

Liquid phase separation of polyaromatics on [Cu₂(BDC)₂(dabco)]

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Table of contents

Synthesis and activation of [Cu ₂ (BDC) ₂ (dabco)]	S2
Characterization	S3
Batch experiments	S6
Additional competitive isotherms	S8

Synthesis and activation of [Cu₂(BDC)₂(dabco)]

[Cu₂(BDC)₂(dabco)] was synthesized based on the procedure described in K. Seki and W. Mori, *J. Phys. Chem. B*, **2002**, *106*, 1380. A solution of 0.31 g Cu^{II}(acetate).H₂O in 12.63 g MeOH was added to a solution of 0.21 g terephthalic acid in 252 g MeOH and 1.64 g formic acid and is allowed to stir for 72 hours at 313 K. A solution of 0.07 g dabco in 14.46 g toluene is added to this mixture and the mixture is divided over several teflon lined steel autoclaves. These autoclaves are sealed and heated at 433 K for 15 hours. The resulting pale blue crystals are washed with MeOH. The material is activated under vacuum at 383 K during 15 hours.

Characterization of $[\text{Cu}_2(\text{BDC})_2(\text{dabco})]$

The X-ray diffractogram of $[\text{Cu}_2(\text{BDC})_2(\text{dabco})]$ is shown in Figure S1.

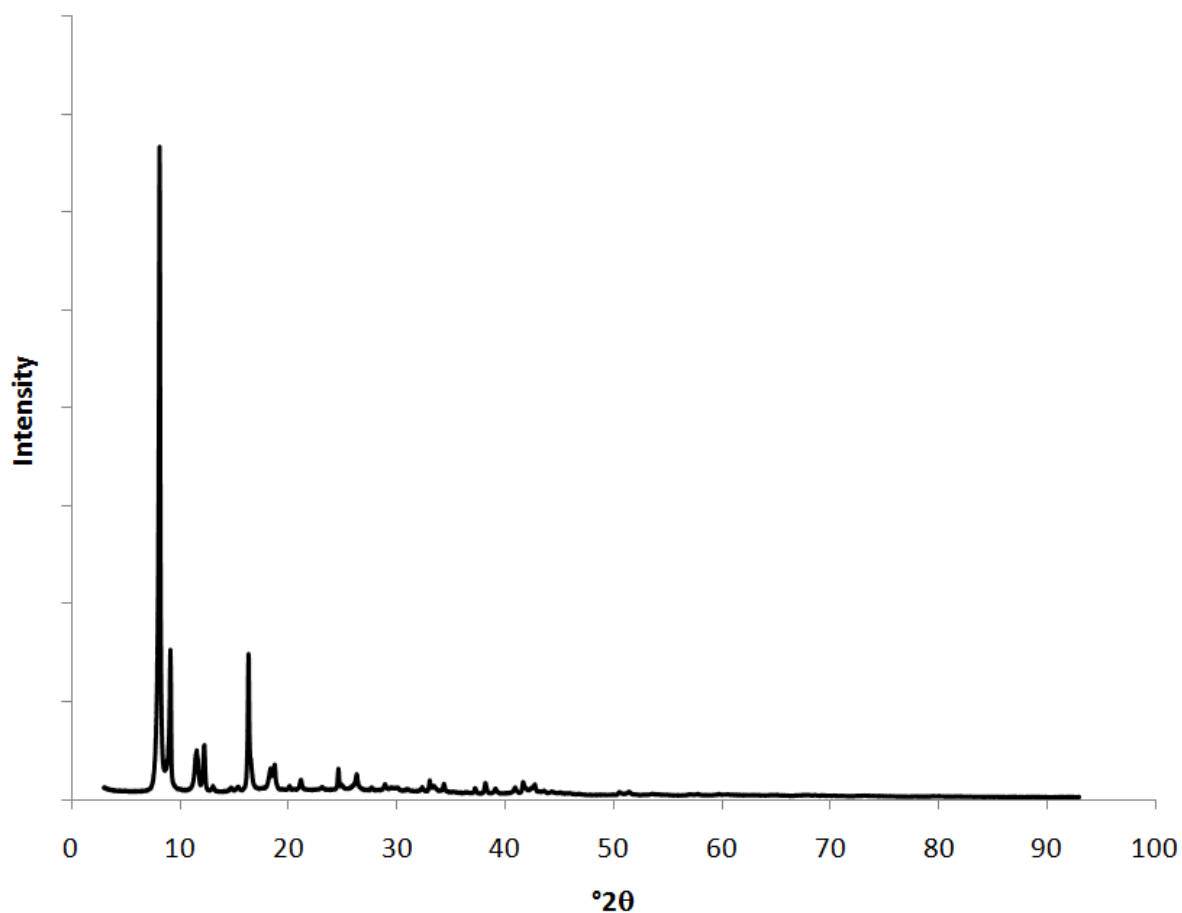


Figure S1. XRD pattern of $[\text{Cu}_2(\text{BDC})_2(\text{dabco})]$.

