Supporting Information

Efficient separation of ethanol-methanol and ethanol-water mixtures using ZIF-8 supported on a hierarchical porous mixed-oxide substrate

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E-mail: s.grecea@uva.nl
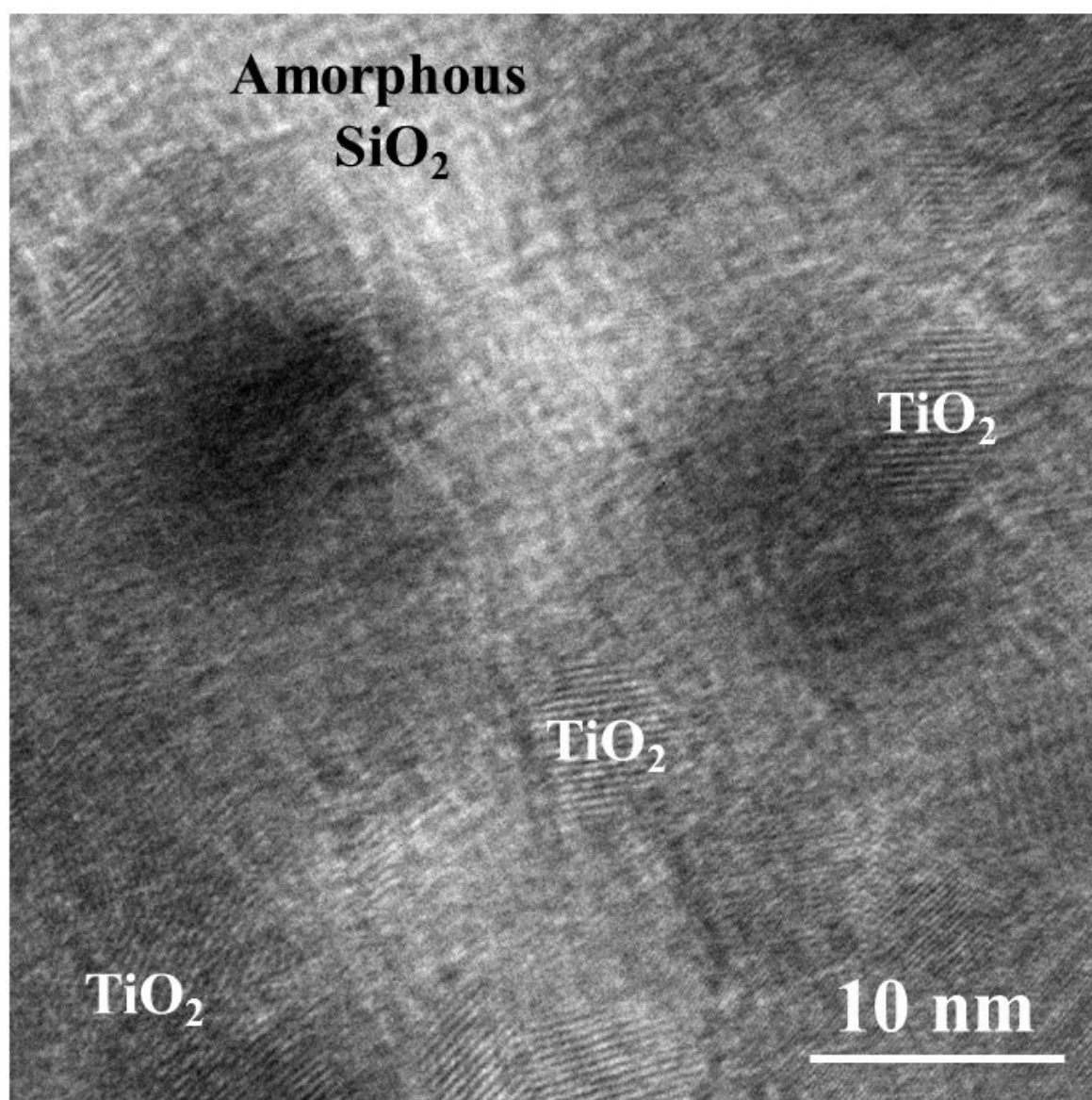
S1. Characterization of the TSO artificial leaf

