipated to improve the electrochemical performance by encouraging charge accumulation and electron transfer between manganese and electrolytes.
3. As battery-type electrodes, Mn-MOFs can be used to assemble supercapattery devices, which are anticipated to have a promising electrochemical performance because Mn can provide some opportunities for redox reactions due to its five stable oxidation states.

1.6 Organisation of thesis

This thesis consists of five chapters and the chapters are organised as follows. Chapter 1 of this research describes the introduction of this research which contains the background of the research, problem statement, objectives and scope of the study. Chapter 2 comprises of design and synthesis of MOFs, crucial aspects of MOFs, the chemistry of 1,2,4-triazoles and the utilisation of MOFs in electrochemical studies were described. The materials and experimental procedures for Mn-MOFs synthesis and electrochemical studies are elaborated in Chapter 3. Chapter 4 demonstrates the facile synthesis, structural elucidation, and electrochemical performances of three novel Mn-MOFs namely UPMOF-4, UPMOF-5 and UPMOF-6 as electrodes in supercapattery device assembly. Finally, the conclusion and recommendations for future works are described in Chapter 5.

REFERENCES

- Akhbari, K. and Morsali, A. (2011) Effect of the guest solvent molecules on preparation of different morphologies of ZnO nanomaterials from the $[Zn_2(1,4\text{-bdc})_2(\text{dabco})]$ metal-organic framework. *Journal of Coordination Chemistry*. 64. 3521-3530.
- Akinwolemiwa, B., Peng, C. and Chen, G. Z. (2015) Redox electrolytes in supercapacitors. *Journal of The Electrochemical Society*. 162. A5054-A5059.
- Allen, G. C. and Tucker, P. M. (1976) Satellite Phenomena in X-ray photoelectron spectra of actinide compounds. *Chemical Physics Letters*. 43. 254-257.
- Allendorf, M. D., Schwartzberg, A., Stavila, V. and Talin, A. A. (2011) A roadmap to implementing metal-organic frameworks in electronic devices: Challenges and critical directions. *Chemistry - A European Journal*. 17. 11372-11388.
- Ameloot, R., Stappers, L., Fransaer, J., Alaerts, L., Sels, B. F. and De Vos, D. E. (2009) Patterned growth of metal-organic framework coatings by electrochemical synthesis. *Chemistry of Materials*. 21. 2580-2582.
- An, H., Li, Y., Long, P., Gao, Y., Qin, C., Cao, C., Feng, Y. and Feng, W. (2016) Hydrothermal preparation of fluorinated graphene hydrogel for high-performance supercapacitors. *Journal of Power Sources*. 312. 146-155.
- Aromí, G., Barrios, L. A., Roubeau, O. and Gamez, P. (2011) Triazoles and tetrazoles: Prime ligands to generate remarkable coordination materials. *Coordination Chemistry Reviews*. 255. 485-546.
- Athouël, L., Moser, F., Dugas, R., Crosnier, O., Bélanger, D. and Brousse, T. (2008) Variation of the MnO_2 birnessite structure upon charge/discharge in an electrochemical supercapacitor electrode in aqueous Na_2SO_4 electrolyte. *Journal of Physical Chemistry C*. 112. 7270-7277.
- Augustyn, V., Simon, P. and Dunn, B. (2014) Pseudocapacitive oxide materials for high-rate electrochemical energy storage. *Energy & Environmental Science*. 7.
- Bai, S. Q., Young, D. J. and Hor, T. S. A. (2011) Nitrogen-rich azoles as ligand spacers in coordination polymers. *Chemistry - An Asian Journal*. 6. 292-304.
- Baltrusaitis, J., Jayaweera, P. M. and Grassian, V. H. (2009) XPS study of nitrogen dioxide adsorption on metal oxide particle surfaces under different environmental conditions. *Phys Chem Chem Phys*. 11. 8295-305.
- Barpanda, P., Fanchini, G. and Amatucci, G. G. (2011) Structure, surface morphology and electrochemical properties of brominated activated carbons. *Carbon*. 49. 2538-2548.