The XRD pattern measured is in accordance with the pattern provided in K. Seki and W. Mori, *J. Phys. Chem. B*, **2002**, *106*, 1380.

The TGA profile of $[\text{Cu}_2(\text{BDC})_2(\text{dabco})]$ is given in Figure S2.

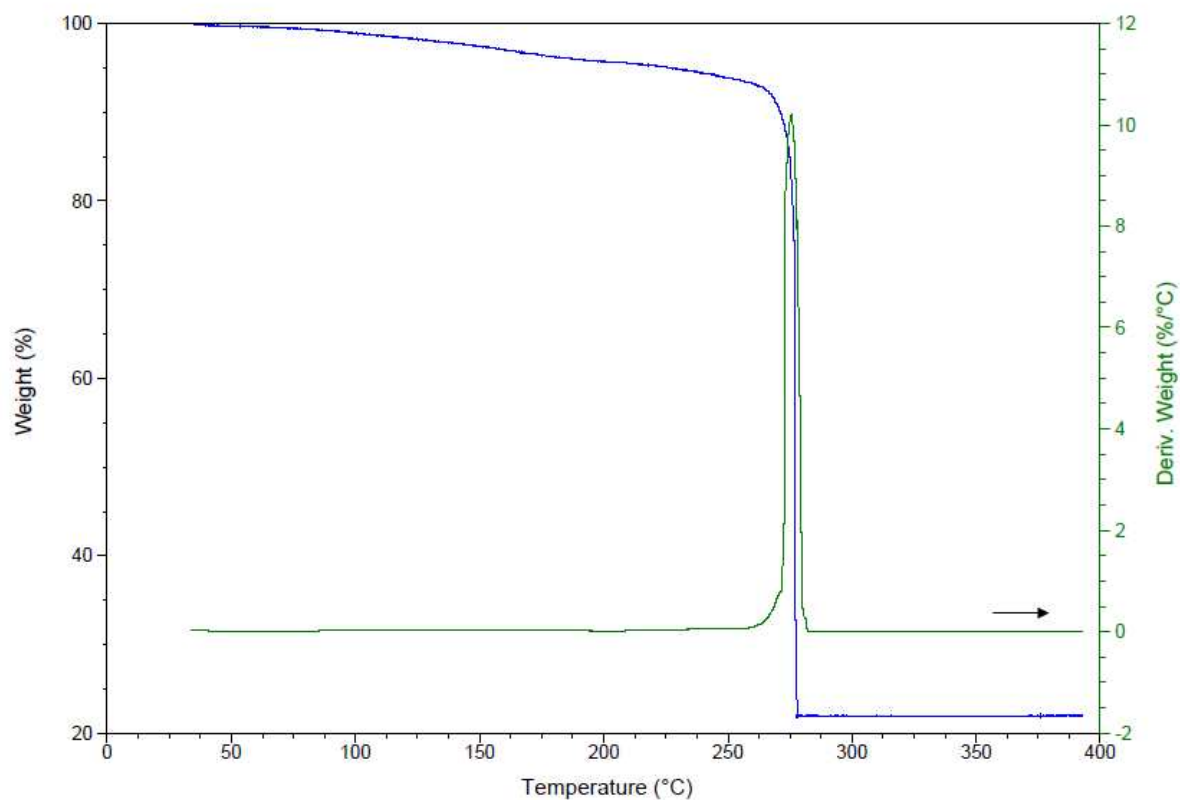


Figure S2. TGA profile of $[\text{Cu}_2(\text{BDC})_2(\text{dabco})]$ under O_2 .

Figure S2 shows a gradual loss of 5 wt% between 50 °C and 150 °C due to the removal of water. From 200 ° till 250 °C a small step is observed that can be ascribed to the loss of any remaining free terephthalic acid. At 260 °C the structure starts to decompose.