Figure S1. The HRTEM image of TSO showing that crystalline TiO_2 is surrounded by amorphous SiO_2.
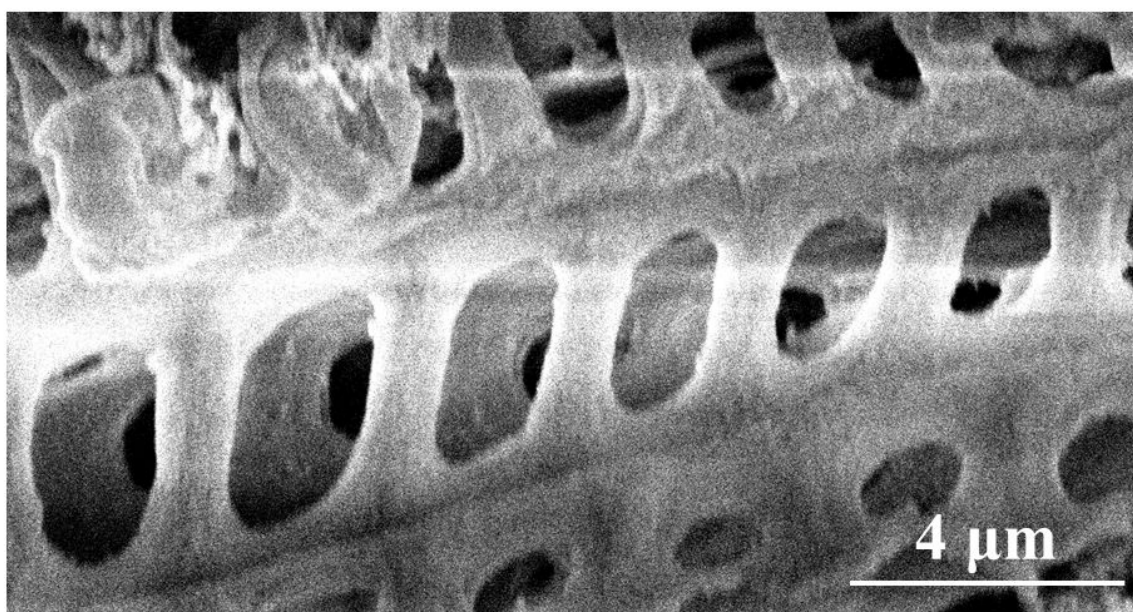
Figure S2. Side view of one channel within the TSO, in which flight deck windows like holes can be observed along the channel. These holes are also shown in **Scheme 2**.
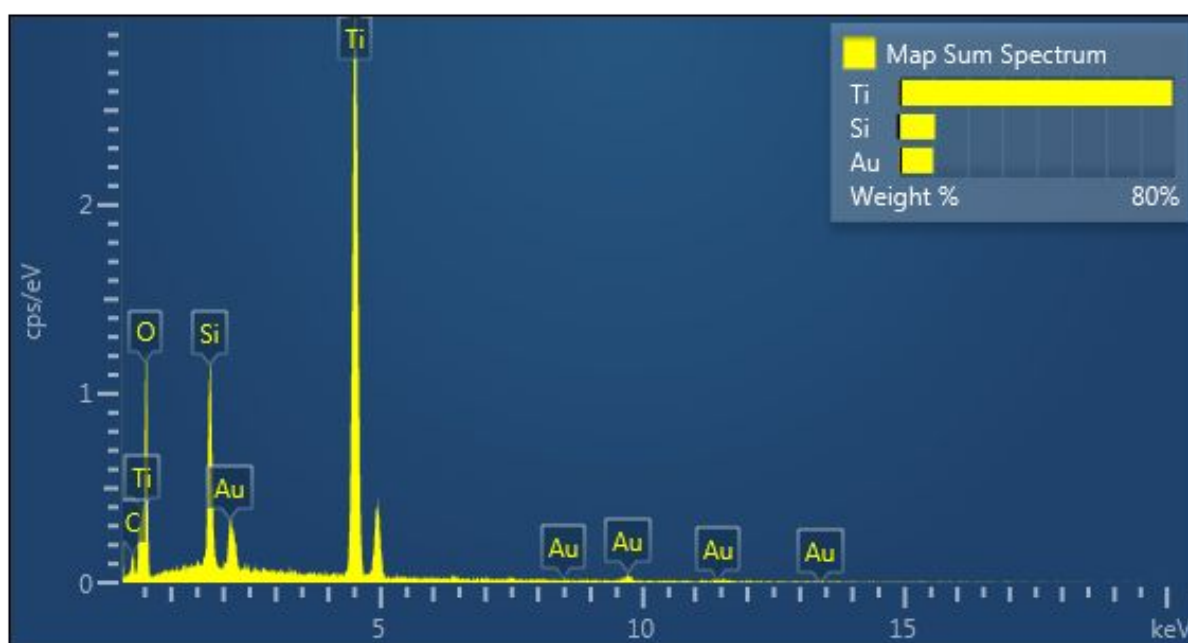

Figure S3. The EDS spectrum of the TSO, corresponding to the red circle in **Figure 1e**.

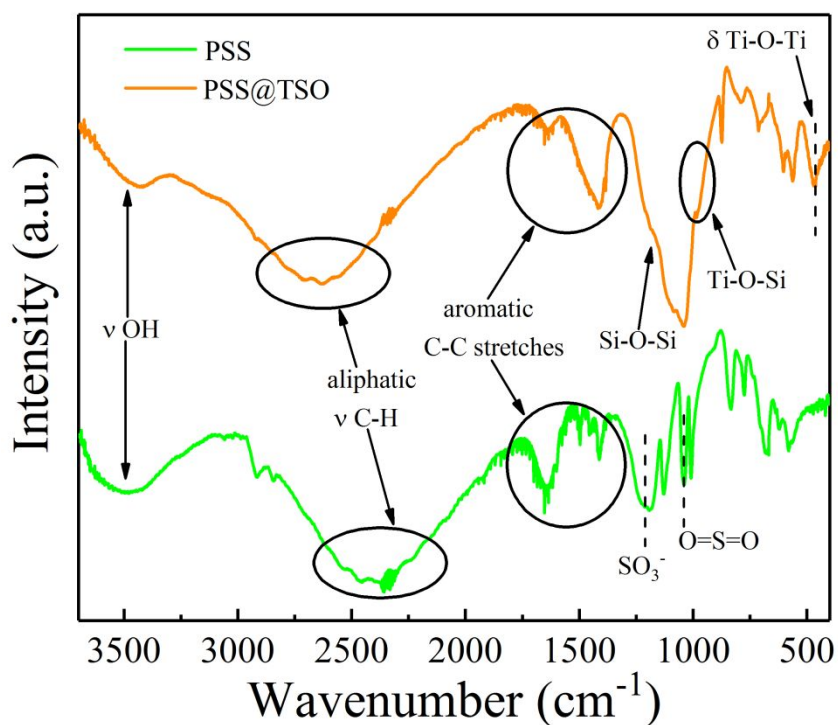# S2. The interaction between TSO and ZIF-8

