Titanium-based Organic Frameworks for Chemical Transformations

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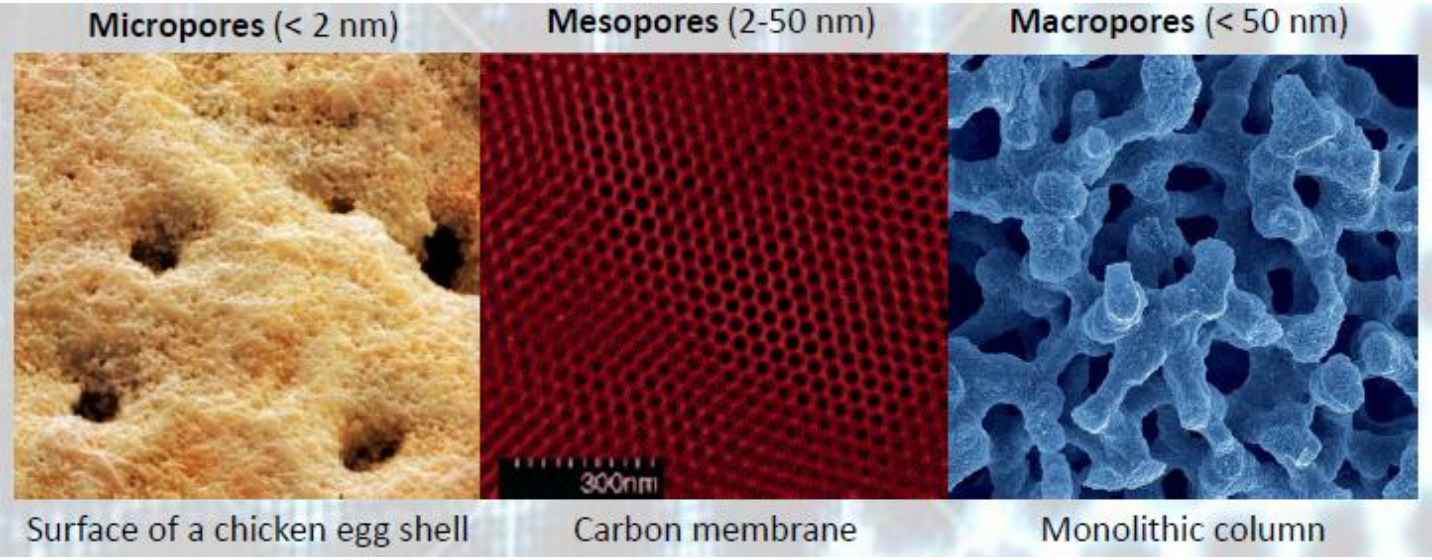
Pore type (Size)t



Microporous material

A microporous material is a material containing pores with diameters less than 2 nm:

1. **Activated Carbons**
2. **Zeolites**
3. **Metal-organic frameworks**
4. **Covalent organic frameworks**
5. **Microporous polymer**

Applications of Microporous Materials

Activated carbons

- Small size of their pores provides greater surface area.
- Can adsorb a large amount of gas directly onto their surface.
- Popular support for several metal catalysts (e.g., Pd & Pt)

Zeolites

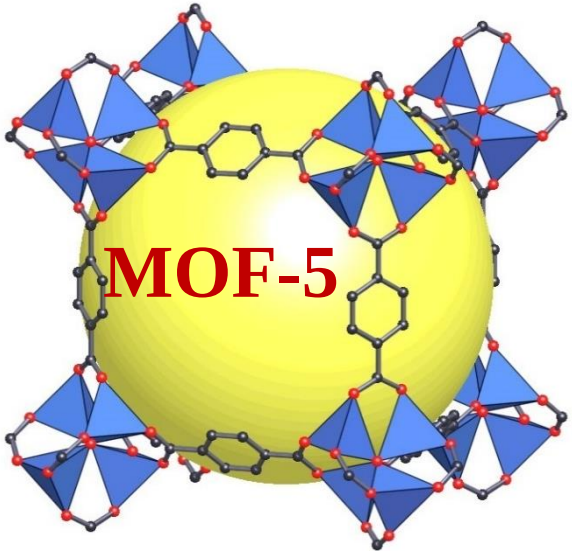
- Narrow size distribution of their pores makes them very useful for gas separation.
- Used as catalysts because of acid sites in the pores.

Metal organic frameworks

- Their huge surface area and pore volume makes them potentially useful for gas sequestration/storage.

Metal-Organic Frameworks (MOF)

- **MOFs are crystalline and porous materials.**
- **Consists of metal ions or clusters coordinated to often rigid organic molecules**

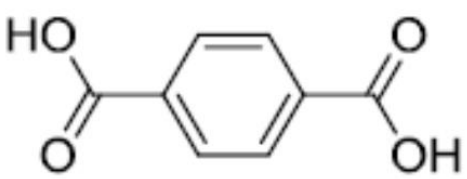


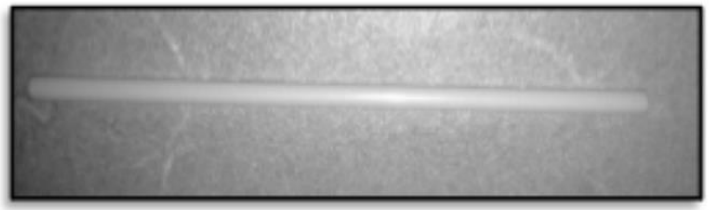
Inorganic-Organic Hybrid, ordered structure

- ***Synthetic materials***
- ***Also named coordination polymers***
- ***Materials without metals are termed COFs (Covalent Organic Frameworks)***
- ***Very active research area coordination polymers***

Zn_4O tetrahedra (blue) are joined by organic linkers (O, red, C, black)

