

Electronic Supplementary Information

Enantioselective Extraction Mediated by a Chiral Cavitand-Salen Covalently Assembled on a Porous Silicon Surface

Alessandro D'Urso, Cristina Tudisco, Francesco P. Ballistreri, Guglielmo G. Condorelli, Rosalba Randazzo, Gaetano A. Tomaselli, Rosa M. Toscano, Giuseppe Trusso Sfrazzetto and Andrea Pappalardo

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General

The NMR experiments were carried out at 27° C on a Varian UNITY Inova 500 MHz spectrometer (¹H at 499.88 MHz, ¹³C-NMR at 125.7 MHz) equipped with pulse field gradient module (Z axis) and a tuneable 5 mm Varian inverse detection probe (ID-PFG). ESI mass spectra were acquired on a ES-MS Thermo-Finnigan LCQ-DECA using MeOH (positive ion mode). CD and UV experiments are carried out by spectropolarimeter JASCO J-710, and spectrophotometer JASCO V-530. α -methyl-4-bromophenyl-benzyl amine and Methyl iodide were purchased by Sigma Aldrich. XPS spectra were run with a PHI 5600 multitechnique ESCA-Auger spectrometer equipped with a monochromated Al K α X-ray source. Analyses were carried out with a photoelectron angle of 45° (relative to the sample surface) with an acceptance angle of $\pm 7^\circ$. The XPS binding energy (B.E) scale was calibrated by centering the C 1s peak due to hydrocarbon moieties and “adventitious” carbon at 285.0 eV^[1]. Racemic mixture of ammonium salt (**Br-MBA**) was prepared dissolving in ultra pure water (obtained with Purelab Flex Elga system by Veolia) the solid.

Synthesis of (\pm)-*N,N,N*-trimethyl- α -methyl-*p*-bromo-benzylammonium iodide (**Br-MBA**)

A solution of α -methyl-4-bromophenyl-benzyl amine in methanol (0.06 M) was stirred in the presence of K₂CO₃ (3 eq.) for 30 minutes at room temperature under nitrogen atmosphere. Then, 6 eq. of CH₃I were added and the mixture was vigorously stirred overnight. The solvent was removed under reduced pressure, the permethylated compound was extracted with DMSO, and after filtration and concentration it was precipitated by addition of dry THF (yield 80%). ¹H NMR (500 MHz, CDCl₃) δ 7.56-7.62 (m, 4H, ArH), 5.46 (q, *J* = 7.5 Hz, 1H, CH), 3.35 (s, 9H, N(CH₃)₃), 1.84 (d, *J* = 7.5 Hz, 3H, CH₃). ESI-MS *m/z* 242 [M]⁺. Anal. Calcd. for C₁₁H₁₇BrIN: C, 35.70; H, 4.63; Br, 21.59; I, 34.29; N, 3.78. Found: C, 35.45; H, 4.53; Br, 21.41; I, 34.13; N, 3.71.