- Barsukova, M. O., Samsonenko, D. G., Sapianik, A. A., Sapchenko, S. A. and Fedin, V. P. (2018) Influence of synthetic conditions on the formation of thermally and hydrolytically stable Sc-based metal–organic frameworks. *Polyhedron*. 144. 219-224.
- Behera, J. N., D'alessandro, D. M., Soheilnia, N. and Long, J. R. (2009) Synthesis and characterization of ruthenium and iron-ruthenium prussian blue analogues. *Chemistry of Materials*. 21. 1922-1926.
- Bhattacharjee, S., Chen, C. and Ahn, W. S. (2014) Chromium terephthalate metal-organic framework MIL-101: Synthesis, functionalization, and applications for adsorption and catalysis. *RSC Advances*. 4. 52500-52525.
- Bo, Q. B., Pang, J. J., Wang, H. Y., Fan, C. H. and Zhang, Z. W. (2015) Hydrothermal synthesis, characterization and photoluminescent properties of the microporous metal organic frameworks with 1,3-propanediaminetetraacetate ligand and its auxiliary ligand. *Inorganica Chimica Acta*. 428. 170-175.
- Bosch, M., Yuan, S., Rutledge, W. and Zhou, H. C. (2017) Stepwise Synthesis of Metal-Organic Frameworks. *Accounts of Chemical Research*. 50. 857-865.
- Bosch, M., Zhang, M. and Zhou, H.-C. (2014) Increasing the stability of metal-organic frameworks. *Advances in Chemistry*. 2014. 1-8.
- Bureekaew, S., Shimomura, S. and Kitagawa, S. (2008) Chemistry and application of flexible porous coordination polymers. *Sci Technol Adv Mater*. 9. 014108.
- Butova, V. V., Soldatov, M. A., Guda, A. A., Lomachenko, K. A. and Lamberti, C. (2016) Metal-organic frameworks: structure, properties, methods of synthesis and characterization. *Russian Chemical Reviews*. 85. 280-307.
- Calbo, J., Golomb, M. J. and Walsh, A. (2019) Redox-active metal–organic frameworks for energy conversion and storage. *Journal of Materials Chemistry A*. 7. 16571-16597.
- Cameron F. Holder, R. E. S. (2019) Tutorial on powder X-ray diffraction for characterizing nanoscale. *ACS Nano*. 7359-7365.
- Cao, W., Liu, Y., Xu, F., Li, J., Li, D., Du, G. and Chen, N. (2020) In Situ Electrochemical Synthesis of Rod-Like Ni-MOFs as Battery-Type Electrode for High Performance Hybrid Supercapacitor. *Journal of The Electrochemical Society*. 167. 050503-050503.
- Che, W., Wei, M., Sang, Z., Ou, Y., Liu, Y. and Liu, J. (2018) Perovskite $\text{LaNiO}_{3-\delta}$ oxide as an anion-intercalated pseudocapacitor electrode. *Journal of Alloys and Compounds*. 731. 381-388.
- Chen, D., Zhao, J., Zhang, P. and Dai, S. (2019a) Mechanochemical synthesis of metal–organic frameworks. *Polyhedron*. 162. 59-64.

- Chen, G. Z. (2016) Supercapacitor and supercapattery as emerging electrochemical energy stores. *International Materials Reviews*. 62. 173-202.
- Chen, H., Zhou, J., Li, Q., Tao, K., Yu, X., Zhao, S., Hu, Y., Zhao, W. and Han, L. (2019b) Core-shell assembly of Co₃O₄@NiO-ZnO nanoarrays as battery-type electrodes for high-performance supercapatteries. *Inorganic Chemistry Frontiers*. 6. 2481-2487.
- Chen, L., Xu, Z., Li, J., Zhou, B., Shan, M., Li, Y., Liu, L., Li, B. and Niu, J. (2014) Modifying graphite oxide nanostructures in various media by high-energy irradiation. *RSC Adv*. 4. 1025-1031.
- Chen, W. and Wu, C. (2018) Synthesis, functionalization, and applications of metal-organic frameworks in biomedicine. *Dalton Transactions*. 47. 2114-2133.
- Colin Mckinstry , E. J. C., Ashleigh J. Fletcher , Siddharth V. Patwardhan , and Jan Sefcik (2013) Effect of Synthesis Conditions on Formation Pathways of Metal Organic Framework (MOF-5) Crystals. *Crystal Growth & Design*. 12. 5481-5486.
- D. W. Engelfriet, W. D. B., G. C. Verschoor and S. Gorter (1979) first report 1,2,4-Triazole Complexes.pdf. *international union of crystallography*. B35. 2922-2927.
- De Oliveira, C. a. F., Da Silva, F. F., Malvestiti, I., Malta, V. R. D. S., Dutra, J. D. L., Da Costa, N. B., Freire, R. O. and Júnior, S. A. (2013) Effect of temperature on formation of two new lanthanide metal-organic frameworks: Synthesis, characterization and theoretical studies of Tm(III)-succinate. *Journal of Solid State Chemistry*. 197. 7-13.
- Devic, T. and Serre, C. (2014) High valence 3p and transition metal based MOFs. *Chemical Society Reviews*. 43. 6097-6115.
- Faisal, M. M., Ali, S. R., K.C, S., Iqbal, M. W., Iqbal, M. Z. and Saeed, A. (2021) Highly porous terpolymer-MOF composite electrode material for high performance supercapattery devices. *Journal of Electroanalytical Chemistry*. 893. 115321.
- Fischer, J., González-Martín, J., Lochyński, P., Dejmková, H., Schwarzová-Pecková, K. and Vega, M. (2020) Voltammetric study of triazole antifungal agent terconazole on sp³ and sp² carbon-based electrode materials. *Journal of Electroanalytical Chemistry*. 863.
- Frisch, A. J. W., USA, 25p (2009) gaussian 09W Reference. 470.
- Furukawa, H., Cordova, K. E., O'keeffe, M. and Yaghi, O. M. (2013) The chemistry and applications of metal-organic frameworks. *Science*. 341. 1230444.