MOF Construction

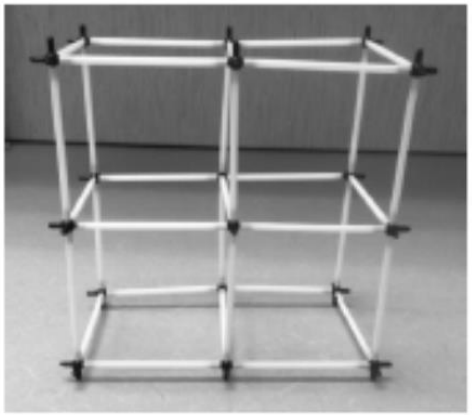




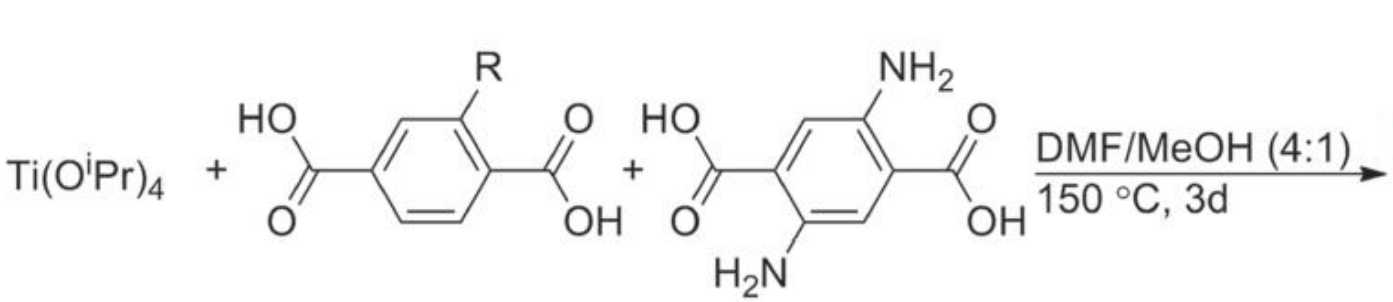
Organic Linkers

Mn^{2+}

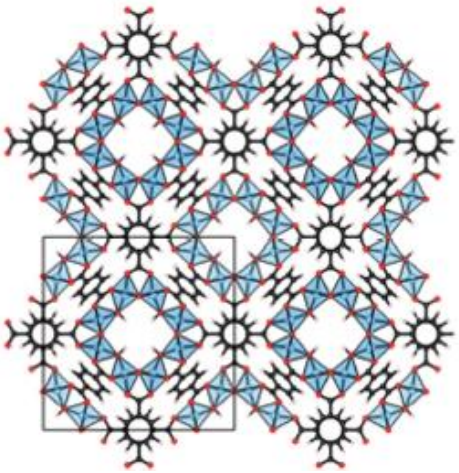
Metal Nodes



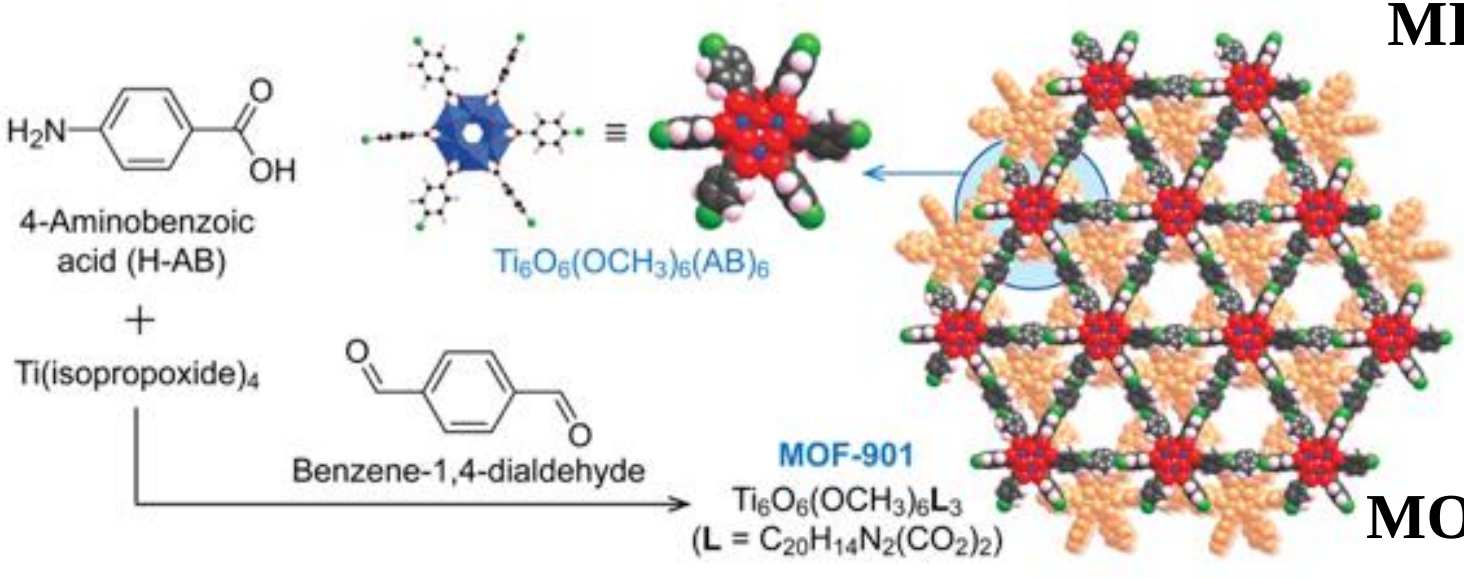
Titanium Based Organic Frameworks



x$_1$(BDC-R; R = H) : y(BDC-(NH$_2$)$_2$)
x$_2$(BDC-R; R = NH$_2$)



MIL-125

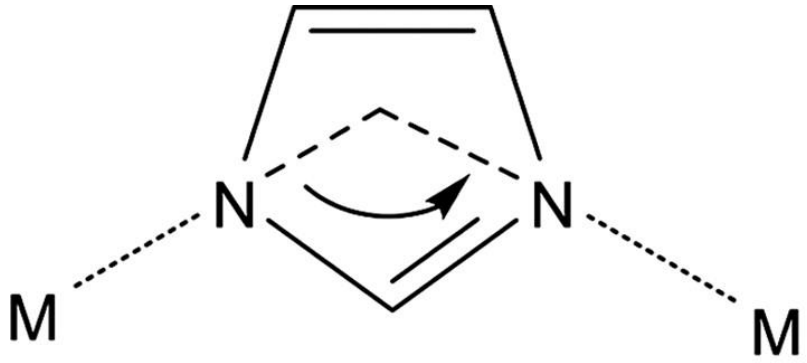


MOF-901

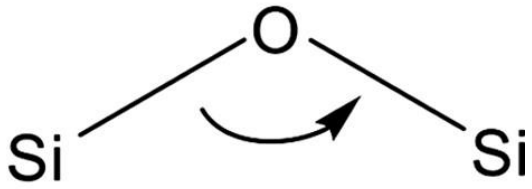
Energy Environ. Sci., 2015, *8*, 1923-1937
J. Am. Chem. Soc., 2016, *138*, 4330.