Figure S4. FTIR spectra of the bulk poly(styrenesulfonate, sodium salt) (PSS) and the surface modified PSS@TSO.
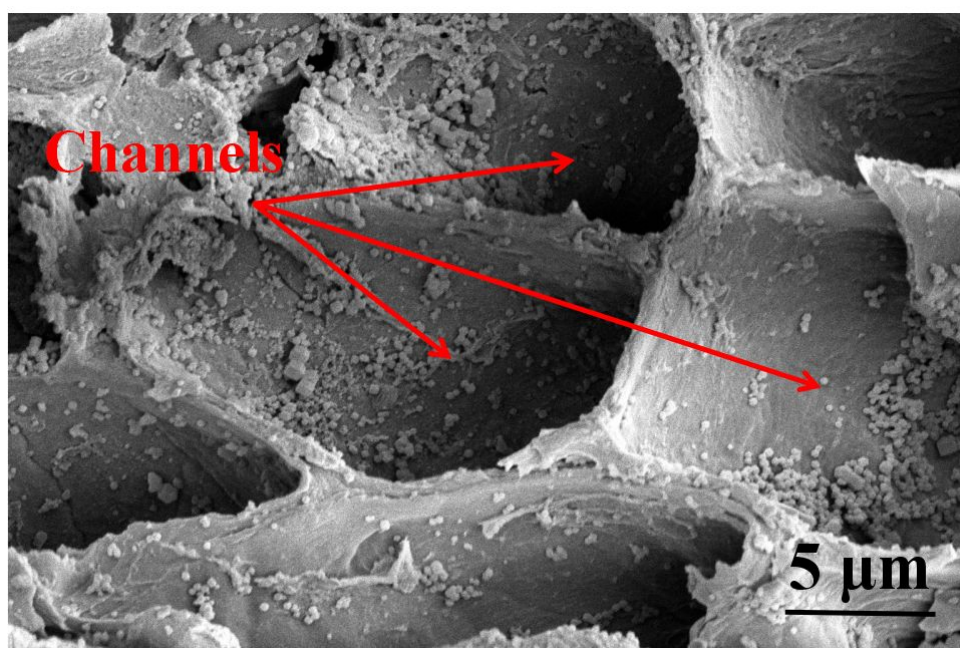

Figure S5. The cross section of the ZIF-8@TSO composite; the TSO support was not pre-treated by PSS.

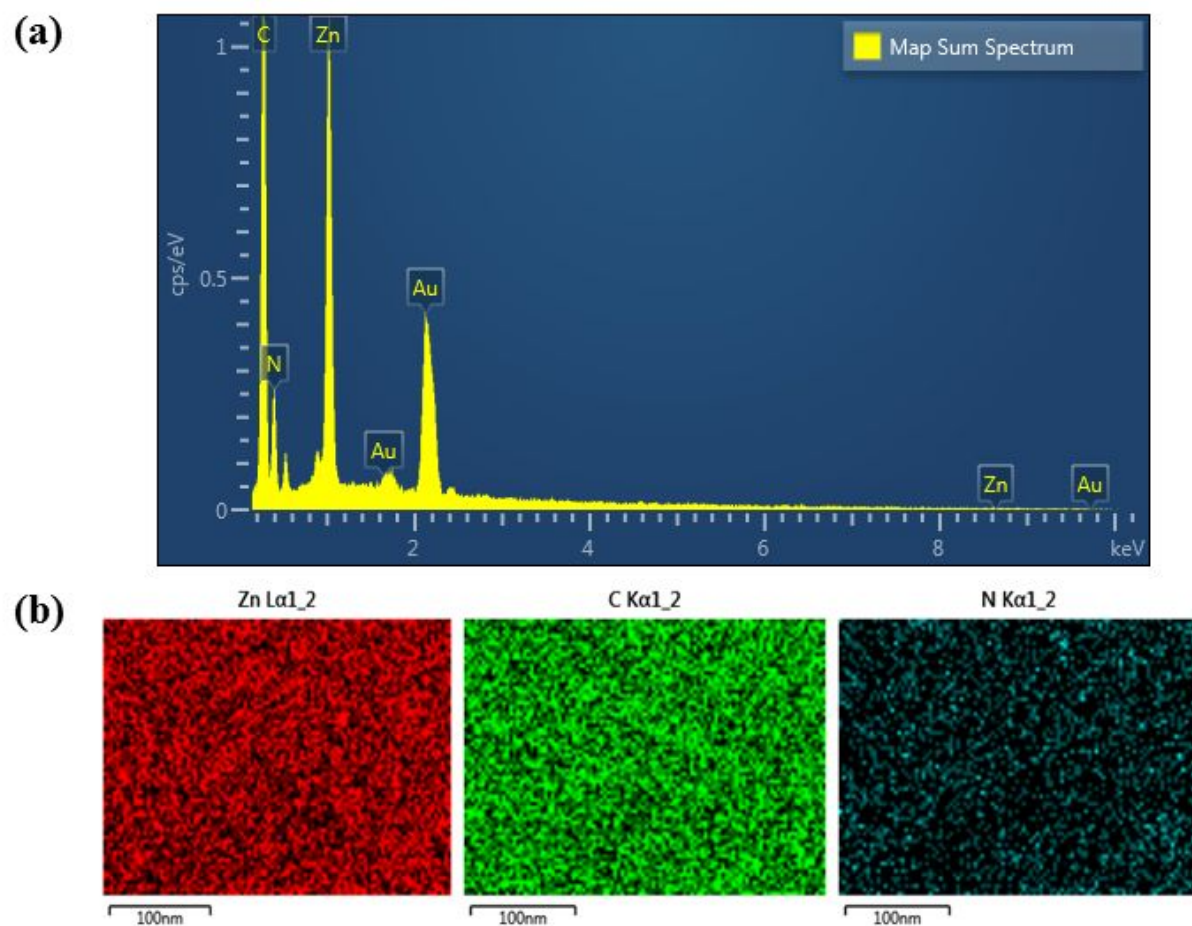# S3. The EDS Spectrum of the bulk crystalline ZIF-8

Figure S6. The EDS spectrum and mapping of the as-synthesised ZIF-8 corresponding to **Figure 4a**.