- Gangu, K. K., Maddila, S., Mukkamala, S. B. and Jonnalagadda, S. B. (2016) A review on contemporary metal-organic framework materials. *Inorganica Chimica Acta*. 446. 61-74.
- Gao, N., Zheng, W. T. and Jiang, Q. (2012) Density functional theory calculations for two-dimensional silicene with halogen functionalization. *Phys Chem Chem Phys*. 14. 257-61.
- Gao, Y., Zhi, C., Cui, P., Zhang, K. a. I., Lv, L. P. and Wang, Y. (2020) Halogen-functionalized triazine-based organic frameworks towards high performance supercapacitors. *Chemical Engineering Journal*. 400. 125967-125967.
- Gonzalez-Nelson, A., Coudert, F. X. and Van Der Veen, M. A. (2019) Rotational dynamics of linkers in metal-organic frameworks. *Nanomaterials*. 9.
- Gu, W. and Yushin, G. (2014) Review of nanostructured carbon materials for electrochemical capacitor applications: advantages and limitations of activated carbon, carbide-derived carbon, zeolite-templated carbon, carbon aerogels, carbon nanotubes, onion-like carbon, and graphene. *Wiley Interdisciplinary Reviews: Energy and Environment*. 3. 424-473.
- Haque, E. and Jhung, S. H. (2011) Synthesis of isostructural metal-organic frameworks, CPO-27s, with ultrasound, microwave, and conventional heating: Effect of synthesis methods and metal ions. *Chemical Engineering Journal*. 173. 866-872.
- He, H., Wang, G., Shen, B., Wang, Y., Lu, Z., Guo, S., Zhang, J., Yang, L., Jiang, Q. and Xiao, Z. (2020) Three isostructural Zn/Ni nitro-containing metal-organic frameworks for supercapacitor. *Journal of Solid State Chemistry*. 288. 121375-121375.
- He, W., Zhao, G., Sun, P., Hou, P., Zhu, L., Wang, T., Li, L., Xu, X. and Zhai, T. (2019) Construction of Longan-like hybrid structures by anchoring nickel hydroxide on yolk-shell polypyrrole for asymmetric supercapacitors. *Nano Energy*. 56. 207-215.
- Hu, Y., Wu, Y. and Wang, J. (2018) Manganese-oxide-based electrode materials for energy storage applications: How close are we to the theoretical capacitance? *Advanced Materials*. 30. 1-21.
- Iqbal, J., Li, L., Numan, A., Rafique, S., Jafer, R., Mohamad, S., Khalid, M., Ramesh, K. and Ramesh, S. (2019) Density functional theory simulation of cobalt oxide aggregation and facile synthesis of a cobalt oxide, gold and multiwalled carbon nanotube based ternary composite for a high performance supercapattery. *New Journal of Chemistry*. 43. 13183-13195.
- Iqbal, M. Z., Faisal, M. M., Ali, S. R. and Alzaid, M. (2020a) A facile approach to investigate the charge storage mechanism of MOF/PANI based supercapattery devices. *Solid State Ionics*. 354. 115411.