Zeolitic Imidazolate Framework (ZIF)

- ZIFs are a class of metal-organic frameworks
- ZIFs have zeolite-like topologies
- Tetrahedrally-coordinated transition metal ions (e.g., Fe, Co, Cu, Zn, etc.) are connected by imidazolate linkers
- Metal-imidazole-metal angle is similar to the 145° Si-O-Si angle in zeolites



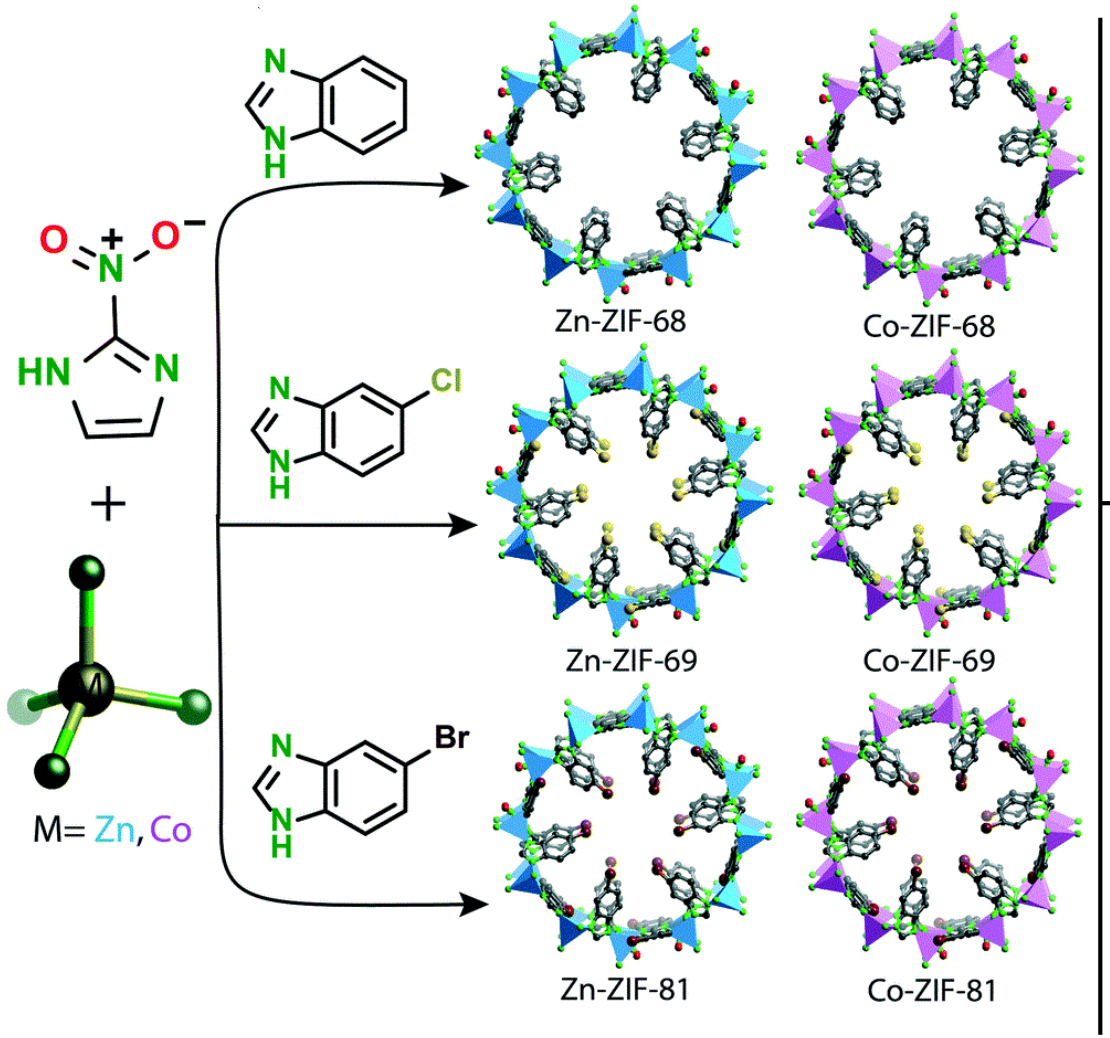
M - IM - M