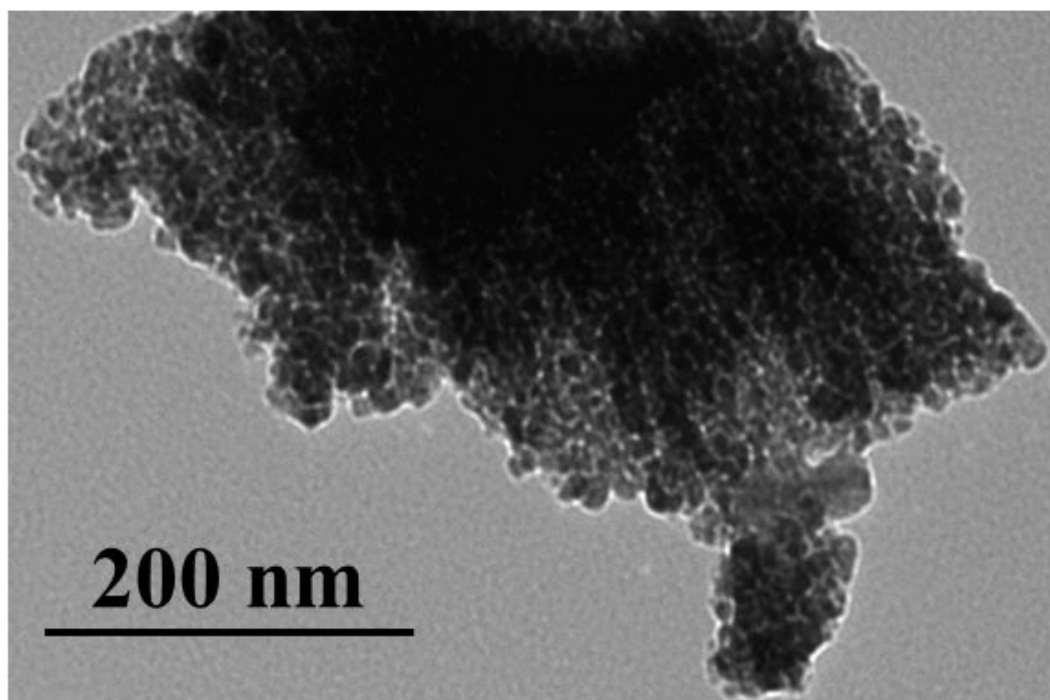## S4. The mesopores within the TSO artificial leaf

Figure S7. The TEM image of the TSO; wormlike meso-pores can be observed.

S5. The Ideal Adsorbed Solution Theory (IAST) selectivity calculations

The IAST (ideal adsorption solution theory) is applied to predict the binary mixture adsorption behavior from single-component adsorption isotherms.[1,2]

Some of the experimental water, methanol and ethanol adsorption isotherms data measured at 303 K are hard to fit any models within IAST method, so the numerical interpolation method was chosen. Some of the experimental adsorption isotherms here did not reach equilibrium at relative saturated pressure, due to the capillary condensation occurred in large pores. Thus, the loading amount at relative saturated pressure in each adsorption isotherm is assigned to the maximum loading amount and which is reasonably extended to a higher pressure to preferably fit the simulation. The fitted data are then applied to predict adsorption selectivity with IAST.
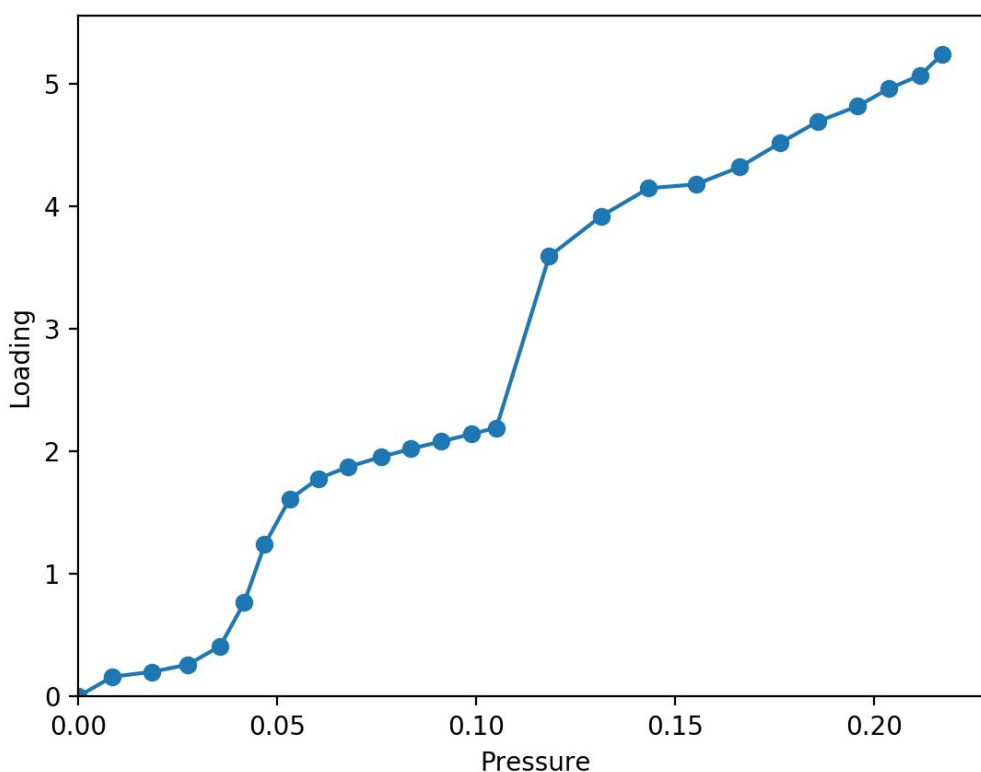

