Isolation of cucurbit[n]uril homologues with imidazolium salts in a recyclable manner

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Supporting Information

Both 20% DCl and the NH₄PF₆ salt are from Alfa Aesar. [C_nmim]Br was synthesised from methyl imidazole (Aldrich) and the appropriate 1-bromo alkyl (Aldrich). [Npmim]Br was synthesised from methyl imidazole (Aldrich) and 2-(bromomethyl) naphthalene (Aldrich). A solution of 1-methyl imidazole (1.47 g, 18 mmol) and 2-(bromomethyl) naphthalene (4.42 g, 20 mmol) (or appropriate 1-bromo alkyl) was refluxed in 100 mL of toluene until a large amount insoluble product was formed. The insoluble compound was isolated and washed with toluene. The starting CB[5]/CB[7] and CB[6]/CB[8] mixtures used in these experiments were synthesised from glycoluril with formaldehyde by basic procedures published by Day and Kim.[1, 2] NMR spectra were recorded on a Bruker DRX-400, and chemical shifts are quoted in parts per million relative to residual proteo species.

CB[5]/CB[7] isolation procedure

The mixture of CB[5] and CB[7] (5 g, including 4 mmol CB[7]) was dissolved in 220 mL water and followed by filtration to removed the insoluble solid. $[C_4mim]Br$ (4.5 mmol, 1 g) was added into the solution. Then, NH₄PF₆ salt was used to exchange the Br counter ion and resulted in the precipitation of CB[7]-[C₄mim]PF₆ as a complex, which was isolated by centrifugation. CB[5] remained in the aqueous solution, which was concentrated and precipitated to yield crude CB[5] solid. The crude CB[5] was further purified by washing with MeOH, and recrystallised in water.

The CB[7]-[C₄mim]PF₆ complex was mixed with [C₄mim]Br (5 mmol, 1.1 g) in 200 mL water and the solution was heated to 80 $^{\circ}$ C until most of the solid dissolved. After the counter ion was exchanged from PF₆ to Br, the CB[7]-[C₄mim]Br complex was precipitated from the solution by addition of MeOH. Finally, CB[7] was purified from CB[7]-[C₄mim]Br complex by SSM decomplexation as depicted in the main article.

CB[6]/CB[8] isolation procedure

A 2 g mixture of CB[6] and CB[8] (appx.18% CB[8], 0.3 g) was dissolved in 200 mL water with [Npmim]Br (0.14 g). The insoluble solid, which was mainly CB[6], was then isolated by centrifugation while the soluble CB[8]-([Npmim]Br)₂ complex remained in the aqueous solution. The crude CB[6] (appx. 1.7 g) was dissolved in water with [C₄mim]Br (0.56 g). CB[6] was then separated from the CB[6]-[C₄mim]Br complex by SSM decomplexation as depicted in the main text.

The CB[8]-([Npmim]Br)₂ complex was precipitated from solution with addition of NH_4PF_6 salt (0.1 g). The solid CB[8]-([Npmim]PF_6)₂ complex was subsequently re-dissolved in an aqueous solution containing [Npmim]Br (0.2 g) at 80 °C for two hours. After ion exchange from PF₆ back to Br, the solution was

cooled down and extracted with DCM to remove $[Npmim]PF_6$ salts from the solution. The CB[8]-([Npmim]Br)₂ complex was precipitated by MeOH and isolated by centrifugation. Finally, CB[8] was separated from the CB[8]-([Npmim]Br)₂ complex by SSM decomplexation as depicted in the main text.

Recycling the imidazolium salts, organic solvents and non-purified CB[n]

The imidazolium salts were first separated and purified forming the "waste" material as discussed in the main text, the organic solvents, MeOH and DCM (collected from each purification steps) were isolated by standard distillation procedures. Experimentally, more than 70% of all the organic solvents used could be recycled, with any loss caused by evaporation during the isolation procedures. When all the solvents were removed, the remaining solid (mainly CB[n]) was kept and used in the next CB[n] isolation cycle.

References

[1] J. Kim, I.-S. Jung, S.-Y. Kim, E. Lee, J.-K. Kang, S. Sakamoto, K. Yamaguchi and K. Kim, *J. Am. Chem. Soc.*, 2000, **122**, 540-541.

[2] A. I. Day, A. P. Arnold, R. J. Blanch and B. Snushall, J. Org. Chem., 2001, 66, 8094-8100.



Figure 1: Detail procedure of isolation CB[6] and CB[8].

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Figure 2: Detail procedure of isolation CB[5] and CB[7].

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Figure 3: 1 H NMR spectra following SSM decomplexation of [C₂mim]Br-CB[6].



Figure 4: ¹H NMR spectra following SSM decomplexation of ([Npmim]Br)₂-CB[8].



Figure 5: ¹H NMR spectrum of recycled [C₂mim]PF₆ (in MeOD) after extraction with DCM from water.



Figure 6: ¹H NMR spectrum of CB[5] in D_2O .



Figure 7: ¹3C NMR spectrum of CB[5] in D_2O .

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Figure 8: ¹H NMR spectrum of CB[7] in D_2O .



Figure 9: ¹3C NMR spectrum of CB[7] in D_2O .