“Choose-a-Size” Control in the Synthesis of Sucrose Based Urea and Thiourea
Macrocycles
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1. The synthesis of monomeric macrocyclic derivative 3 in a flow mode

![Diagram of the synthesis of monomeric macrocyclic derivative 3]

2. The synthesis of monomeric macrocyclic derivative 5 in a flow mode

![Diagram of the synthesis of monomeric macrocyclic derivative 5]
2. Copies of NMR spectra

**a)**

Fig. S1. $^1$H NMR (600 MHz) and $^{13}$C NMR (151 MHz) spectra of compound 2a in DMF-$d_6$. 

**b)**
Fig. S2. COSY (¹H-¹H) spectra of compound 2a in DMF-d₆.
Fig. S3. HSQC (\textsuperscript{1}H-\textsuperscript{13}C) spectra of compound 2a in DMF-\textit{d}_6.
**Fig. S4.** $^1$H NMR (600 MHz) and $^{13}$C NMR (151 MHz) spectra of compound 2b in acetone-$d_6$. 
Fig. S5. COSY ($^1$H-$^1$H) spectra of compound 2b in acetone-$d_6$. 
Fig. S6. HSQC ($^1$H-$^{13}$C) spectra of compound 2b in acetone-$d_6$. 
Fig. S7. $^1$H NMR (600 MHz) and $^{13}$C NMR (151 MHz) spectra of compound 3 in acetone-$d_6$. 
Fig. S8. COSY (¹H-¹H) spectra of compound 3 in acetone-$d_6$. 
Fig. S9. HSQC ($^1$H-$^{13}$C) spectra of compound 3 in acetone-$d_6$. 
Fig. S10. $^1$H NMR (600 MHz) and $^{13}$C NMR (151 MHz) spectra of compound 3 in acetone-$d_6$. 
Fig. S11. COSY (1H-1H) spectra of compound 5 in acetone-$d_6$. 
Fig. S12. HSQC (\(^1\)H-\(^{13}\)C) spectra of compound 5 in acetone-\(d_6\).
3. Titration experiments

All solutions were prepared in the HPLC gradient-grade acetonitrile. TBA salts (TBAHCl, TBAH$_2$PO$_4$, CH$_3$COOTBA, and PhCOOTBA) were dried overnight at room temperature under high vacuum (1 mbar) directly before use. A 1 cm cuvette was filled with ~2.2 mL of the host solution and aliquots of the guest solution were added by a syringe pump. UV-Vis spectrum was recorded after each step once the mixture was homogenised by magnetic stirrer (30 s). The collected data were then analysed by HyperSpec. In case of hosts 3 and 5, addition of guest had no effect on the spectra. In case of 2a and 2b the data were fitted with 1:1 and 1:1+1:2 models. Low values of the residuals are obtained with simple 1:1 model and no significant improvement in fitting quality is observed with 1:1+1:2 model. The residuals are most likely to arise from small errors in concentrations of the reagents.
Fig. 13 Plots of UV-Vis titration of host 2a with TBACl.
Fig. 14 Plots of UV-Vis titration of host 2a with AcOTBA.
**2b + Cl⁻**

C₀(Host) 4.82E-5 M  
C₀(Guest) 0.0372 M  
V₀ 2.235 mL  
titration steps: 10x2.5ul, 10x5ul, 10x10ul  
Kₐ = 520 M⁻¹

**Fig. 15** Plots of UV-Vis titration of host 2b with TBACl.
2b + AcO⁻

C₀(Host)  4.82E-5 M
C₀(Guest)  0.0155 M
V₀        2.237 mL
titration steps:
10x2.5µl, 10x5µl, 10x10µl

Kₐ = 28 800 M⁻¹

Fig. 16 Plots of UV-Vis titration of host 2b with AcOTBA.
4. Single crystal X-ray measurement

Single crystal X-ray diffraction measurements were carried out on a Agilent Supernova diffractometer, at 100K with monochromated Mo Kα radiation (0.7107Å). The data reduction was made by using CrysAlisPRO [1] software. The structures were solved by direct methods and refined on F² by full-matrix least-squares by using SHELXS97 and SHELXL97 [2]. All non-hydrogen atoms were refined as anisotropic while hydrogen atoms were placed in calculated positions, and refined in riding mode.

Crystal of 3. orthorhombic, P212121, a= 11.1611(7), b=18.4375(11), c= 23.2735(12)Å, V= 4789.3(5)Å³, Z=4, D_{calc}=1.385g cm⁻¹, μ=1.782 mm⁻¹, R1=0.0635 for 6643 [ Fo > 4σ(Fo)] and 0. 1075 for all data, wR²=0. 1795, S=0. 911

CCDC 1584391 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif

5. References