Figure S8. The methanol adsorption isotherm of the ZIF-8@TSO composite along with the numerical interpolation method (Unit: Pressure in bar; Loading in mmol·g^{-1}).
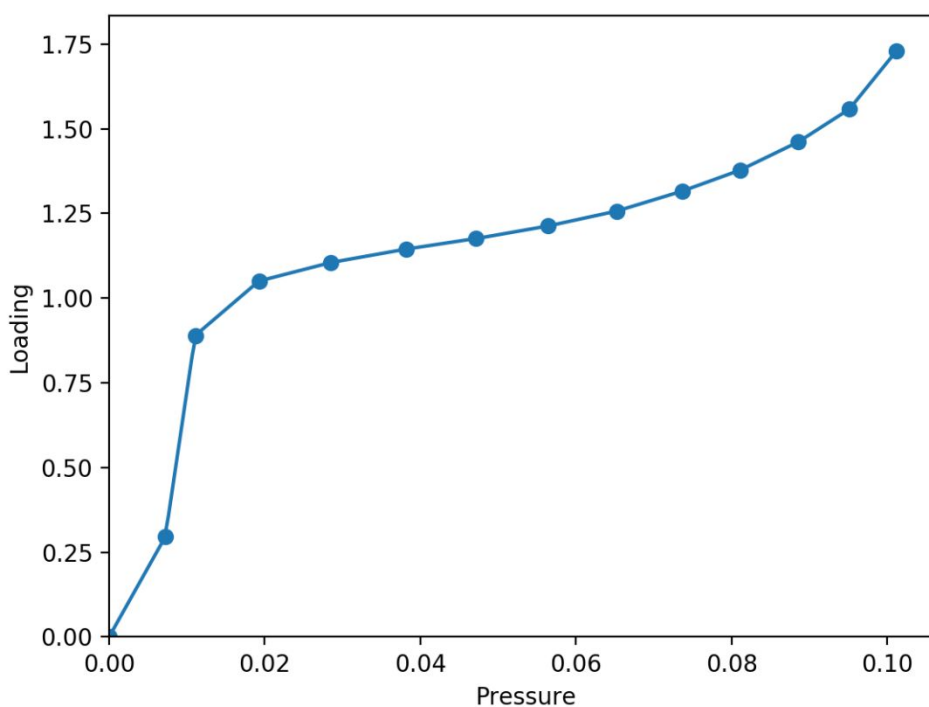
Figure S9. The ethanol adsorption isotherm of the ZIF-8@TSO composite along with the numerical interpolation method (Unit: Pressure in bar; Loading in mmol·g^{-1}).
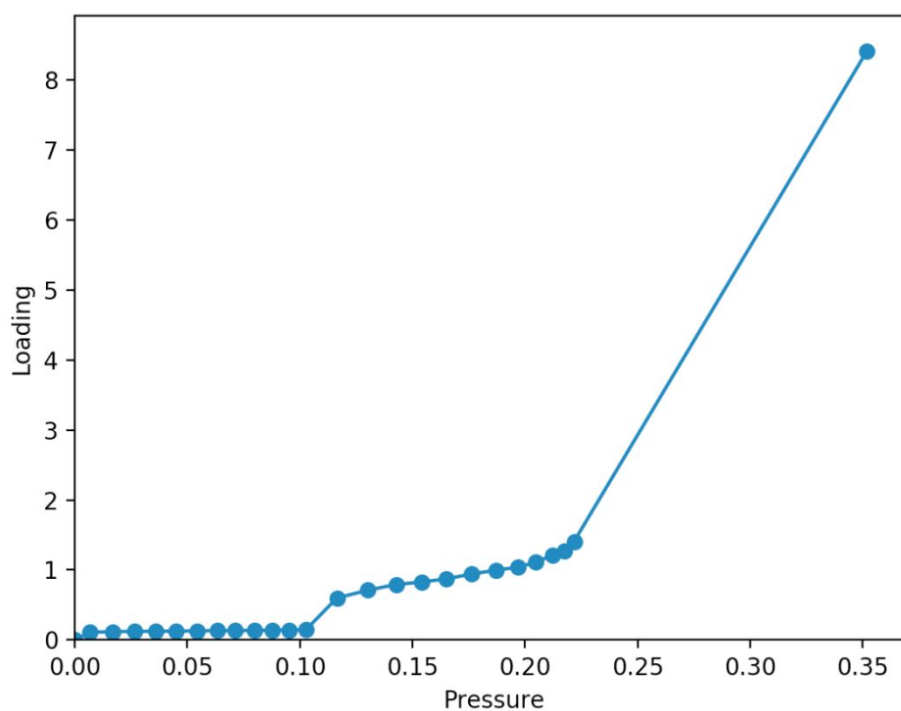

Figure S10. The methanol adsorption isotherm of the TSO along with the numerical interpolation method (Unit: Pressure in bar; Loading in mmol·g^{-1}).

Figure S11. The ethanol adsorption isotherm of the TSO along with the numerical interpolation method (Unit: Pressure in bar; Loading in mmol·g^{-1}).
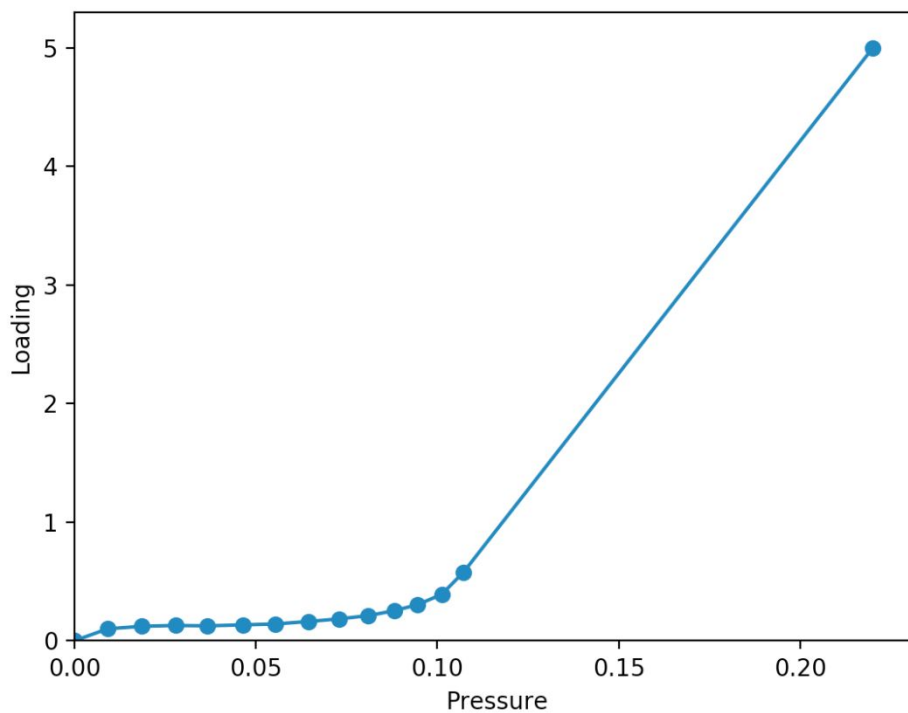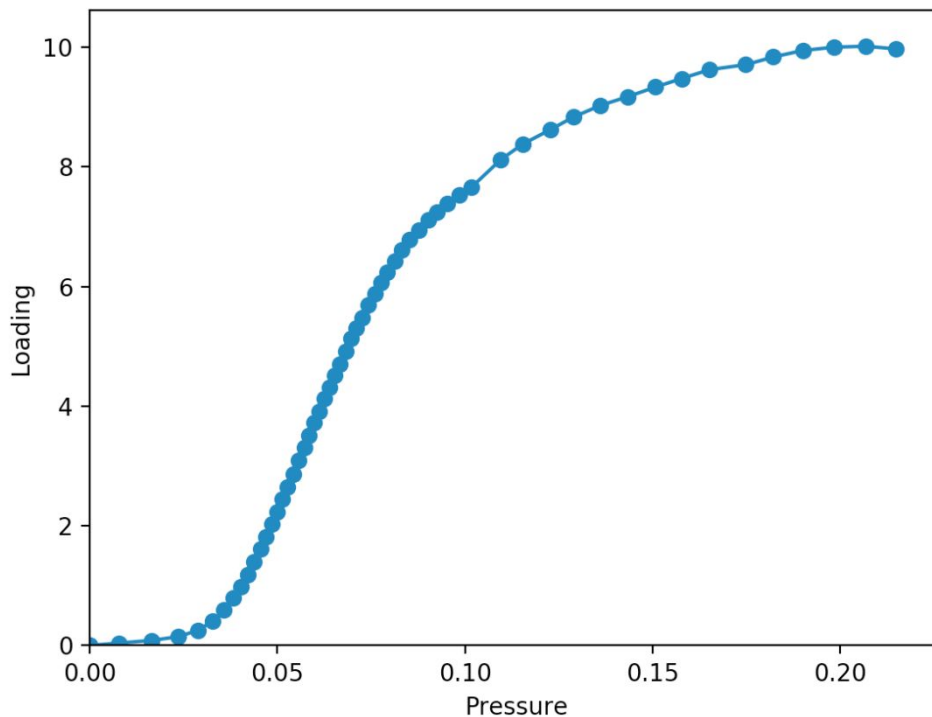