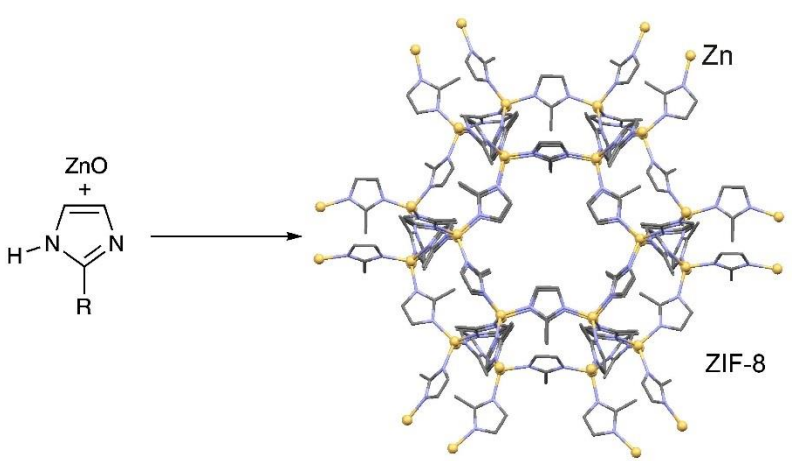


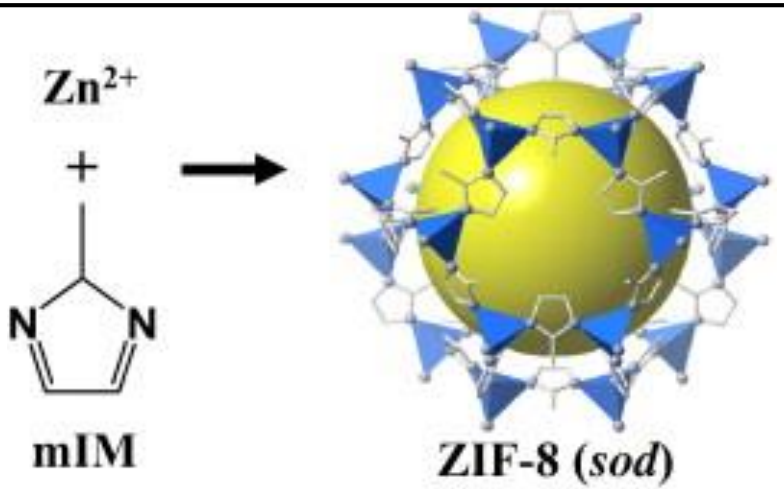
Si - O - Si

J. Mater. Chem. A, 2014, *2*, 16811-16831

Common Types of ZIFs





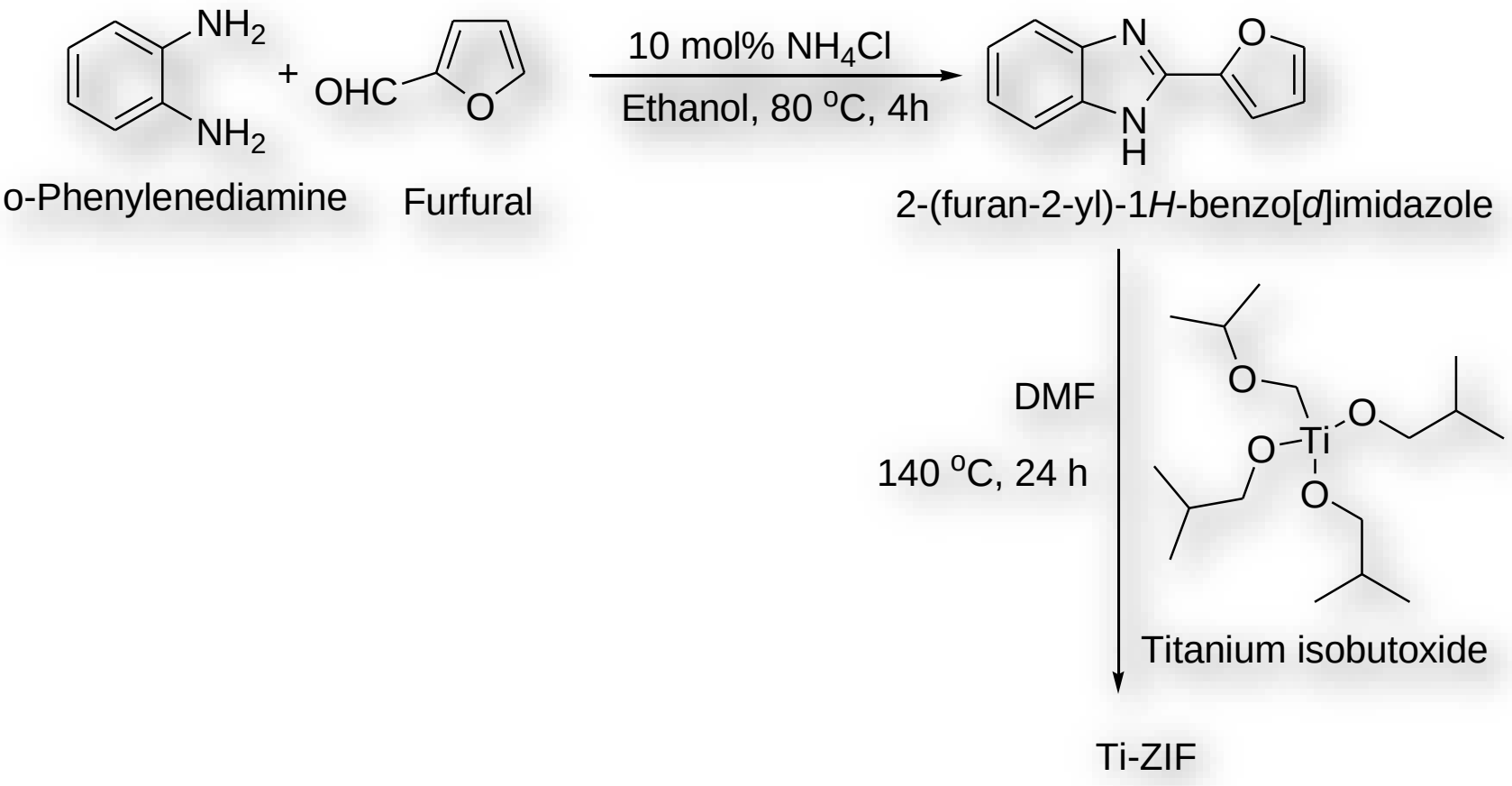


J. Mater. Chem. A, 2014, *2*, 16811-16831

CrystEngComm, 2014, *16*, 4677-4680

Titanium Based Zeolitic Imidazolate Framework for Chemical Fixation of Carbon Dioxide