- Iqbal, M. Z., Faisal, M. M., Ali, S. R., Farid, S. and Afzal, A. M. (2020b) Co-MOF/polyaniline-based electrode material for high performance supercapattery devices. *Electrochimica Acta*. 346. 136039.
- Jahan, M., Bao, Q., Yang, J. X. and Loh, K. P. (2010) Structure-directing role of graphene in the synthesis of metal-organic framework nanowire. *Journal of the American Chemical Society*. 132. 14487-14495.
- James, S. L. (2003) Metal-organic frameworks. *Chemical Society Reviews*. 32. 276-288.
- Jankovsky, O., Simek, P., Klimova, K., Sedmidubsky, D., Matejkova, S., Pumera, M. and Sofer, Z. (2014) Towards graphene bromide: bromination of graphite oxide. *Nanoscale*. 6. 6065-74.
- Jasmina Hafizovic Cavka, S. J., Unni Olsbye, Nathalie Guillou, Carlo Lamberti, Silvia Bordiga, and Karl Petter Lilleru (2008) A New Zirconium Inorganic Building Brick Forming Metal Organic Frameworks with Exceptional Stability. *J Am Chem Soc*. 130. 13850-13851.
- Jensen, F. (2010) Describing Anions by Density Functional Theory: Fractional Electron Affinity. *Journal of Chemical Theory and Computation*. 6. 2726-2735.
- Jiang, Y. and Liu, J. (2019) Definitions of pseudocapacitive materials: A brief review. *Energy & Environmental Materials*. 2. 30-37.
- Kannangara, Y. Y., Rathnayake, U. A. and Song, J.-K. (2019) Hybrid supercapacitors based on metal organic frameworks using p-phenylenediamine building block. *Chemical Engineering Journal*. 361. 1235-1244.
- Karozis, S., Charalambopoulou, G., Steriotis, T., Stubos, A. and Kainourgiakis, M. (2017) Determining the specific surface area of Metal Organic Frameworks based on a computational approach. *Colloids and Surfaces A: Physicochemical and Engineering Aspects*. 526. 14-19.
- Kim, J., Yang, S. T., Choi, S. B., Sim, J., Kim, J. and Ahn, W. S. (2011) Control of catenation in CuTATB-n metal-organic frameworks by sonochemical synthesis and its effect on CO₂ adsorption. *Journal of Materials Chemistry*. 21. 3070-3076.
- Kim, M.-H., Yang, J.-H., Kang, Y.-M., Park, S.-M., Han, J. T., Kim, K.-B. and Roh, K. C. (2014) Fluorinated activated carbon with superb kinetics for the supercapacitor application in nonaqueous electrolyte. *Colloids and Surfaces A: Physicochemical and Engineering Aspects*. 443. 535-539.
- Kitagawa, S., Kitaura, R. and Noro, S. (2004) Functional porous coordination polymers. *Angew Chem Int Ed Engl*. 43. 2334-75.

- Kuaibing Wang, Z. W., Xin Wang, Xueqin Zhou, Yuehong Tao and Hua Wu (2018) Flexible long-chain-linker constructed Ni-based metal-organic frameworks with 1D helical channel and their pseudo-capacitor behavior studies. *Journal of Power Sources*. 377. 44-51.
- Lee, Y. R., Kim, J. and Ahn, W. S. (2013) Synthesis of metal-organic frameworks: A mini review. *Korean Journal of Chemical Engineering*. 30. 1667-1680.
- Li, G., Cai, H., Li, X., Zhang, J., Zhang, D., Yang, Y. and Xiong, J. (2019a) Construction of Hierarchical NiCo₂O₄@Ni-MOF Hybrid Arrays on Carbon Cloth as Superior Battery-Type Electrodes for Flexible Solid-State Hybrid Supercapacitors. *ACS Appl Mater Interfaces*. 11. 37675-37684.
- Li, L., Wang, S., Chen, T., Sun, Z., Luo, J. and Hong, M. (2012) Solvent-Dependent Formation of Cd(II) Coordination Polymers Based on a C₂-Symmetric Tricarboxylate Linker. *Crystal Growth & Design*. 12. 4109-4115.
- Li, N., Xu, J., Feng, R., Hu, T. L. and Bu, X. H. (2016) Governing metal-organic frameworks towards high stability. *Chemical Communications*. 52. 8501-8513.
- Li, Q., Yu, M. H., Xu, J., Li, A. L., Hu, T. L. and Bu, X. H. (2017) Two new metal-organic frameworks based on tetrazole-heterocyclic ligands accompanied by in situ ligand formation. *Dalton Transactions*. 46. 3223-3228.
- Li, Q., Zhou, J., Liu, R. and Han, L. (2019b) An amino-functionalized metal-organic framework nanosheet array as a battery-type electrode for an advanced supercapattery. *Dalton Trans*. 48. 17163-17168.
- Li, S., Huang, W., Yang, Y., Ulstrup, J., Ci, L., Zhang, J., Lou, J. and Si, P. (2018) Hierarchical layer-by-layer porous FeCo₂S₄@Ni(OH)₂ arrays for all-solid-state asymmetric supercapacitors. *Journal of Materials Chemistry A*. 6. 20480-20490.
- Liping Zhang, A. a. S. G., Mietek Jaroniec (2020) Identification of preferentially exposed crystal facets by X-ray diffraction. *RSC Advances*. 5585-5589.
- Liu, H., Guo, H., Yao, W., Zhang, L., Wang, M., Fan, T., Yang, W. and Yang, W. (2020) Spear-shaped Mn/Ni bimetallic hydroxide derived from metal-organic frameworks as electrode materials for aqueous and all-solid-state hybrid supercapacitors. *Colloids and Surfaces A: Physicochemical and Engineering Aspects*. 601. 125011-125011.
- Liu, Y., Qi, Y., Su, Y.-H., Zhao, F.-H., Che, Y.-X. and Zheng, J.-M. (2010) Five novel cobalt coordination polymers: effect of metal–ligand ratio and structure characteristics of flexible bis(imidazole) ligands. *CrystEngComm*. 12.
- Lu, C., Ben, T., Xu, S. and Qiu, S. (2014) Electrochemical synthesis of a microporous conductive polymer based on a metal-organic framework thin film. *Angewandte Chemie - International Edition*. 53. 6454-6458.