Figure S12. The methanol adsorption isotherm of the bulk crystalline ZIF-8 along with the numerical interpolation method (Unit: Pressure in bar; Loading in mmol·g^{-1}).
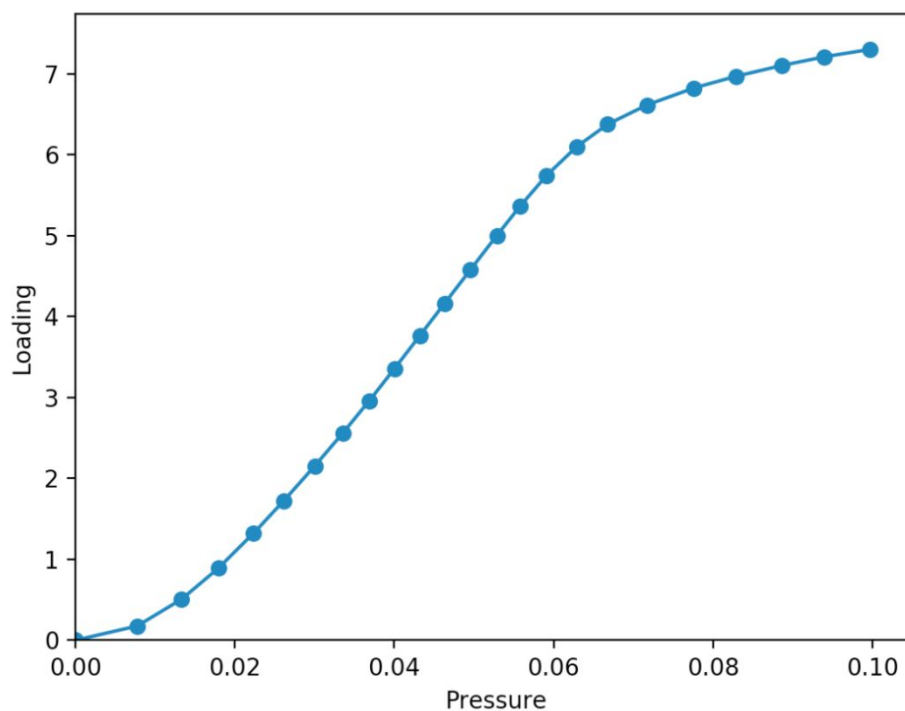
Figure S13. The ethanol adsorption isotherm of the as-synthesised ZIF-8 along with the numerical interpolation method (Unit: Pressure in bar; Loading in mmol·g^{-1}).
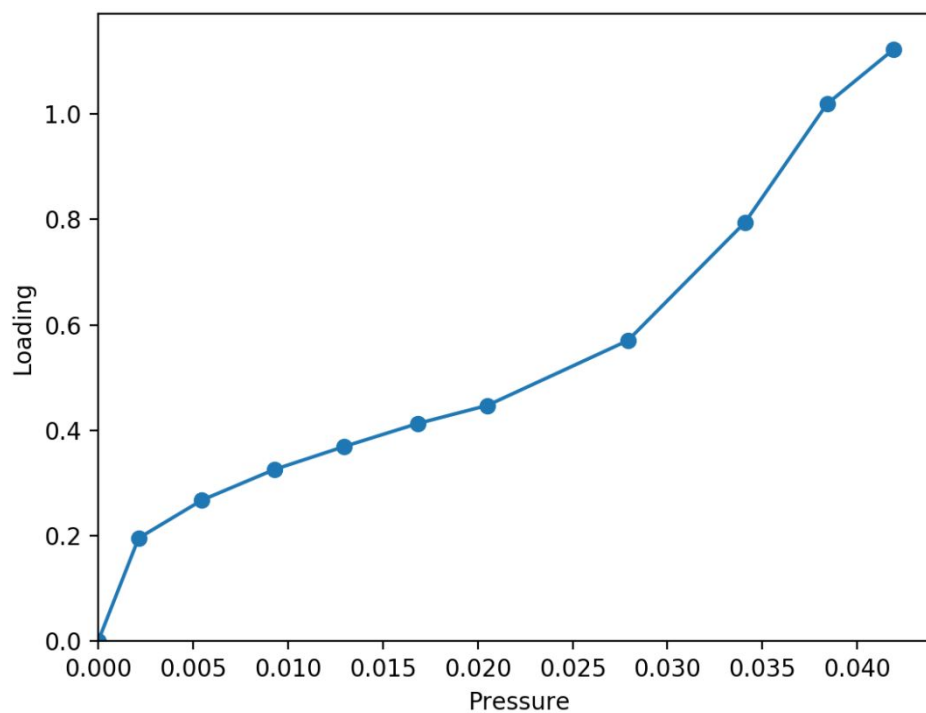

Figure S14. The water adsorption isotherm of the ZIF-8@TSO composite along with the numerical interpolation method (Unit: Pressure in bar; Loading in mmol·g^{-1}).