Synthesis of Ti-ZIF



o-Phenylenediamine Furfural

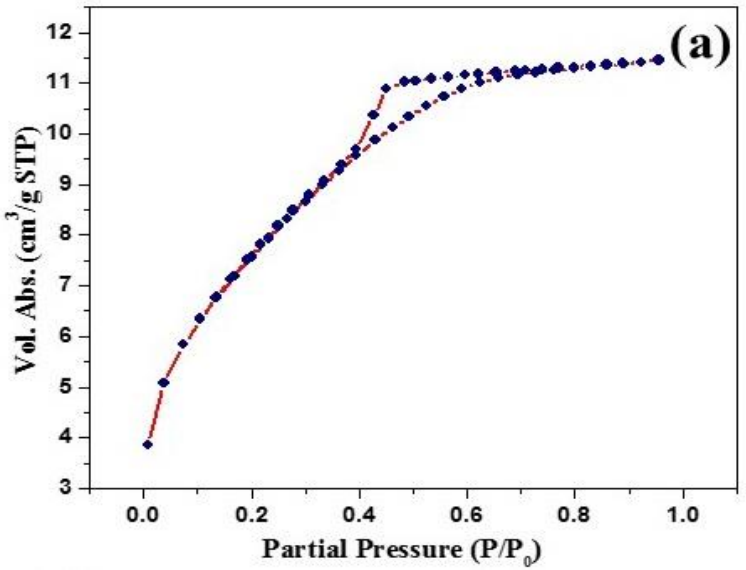
2-(furan-2-yl)-1*H*-benzo[*d*]imidazole

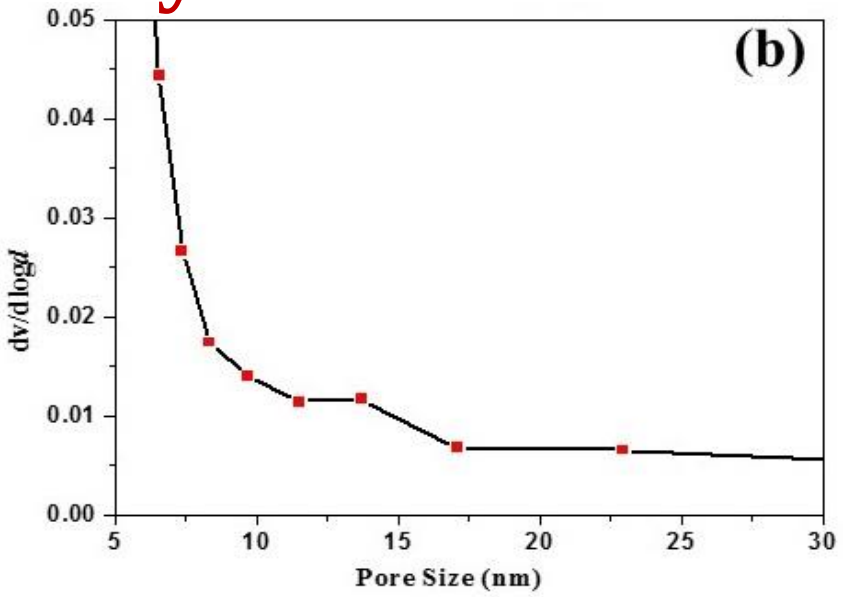
Titanium isobutoxide

Ti-ZIF

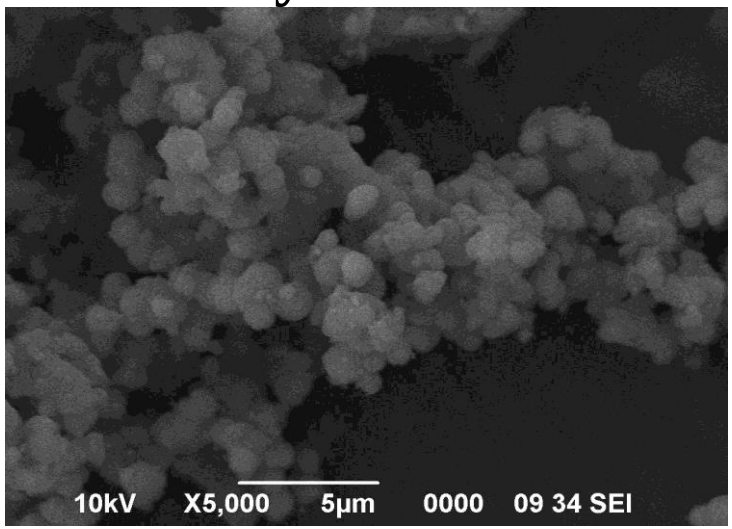
Varma *et al*. *Green Chem*., 2016, *18* , 4855-4858 (Cover Page)