- M. R. Atkinson, J. B. P. (1952) Einhorn–Brunner reaction to synthesis triazole. *journal of chemical society*. 11. 3418-3422.
- M. V, V. and Nageswaran, G. (2020) Review—Direct Electrochemical Synthesis of Metal Organic Frameworks. *Journal of The Electrochemical Society*. 167.
- Ma, X., Wei, X., Wei, Z., Guo, Y., Wang, W., Zhang, C. and Jiang, Z.-Y. (2021) Metal-organic frameworks based on Schiff base condensation reaction as battery-type electrodes for supercapattery. *Electrochimica Acta*. 385. 138434.
- Makino, S., Shinohara, Y., Ban, T., Shimizu, W., Takahashi, K., Imanishi, N. and Sugimoto, W. (2012) 4 V class aqueous hybrid electrochemical capacitor with battery-like capacity. *RSC Advances*. 2. 12144-12147.
- Mariappan, V. K., Krishnamoorthy, K., Pazhamalai, P., Sahoo, S. and Kim, S. J. (2019) Carbyne-enriched carbon anchored on nickel foam: a novel binder-free electrode for supercapacitor application. *Journal of Colloid and Interface Science*. 556. 411-419.
- Martin, R. L., Kowalczyk, S. P. and Shirley, D. A. (1978) The relation between satellite peaks in x-ray emission and x-ray photoemission spectra. *The Journal of Chemical Physics*. 68. 3829-3836.
- Matern, J., Baumer, N. and Fernandez, G. (2021) Unraveling Halogen Effects in Supramolecular Polymerization. *J Am Chem Soc*. 143. 7164-7175.
- Mathieu Toupin, T. B., And Daniel Bélanger (2004) Charge Storage Mechanism of MnO₂ Electrode Used in Aqueous Electrochemical Capacitor.pdf. *chemistry of Materials*. 16. 3184-3190.
- Mohamed Eddaoudi, D. B. M., Hailian Li,† Banglin Chen, Theresa M. Reineke, Michael O'keeffe, and Omar M. Yaghi (2001) Modular Chemistry Secondary Building Units as a Basis for the Design of Highly Porous and Robust Metal–Organic Carboxylate Frameworks. *Accounts of Chemical Research*. 34. 319-330.
- Mohanadas, D., Mohd Abdah, M. a. A., Azman, N. H. N., Ravooof, T. B. S. A. and Sulaiman, Y. (2021) Facile synthesis of PEDOT-rGO/HKUST-1 for high performance symmetrical supercapacitor device. *Scientific Reports*. 11. 11747.
- Morosin, B. (1967) Crystal Structure of Manganese (II) and Cobalt (II) Bromide Dihydrate. *The Journal of Chemical Physics*. 47. 417-420.
- Morozan, A. and Jaouen, F. (2012) Metal organic frameworks for electrochemical applications. *Energy and Environmental Science*. 5. 9269-9290.
- Müller-Buschbaum, K. and Mokaddem, Y. (2006) Three-dimensional networks of lanthanide 1,2,4-triazolates: $\infty^3[\text{Yb}(\text{Tz})_3]$ and $\infty^3[\text{Eu}_2(\text{Tz})_5(\text{TzH})_2]$, the first 4f networks with complete nitrogen coordination. *Chemical Communications*. 2060-2062.