The experimental water adsorption isotherms data measured at 303 K for the TSO artificial leaf are fitted well with the *Langmuir* equation:

$$n_i^o(P) = M\frac{KP}{1 + KP}$$

Here, P is the pressure of the bulk water equilibrium with the adsorbed phase water (bar), M refers to the adsorbed water amount per mass of adsorbent (mmol·g⁻¹; M= 2.7195 for TSO). K is the Langmuir constant that describes the affinity of the water with the adsorbent, a half of the adsorption sites are occupied when the pressure *P=1/K* (K= 6.2047 for TSO). The fitted data are then applied to predict adsorption selectivity with IAST.

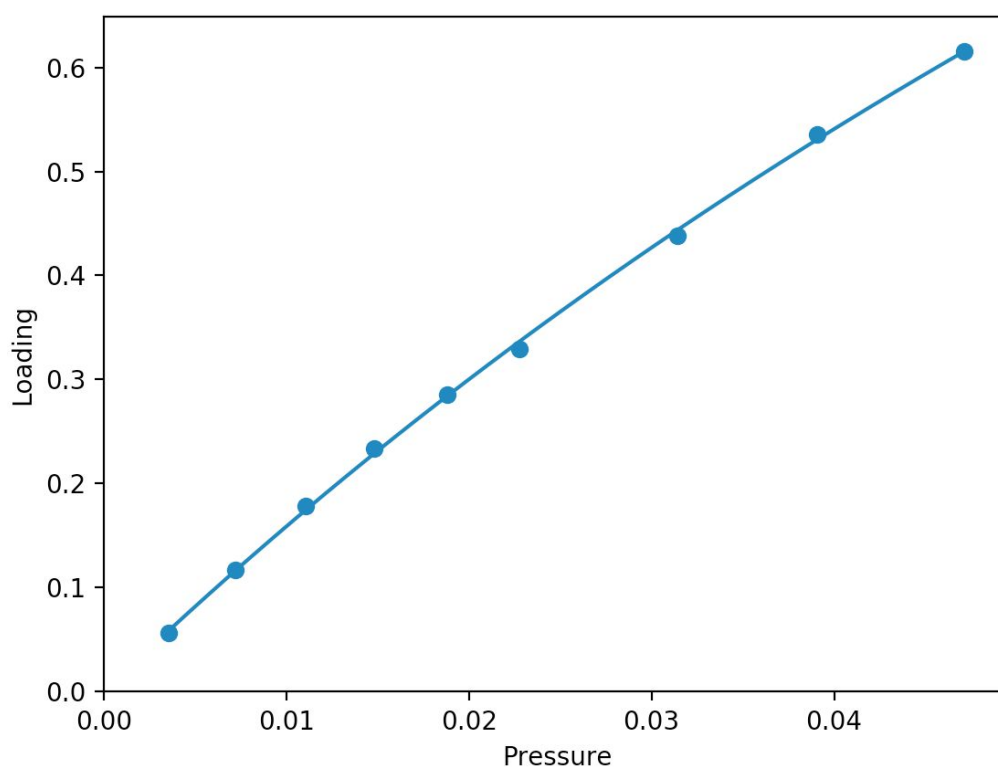**Figure S15.** The water adsorption isotherm of the TSO along with the Langmuir model (Unit: Pressure in bar; Loading in mmol·g⁻¹).

The experimental water adsorption isotherm data measured at 303 K for the as-synthesised ZIF-8 are fitted well with the *Henry's law* equation:

$$n_i^o(P) = K_H P$$

Here, P is the pressure of the bulk water equilibrium to the adsorbed phase water (bar), K_H is the Henry coefficient (K_H=1.8073 for the ZIF-8). The fitted data are then applied to predict adsorption selectivity with IAST.
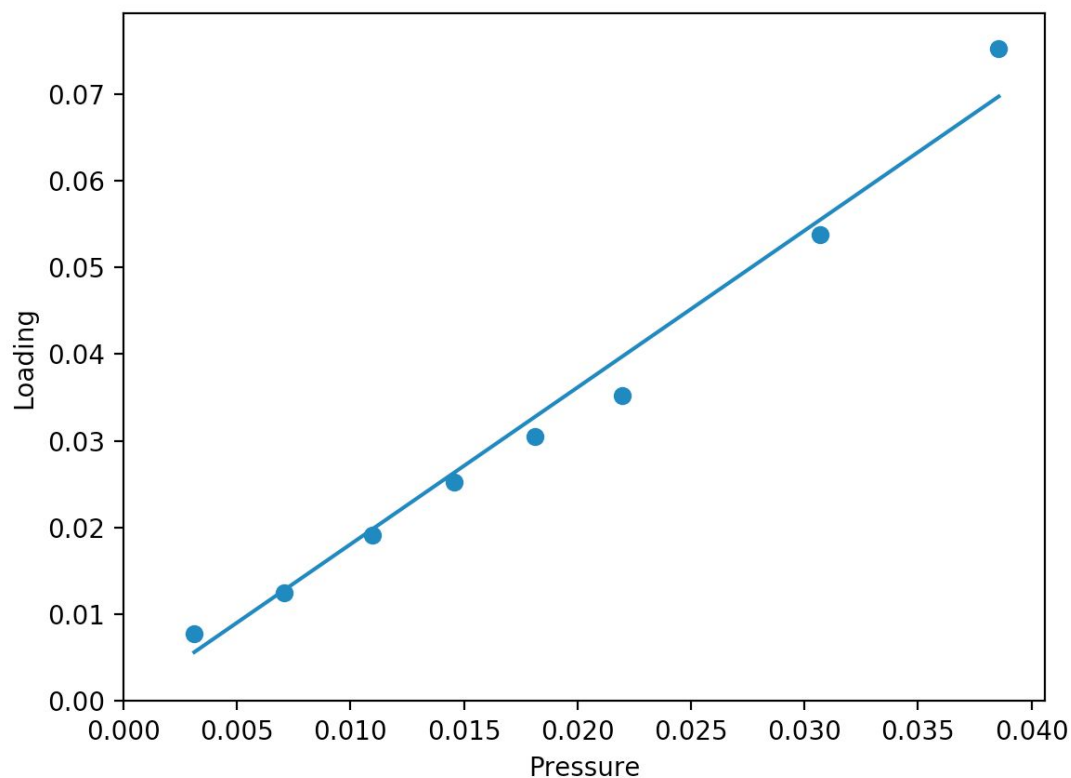