BET analysis





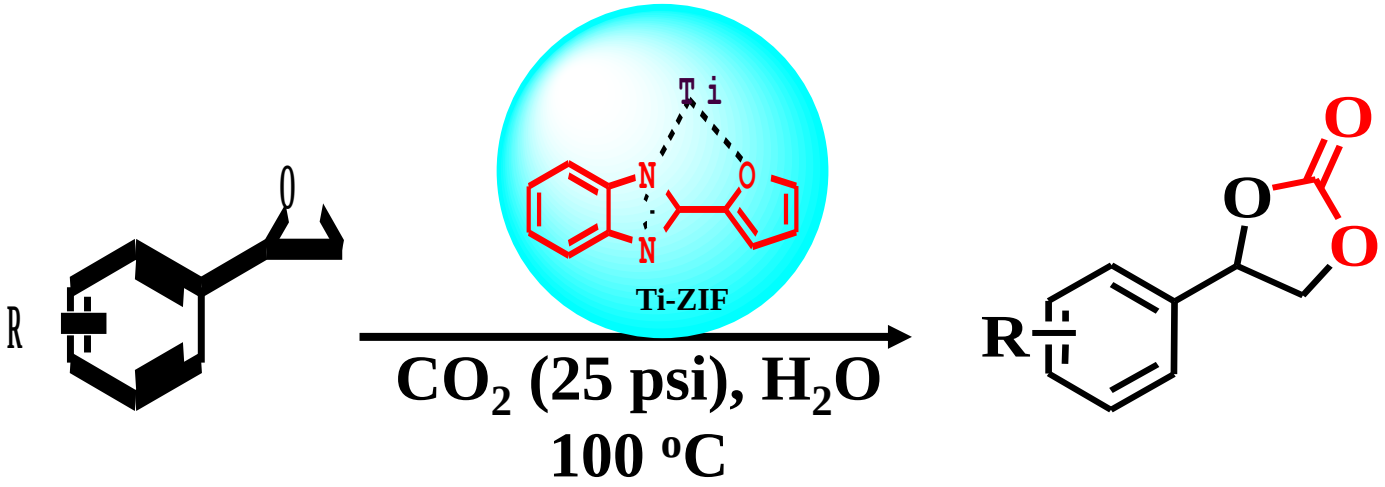
SEM analysis

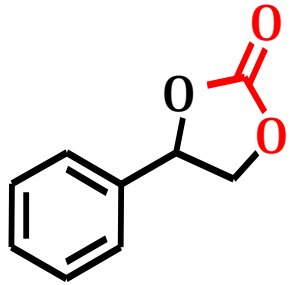


BET surface area= 369.01 m^2g^{-1}

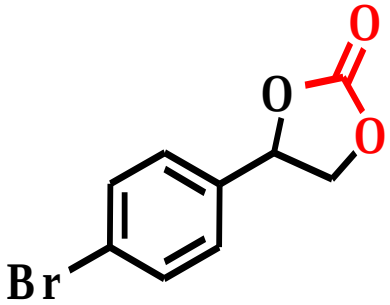
Varma *et al. Green Chem.*, 2016, *18* , 4855-4858 (Cover Page)

Application of Ti-ZIF: Synthesis of Cyclic Carbonates





98%



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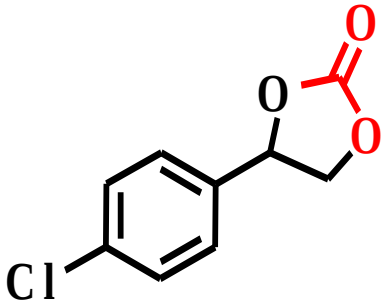

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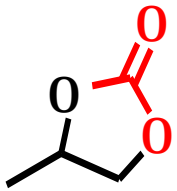

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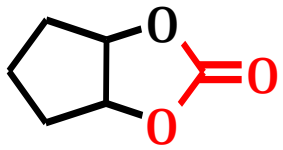

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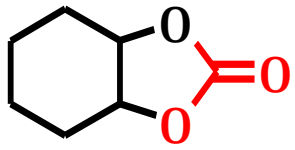

95%

Varma *et al. Green Chem.*, 2016, *18* , 4855-4858 (Cover Page)

Mechanism

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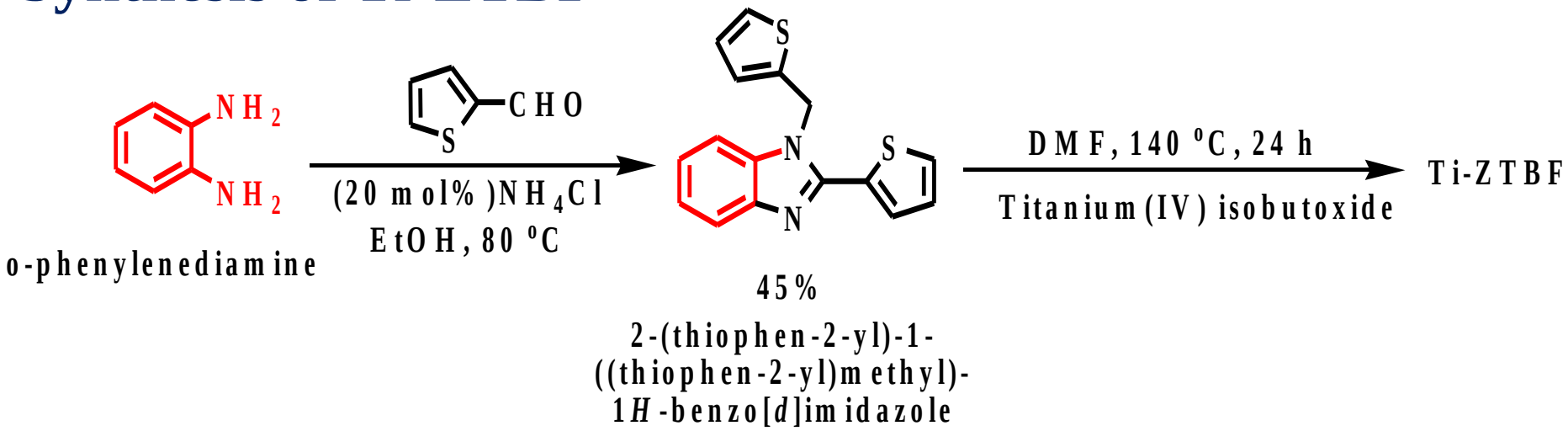
Fixation of Carbon Dioxide into Dimethyl Carbonate