The nitrogen physisorption isotherm of $[\text{Cu}_2(\text{BDC})_2(\text{dabco})]$ (77 K) is shown in Figure S3.

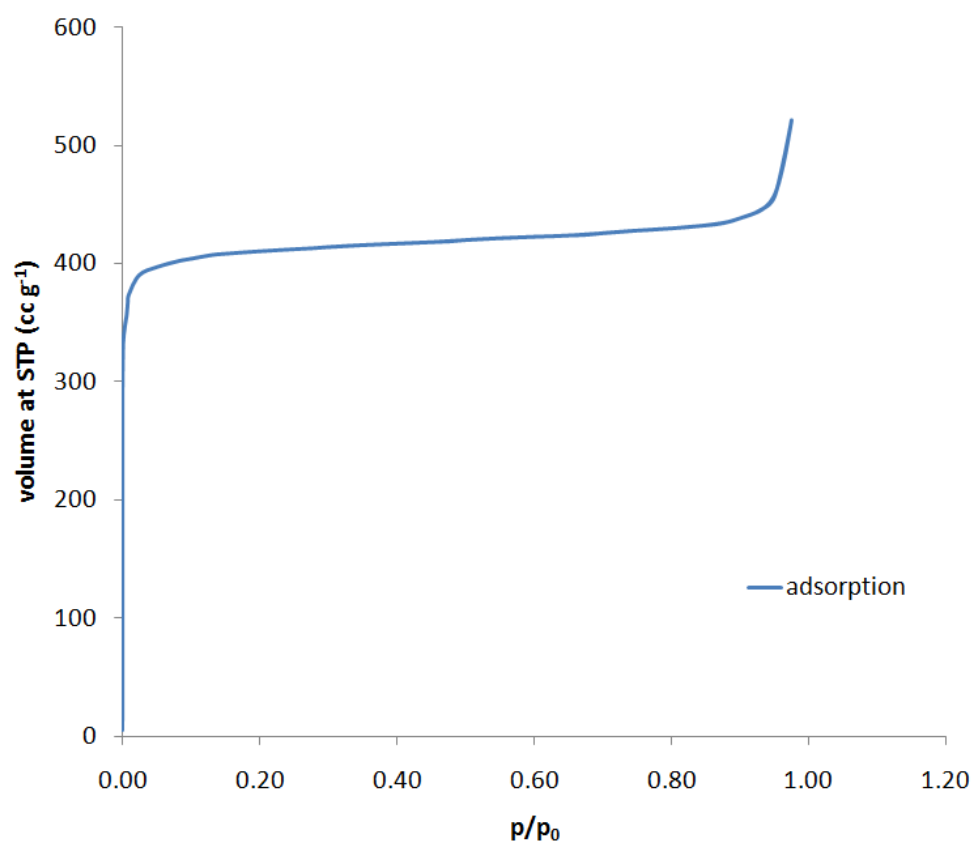


Figure S3. Nitrogen fysisorption on [Cu₂(BDC)₂(dabco)].

The obtained BET surface is 1240 m² g⁻¹ and the pore volume has been determined to be 0.64 ml g⁻¹. The pore size has been reported in reference 17 as being approximately 7.4 Å.

Batch experiments

Liquid phase batch adsorption experiments were carried out at 298 K in 1.8 ml glass vials filled with 0.025 g of adsorbent and a heptane solution containing alkylaromatics or 50:50 mixtures of alkylaromatics following a literature procedure (L. Alaerts, C. Kirschock, M. Maes, M. van der Veen, V. Finsy, A. Depla, J. Martens, G. Baron, P. Jacobs, J. Denayer, D. De Vos, *Angew. Chem. Int. Ed.*, **2007**, 46, 4372; L. Alaerts, M. Maes, M. van der Veen, P. Jacobs, D. De Vos, *Phys. Chem. Chem. Phys.*, **2009**, 11, 2903). An aliphatic solvent has been selected to dissolve the naphthalenes, since these solvents are known not to interact strongly with the host and are thus unlikely to influence the adsorption of naphthalene compounds. For each adsorbed compound, the percentual uptake is calculated from GC data using formula 1:

$$q(\%) = \left(1 - \frac{\text{relative peak area } \%_S}{\text{relative peak area } \%_R} \right) * 100 \quad (1)$$

in which S stands for the sample containing the adsorbent material, and R for a reference sample without adsorbent. The uptake (wt%) is calculated according to formula 2:

$$\text{uptake (wt\%)} = \left(\frac{q(\%) * m_{\text{component}}}{100 * m_{\text{adsorbent}}} \right) \quad (2)$$

in which m stands for mass (g); $m_{\text{component}}$ is the mass of adsorbate initially offered.