Figure S16. The water adsorption isotherm of the as-synthesised ZIF-8 along with the *Henry's law* model (Unit: Pressure in bar; Loading in mmol·g⁻¹).

The adsorption selectivity of the adsorbate **a** over adsorbate **b** in a binary mixture is defined as:

$$S_{a/b} = \frac{x_a/y_a}{x_b/y_b}$$

Here, x and y are the mole fractions of **a** and **b** in the adsorbed and bulk phases, respectively.

In order to preferably fit the simulation, the experimental maximum adsorption amount at relative saturated pressure in several isotherms were reasonably extended to higher pressure. However, considering the experimental saturated pressure at 303 K for water, ethanol and methanol is 4 KPa, 10 KPa and 21 KPa, respectively, and the accuracy of the simulation, the total pressure in simulation was restricted as 10 KPa for both the equimolar mixture of methanol-ethanol and water-ethanol.

S6. The adsorption selectivity for as-synthesised ZIF-8 and the TSO support
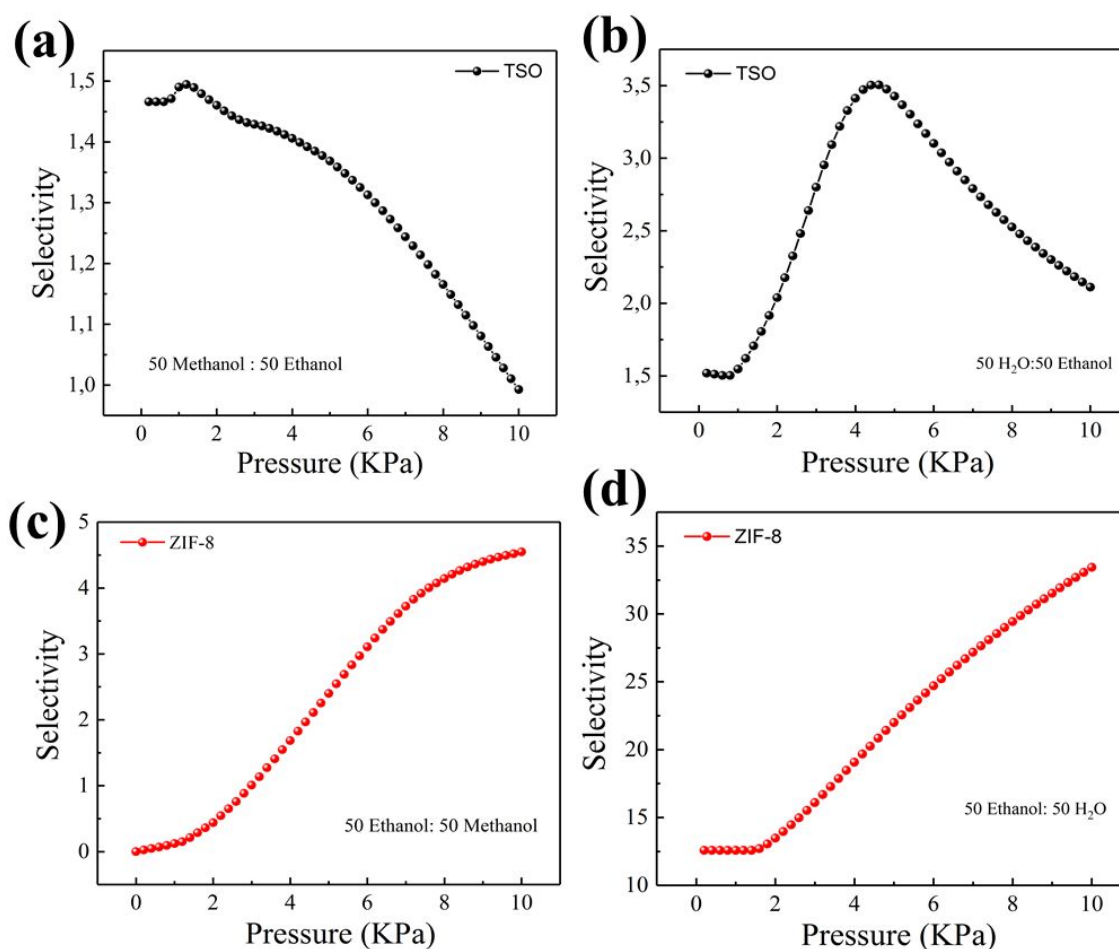

Figure S17. The IAST-calculated equimolar mixture of methanol-ethanol and water-ethanol selectivities for TSO at 303 K (a&b). The IAST-calculated equimolar mixture of ethanol-methanol and ethanol-water selectivities for the as-synthesised ZIF-8 at 303 K (c&b).

References

1 Myers, A. L. and Prausnitz, J. M. Thermodynamics of mixed-gas adsorption. *AIChE. J.,* **1965**, 11, 121-127.

2 Simon, C. Smit, B. Haranczyk, M. pyIAST: Ideal adsorbed solution theory (IAST) Python package. *Comput. Phys. Commun.* **2016**, 200, 364-380.