- Muñoz-Páez, A. (1994) Transition metal oxides: Geometric and electronic structures - introducing solid state topics in inorganic chemistry courses. *Journal of Chemical Education*. 71. 381-387.
- Nasri, S., Bayat, M. and Kochia, K. (2021) Strategies for synthesis of 1,2,4-triazole-containing scaffolds using 3-amino-1,2,4-triazole. *Mol Divers*.
- Norková, R., Dyrtrtová, J. J., Jakl, M. and Schröder, D. (2011) Formation of tebuconazole complexes with cadmium(II) investigated by electrospray ionization mass spectrometry. *Water, Air, & Soil Pollution*. 223. 2633-2640.
- Numan, A., Zhan, Y., Khalid, M. and Hatamvand, M. (2021) Introduction to supercapattery. *Advances in Supercapacitor and Supercapattery*.
- Ouellette, W., Yu, M. H., O'connor, C. J., Hagrman, D. and Zubieta, J. (2006) Hydrothermal chemistry of the copper-triazolate system: A microporous metal-organic framework constructed from magnetic $\{\text{Cu}_3(\mu_3\text{-OH})(\text{triazolate})_3\}^{2+}$ building blocks, and related materials. *Angew Chem Int Ed Engl*. 45. 3497-500.
- Perry, J. J., Perman, J. A. and Zaworotko, M. J. (2009) Design and synthesis of metal-organic frameworks using metal-organic polyhedra as supermolecular building blocks. *Chemical Society Reviews*. 38. 1400-1417.
- Pichon, A. and James, S. L. (2008) An array-based study of reactivity under solvent-free mechanochemical conditions - Insights and trends. *CrystEngComm*. 10. 1839-1847.
- Pichon, A., Lazuen-Garay, A. and James, S. L. (2006) Solvent-free synthesis of a microporous metal-organic framework. *CrystEngComm*. 8. 211-214.
- Qiu, L. G., Li, Z. Q., Wu, Y., Wang, W., Xu, T. and Jiang, X. (2008) Facile synthesis of nanocrystals of a microporous metal-organic framework by an ultrasonic method and selective sensing of organoamines. *Chemical Communications*. 3642-3644.
- Rui-Bo Zhang, Z.-J. L., Ye-Yan Qin, Jian-Kai Cheng, Jian Zhang, and Yuan-Gen Yao (2008) Synthesis, Structure, and Physical Properties of a New Anions-Controlled Cd(II)-Guanazole (3,5-Diamino-1,2,4-triazole) Hybrid Family. *Inorganic Chemistry*. 47. 4861-4876.
- S.A.Lawrence (2004) Amines: Synthesis Properties and Applications. *Cambridge University Press*.
- Saha, D., Maity, T. and Koner, S. (2014) Alkaline earth metal-based metal-organic framework: Hydrothermal synthesis, X-ray structure and heterogeneously catalyzed Claisen-Schmidt reaction. *Dalton Transactions*. 43. 13006-13017.