Synthesis of Ti-ZTBF



o-phenylenediamine

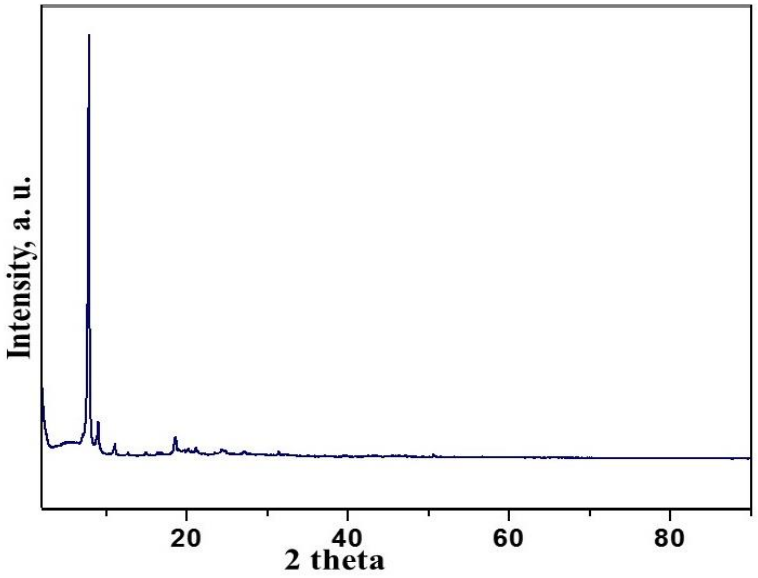
45%

2-(thiophen-2-yl)-1-((thiophen-2-yl)methyl)-1*H*-benzo[*d*]imidazole

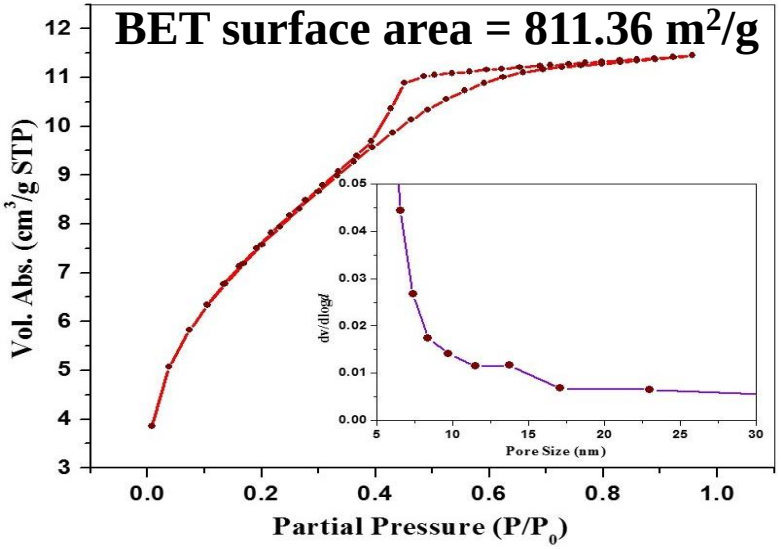
Application of Ti-ZTBF: Synthesis of DMC

Varma *et al*. Scientific Reports 2017, (in press)

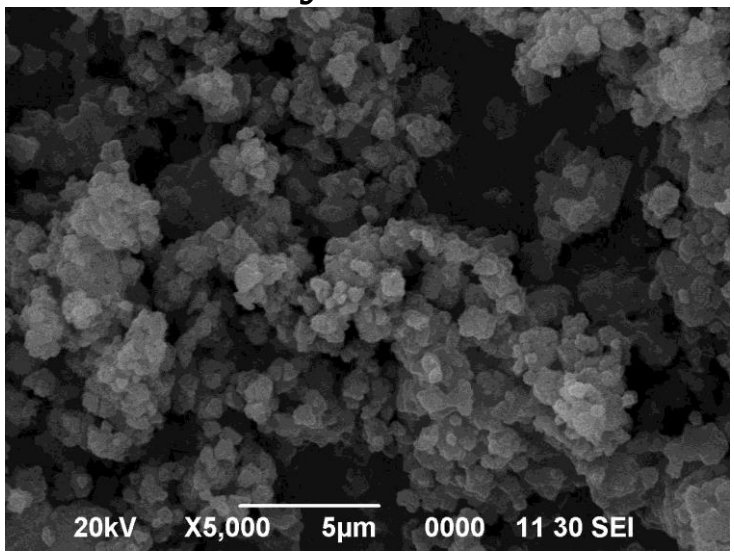
XRD analysis



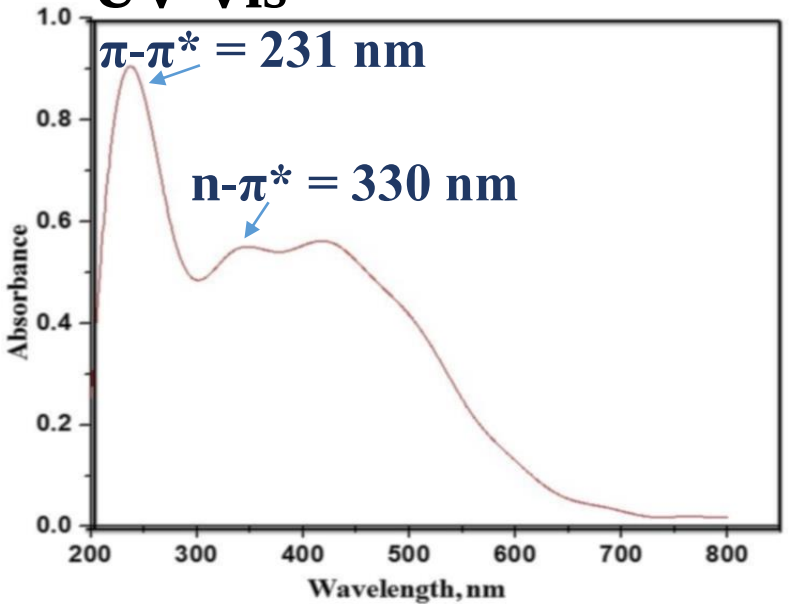
BET analysis



SEM analysis



UV-Vis



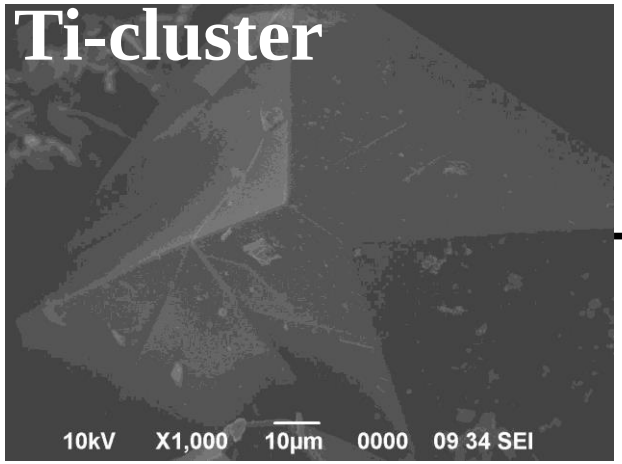
Varma *et al*. Scientific Reports 2017, (in press)