Repeated GC injections and data analysis showed a relative uncertainty of 2.5 % on the relative peak areas. To calculate uncertainties on the wt% uptake, the uncertainty on the percentual uptake is first calculated. The percentual uptake is calculated via the quotient of two relative peak areas; hence the rules for error propagation as shown in formula 3 are used:

$$u\left(\frac{A}{B}\right) = \sqrt{u(A)^2 + u(B)^2} \quad (3)$$

with u being the relative uncertainty. Both $u(A)$ and $u(B)$ were determined to be 2.5%. Based on the relative uncertainty in percentual uptakes, the error bars for the wt% uptake in Figure 1 can be calculated. As the wt% influences the equilibrium concentration, error bars for the equilibrium concentrations have been provided as well based directly on the error of the wt% uptake.

Since these variations are similar for both compounds in the competitive batch mode, error bars have been omitted for clarity.

Additional competitive isotherms of 1-methylnaphthalene vs. naphthalene and 1-methylnaphthalene vs. 1,4-dimethylnaphthalene

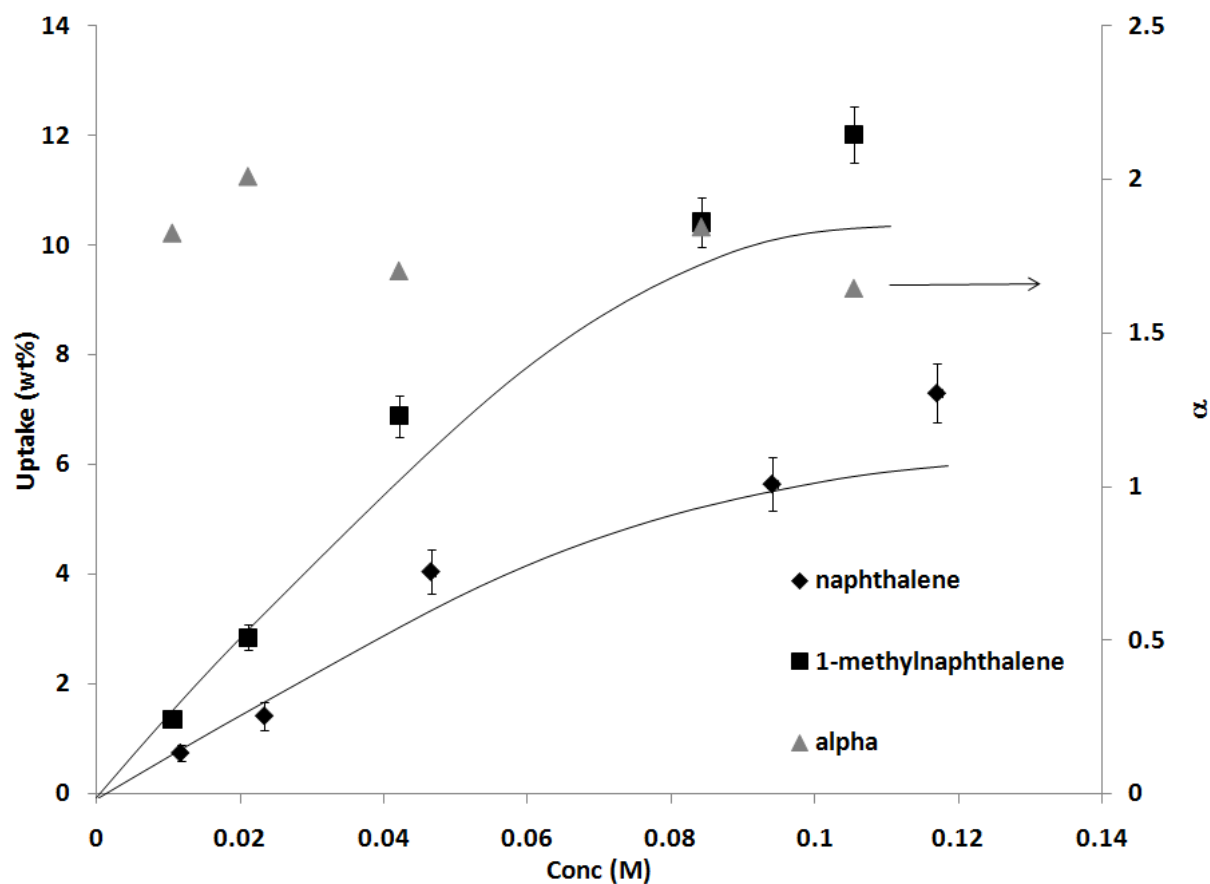


Figure S5. Competitive adsorption on $[\text{Cu}_2(\text{BDC})_2(\text{dabco})]$ in batch mode: uptake (wt%) from an equimolar mixture of 1-methylnaphthalene and naphthalene in heptane at room temperature as a function of equilibrium liquid phase concentration of each compound. Separation factors α are given on the right axis.

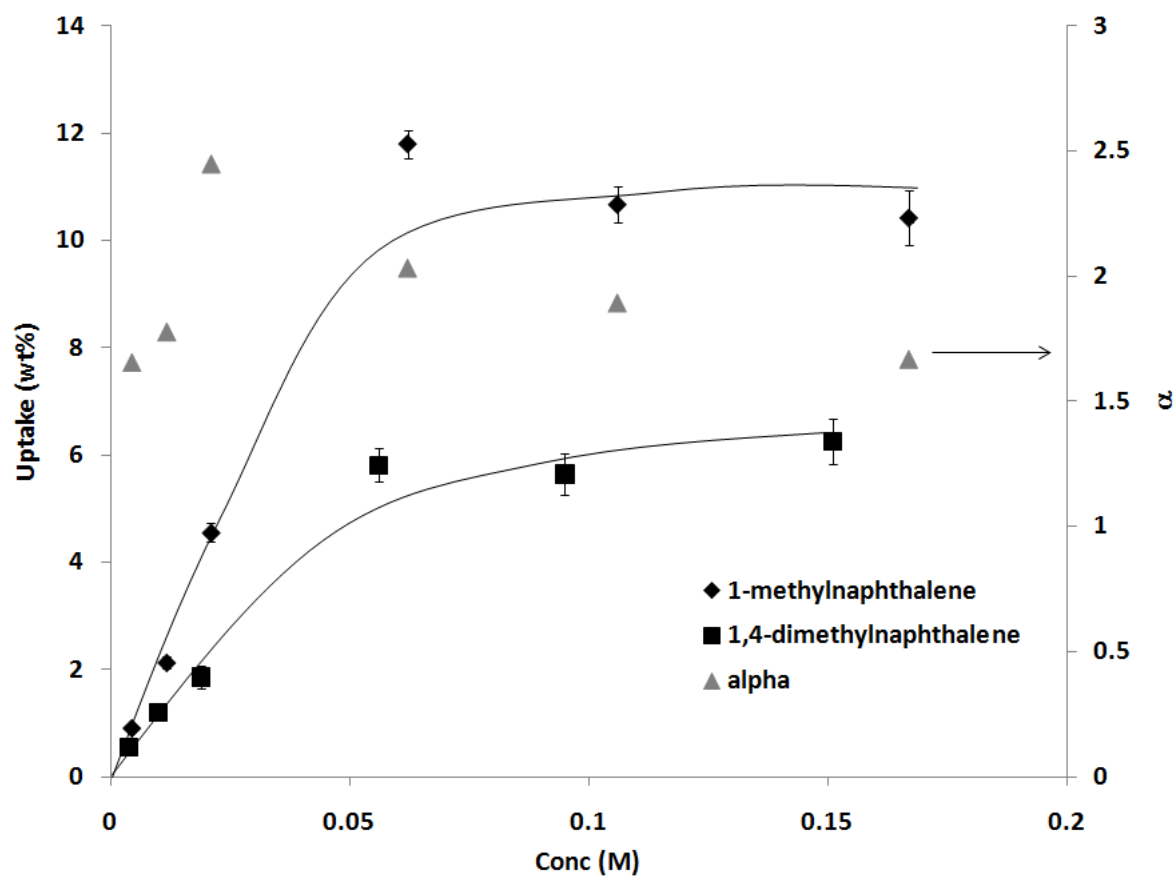


Figure S6. Competitive adsorption on [Cu₂(BDC)₂(dabco)] in batch mode: uptake (wt%) from an equimolar mixture of 1-methylnaphthalene and 1,4-dimethylnaphthalene in heptane at room temperature as a function of equilibrium liquid phase concentration of each compound. Separation factors α are given on the right axis.