- Seetharaj, R., Vandana, P. V., Arya, P. and Mathew, S. (2019) Dependence of solvents, pH, molar ratio and temperature in tuning metal organic framework architecture. *Arabian Journal of Chemistry*. 12. 295-315.
- Seo, Y., Shinde, P. A., Park, S. and Chan Jun, S. (2020) Self-assembled bimetallic cobalt–manganese metal–organic framework as a highly efficient, robust electrode for asymmetric supercapacitors. *Electrochimica Acta*. 335. 135327-135327.
- Shao, H., Lin, Z., Xu, K., Taberna, P.-L. and Simon, P. (2019) Electrochemical study of pseudocapacitive behavior of $\text{Ti}_3\text{C}_2\text{T}_x$ MXene material in aqueous electrolytes. *Energy Storage Materials*. 18. 456-461.
- Sharanyakanth, P. S. and Radhakrishnan, M. (2020) Synthesis of metal-organic frameworks (MOFs) and its application in food packaging: A critical review. *Trends in Food Science & Technology*. 104. 102-116.
- Shashank Sundriyal, S. M., Akash Deep (2019) Study of Manganese-1,4-Benzenedicarboxylate Metal Organic Framework Electrodes Based Solid State Symmetrical Supercapacitor. *Energy Procedia*. 158. 5817-5824.
- Shinde, P. A., Seo, Y., Lee, S., Kim, H., Pham, Q. N., Won, Y. and Chan Jun, S. (2020) Layered manganese metal-organic framework with high specific and areal capacitance for hybrid supercapacitors. *Chemical Engineering Journal*. 387. 122982-122982.
- Skoda, D., Kazda, T., Munster, L., Hanulikova, B., Styskalik, A., Eloy, P., Debecker, D. P., Vyroubal, P., Simonikova, L. and Kuritka, I. (2019) Microwave-assisted synthesis of a manganese metal–organic framework and its transformation to porous MnO/carbon nanocomposite utilized as a shuttle suppressing layer in lithium–sulfur batteries. *Journal of Materials Science*. 54. 14102-14122.
- Soni, S., Bajpai, P. K. and Arora, C. (2018) A review on metal-organic framework: synthesis, properties and application. *Characterization and Application of Nanomaterials*. 2. 1-20.
- Stock, N. and Biswas, S. (2012) Synthesis of metal-organic frameworks (MOFs): routes to various MOF topologies, morphologies, and composites. *Chem Rev*. 112. 933-69.
- Sun, Y.-X. and Sun, W.-Y. (2014) Influence of temperature on metal-organic frameworks. *Chinese Chemical Letters*. 25. 823-828.
- Tanaka, S. (2020) Mechanochemical synthesis of MOFs. *Metal-Organic Frameworks for Biomedical Applications*.
- Tang, M. L. and Bao, Z. (2011) Halogenated Materials as Organic Semiconductors. *Chemistry of Materials*. 23. 446-455.

- Trivedi, M. K. and Tallapragada, R. M. (2015) Characterization of Physical, Spectral and Thermal Properties of Biofield Treated 1,2,4-Triazole. *Journal of Molecular Pharmaceutics & Organic Process Research*. 03.
- Wang, G., Zhang, L. and Zhang, J. (2012) A review of electrode materials for electrochemical supercapacitors. *Chemical Society Reviews*. 41. 797-828.
- Wang, K., Lv, B., Wang, Z., Wu, H., Xu, J. and Zhang, Q. (2020) Two-fold interpenetrated Mn-based metal-organic frameworks (MOFs) as battery-type electrode materials for charge storage. *Dalton Transactions*. 49. 411-417.
- Wang, X., Liu, X., Rong, H., Song, Y., Wen, H. and Liu, Q. (2017) Layered manganese-based metal-organic framework as a high capacity electrode material for supercapacitors. *RSC Advances*. 7. 29611-29617.
- Wayne Ouellette, A. V. P., Jamie Valeich, Kim R. Dunbar, and Jon Zubietta (2007) Hydrothermal Synthesis, Structural Chemistry, and Magnetic Properties of Materials of the M(II)/Triazololate/Anion Family, Where M(II) = Mn, Fe, and Ni. *Inorganic Chemistry*. 46. 9067-9082.
- Won, J., Kaewsuk, J., Jo, J., Lim, D.-H. and Seo, G. (2015) A Density Functional Theory Study on the Ozone Oxidation of Sulfonamide Antibiotics. *Journal of Advanced Oxidation Technologies*. 18.
- Xiong, X., Zhou, L., Cao, W., Liang, J., Wang, Y., Hu, S., Yu, F. and Li, B. (2017) Metal-organic frameworks based on halogen-bridged dinuclear-Cu-nodes as promising materials for high performance supercapacitor electrodes. *CrystEngComm*. 19. 7177-7184.
- Xu, B., Zhang, H., Mei, H. and Sun, D. (2020) Recent progress in metal-organic framework-based supercapacitor electrode materials. *Coordination Chemistry Reviews*. 420. 213438-213438.
- Xu, J., Yang, Y., Wang, Y., Cao, J. and Chen, Z. (2019) Enhanced electrochemical properties of manganese-based metal-organic framework materials for supercapacitors. *Journal of Applied Electrochemistry*. 49. 1091-1102.
- Yaghi, O. M. (2019) Reticular chemistry in all dimensions. *ACS Central Science*. 5. 1295-1300.
- Yakovenko, A. A., Wei, Z., Wriedt, M., Li, J. R., Halder, G. J. and Zhou, H. C. (2014) Study of guest molecules in metal-organic frameworks by powder X-ray diffraction: Analysis of difference envelope density. *Crystal Growth and Design*. 14. 5397-5407.
- Yan, A. L., Wang, X. C. and Cheng, J. P. (2018) Research Progress of NiMn Layered Double Hydroxides for Supercapacitors: A Review. *Nanomaterials (Basel)*. 8.
- Yang-I Lin, S. a. L., Jr., Maurice F. Lovell, and Nancy A. Perkinson (1979) Pellizzari reaction synthesis of triazoles. *J Am Chem Soc*. 44. 4161-4164.