Aerobic Oxidation of Alcohols in Visible Light on Pd-grafted Ti-cluster

Synthesis of Ti-cluster

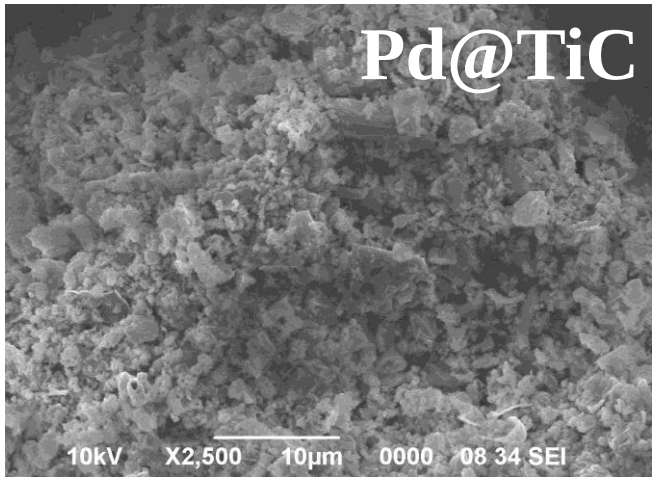
Titanium (IV) isopropoxide (0.518 mL) + 4-aminobenzoic acid (0.96 g, 7.0 mmol)

Isopropanol, 120 °C
72 h, Pressure reactor



Isopropanol

$Pd(NO_3)_2$

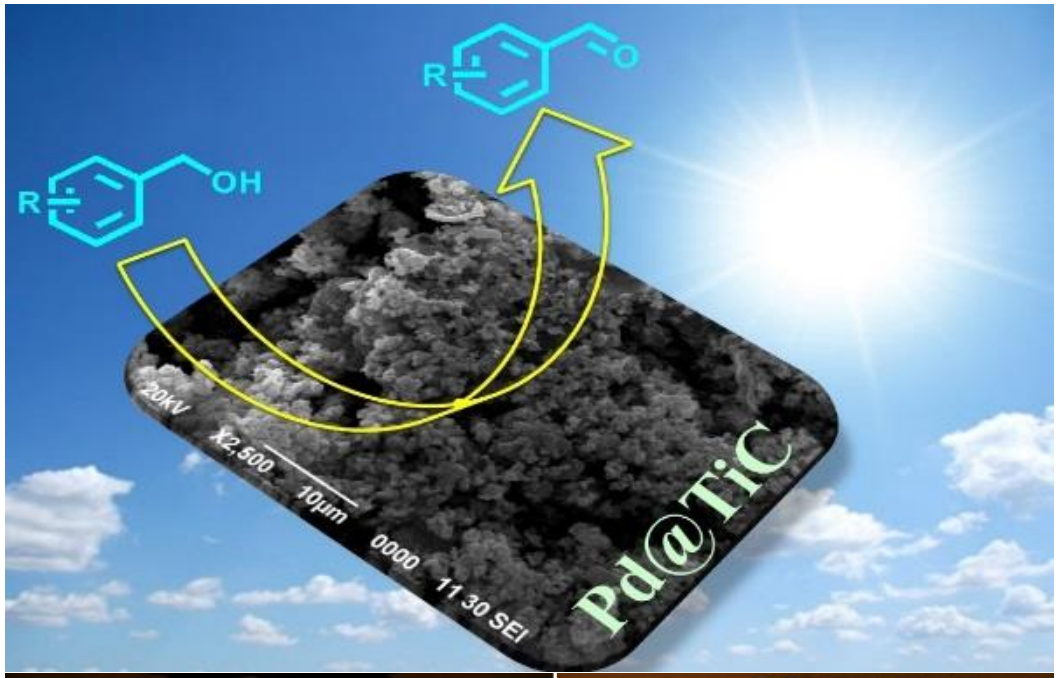


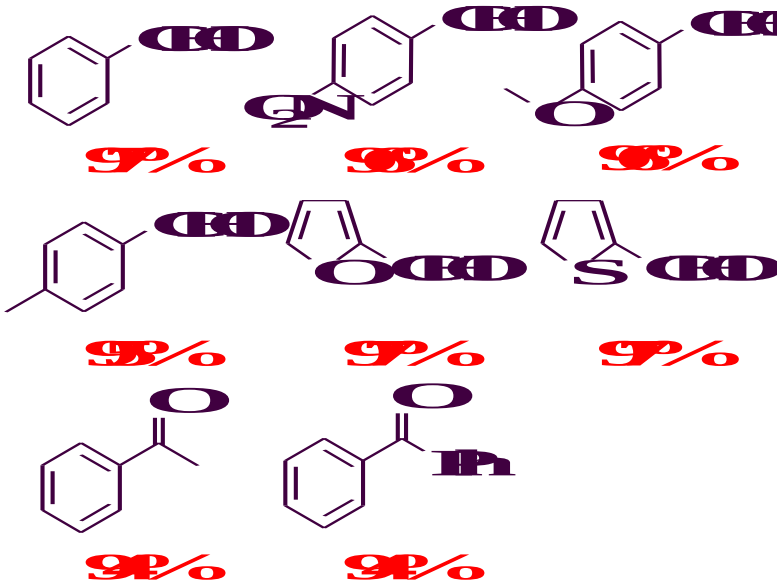
Ti cluster = $Ti_6O_6(O^iPr)_6(abz)_6$

O^iPr= isopropoxide
abz = aminobenzoic acid

Varma *et al. Tetrahedron*, DOI: 10.1016/j.tet.2016.07.070.

Application of Pd@TiC: Aerobic Oxidation of alcohols





Varma *et al*. *Tetrahedron*, 2016, DOI: 10.1016/j.tet.2016.07.070.

Conclusions

Ultimate goal: ***Development of Eco-friendly Synthetic Methodologies***

- **Synthesis of highly porous titanium based imidazolate framework**
- **Utilization of carbon dioxide to dimethyl carbonate**
- **Chemical fixation of carbon dioxide/waste to valued chemicals**
- **Use of titanium cluster as a photo-catalyst**

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