- Yang, W., Shi, X., Li, Y. and Pang, H. (2019) Manganese-doped cobalt zeolitic imidazolate framework with highly enhanced performance for supercapacitor. *Journal of Energy Storage*. 26. 1-7.
- Yin, P. X., Zhang, J., Qin, Y. Y., Cheng, J. K., Li, Z. J. and Yao, Y. G. (2011) Role of molar-ratio, temperature and solvent on the Zn/Cd 1,2,4-triazolate system with novel topological architectures. *CrystEngComm*. 13. 3536-3544.
- Yuan, C., Li, J., Hou, L., Zhang, X., Shen, L. and Lou, X. W. D. (2012) Ultrathin Mesoporous NiCo₂O₄ Nanosheets Supported on Ni Foam as Advanced Electrodes for Supercapacitors. *Advanced Functional Materials*. 22. 4592-4597.
- Zhang, D., Han, X., Kong, X., Zhang, F. and Lei, X. (2020) The Principle of Introducing Halogen Ions Into β -FeOOH: Controlling Electronic Structure and Electrochemical Performance. *Nano-Micro Letters*. 12. 1-13.
- Zhang, J.-P., Zhang, Y.-B., Lin, J.-B. and Chen, X.-M. (2012) Metal azolate frameworks. 1001-1033.
- Zhang, W., Zhao, L., Li, H., Manasa, P. and Ran, F. (2021) Hydrated halide clusters on electrode materials for aqueous supercapacitor. *Journal of Power Sources*. 491.
- Zhang, X., Da Silva, I., Fazzi, R., Sheveleva, A. M., Han, X., Spencer, B. F., Sapchenko, S. A., Tuna, F., McInnes, E. J. L., Li, M., Yang, S. and Schröder, M. (2019) Iodine adsorption in a redox-active metal-organic framework: electrical conductivity induced by host-guest charge-transfer. *Inorganic Chemistry*. 58. 14145-14150.
- Zhang, Y., Lin, B., Sun, Y., Zhang, X., Yang, H. and Wang, J. (2015) Carbon nanotubes@metal-organic frameworks as Mn-based symmetrical supercapacitor electrodes for enhanced charge storage. *RSC Advances*. 5. 58100-58106.
- Zhang, Y. Z., Cheng, T., Wang, Y., Lai, W. Y., Pang, H. and Huang, W. (2016) A simple approach to boost capacitance: Flexible supercapacitors based on manganese oxides@MOFs via chemically induced in situ self-transformation. *Advanced Materials*. 28. 5242-5248.
- Zhao, N., Shi, Z., Chenitz, R., Girard, F. and Mokrini, A. (2020) Effects of 1, 2, 4-Triazole Additive on PEM Fuel Cell Conditioning. *Membranes (Basel)*. 10.
- Zhao, Z., Li, H., Zhao, K., Wang, L. and Gao, X. (2022) Microwave-assisted synthesis of MOFs: Rational design via numerical simulation. *Chemical Engineering Journal*. 428.
- Zheng, X., Han, X., Zhao, X., Qi, J., Ma, Q., Tao, K. and Han, L. (2018) Construction of Ni-Co-Mn layered double hydroxide nanoflakes assembled hollow

nanocages from bimetallic imidazolate frameworks for supercapacitors. *Materials Research Bulletin*. 106. 243-249.

Zhi, M., Xiang, C., Li, J., Li, M. and Wu, N. (2013) Nanostructured carbon-metal oxide composite electrodes for supercapacitors: A review. *Nanoscale*. 5. 72-88.

Zhou, E., Tian, L., Cheng, Z. and Fu, C. (2019) Design of NiO flakes@CoMoO₄ nanosheets core-shell architecture on Ni Foam for high-performance supercapacitors. *Nanoscale Res Lett*. 14. 221.