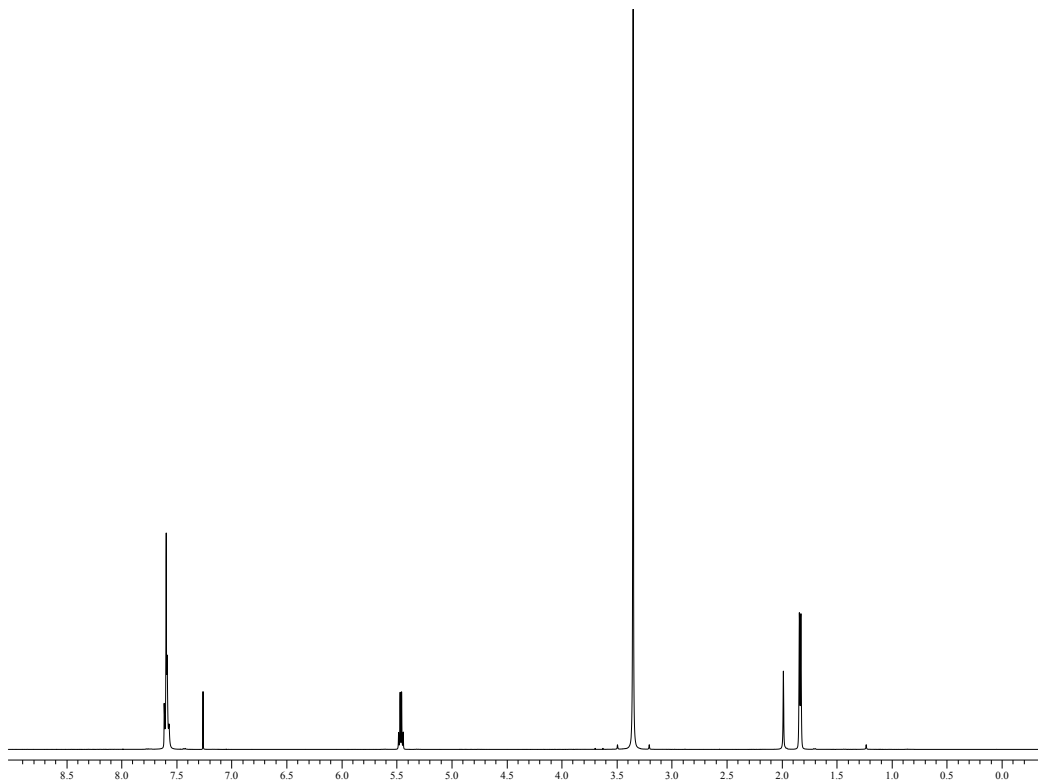


Figure S1: ¹H NMR spectrum of **Br-MBA** in CDCl₃

Porous Silicon (PSi) preparation

Porous silicon (PSi) has been obtained by wet metal-assisted chemical etching according to the procedure reported by Chartier et al.^[2] Silver particles were deposited on the surfaces of the Si(100) *p*-doped (Boron doped, resistivity 1.5-4 Ω cm) by immersing the samples in an aqueous solution of HF (0.14 M) and AgNO₃ (5x10⁻⁴ M) for 5 min. The slides were then etched in aqueous solutions containing HF, H₂O₂ and pure H₂O (40% HF, 30% H₂O₂ and H₂O in a 25:10:4 ratio) for 1 min, and after etching the samples were rinsed with ultra-pure water and dried with prepurified N₂.

This method allows the reproducible preparation of PSi with easily accessible columnar pores formed according to the literature along the (100) direction.^[3]

To graft **SalCav** onto porous substrates, PSi was etched in 10% HF solution for 1 h, washed with ultra-pure water for 20 s, dried with N₂, and immediately placed in the deoxygenated solution of **SalCav**. The solution was then refluxed at 200 °C for 5 h, with a slow stream of N₂ bubbling through the solution to prevent bumping. After grafting, both the sample was removed from the solution of **SalCav** (after cooling to room temperature) and cleaned by two rinsing cycles of ultrasonic cleaner (5 min each) in dichloromethane.

Procedure for the Br-MBA extraction

PSi-SalCav was dipped into 2 mL of racemic mixture of **R/S-Br-MBA** (1 mM). After two hours, **PSi-SalCav** was removed and XPS analysis was performed to detect the presence of the guest. The resulting solution of **Br-MBA** was diluted from 1 mM to 30 μM and then analyzed by UV and CD measurements. Decomplexation was performed by immersing the **PSi-SalCav•Br-MBA** in 2 mL of water for 15 min. Whole decomplexation was confirmed combining XPS analysis of the **PSi-SalCav**, and the CD analysis of the remaining water solution.

XPS and CD data using an unfunctionalized PSi surface

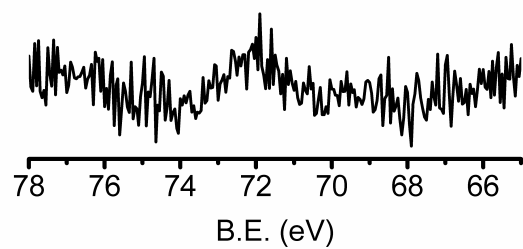


Figure S2: Br 3d XPS spectral region of the unfunctionalized PSi surface after the dipping in the **Br-MBA** solution for 2h.

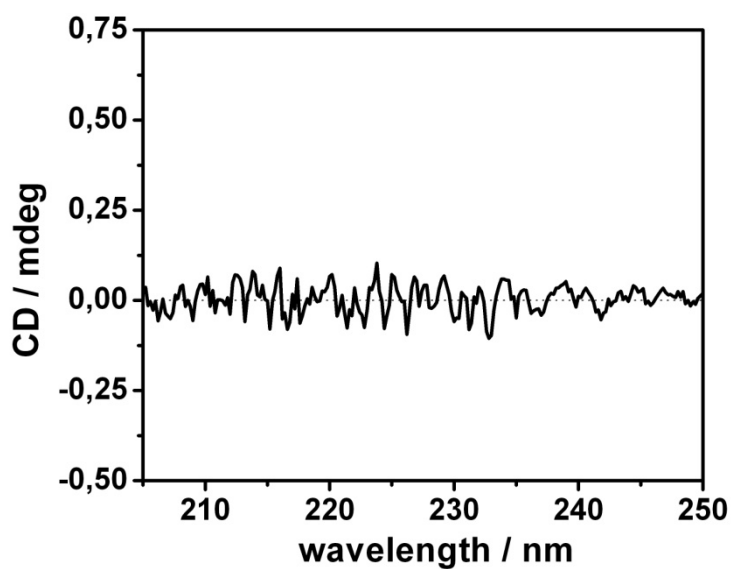


Figure S3: CD spectra of the solution of **Br-MBA** after the dipping of the unfunctionalized PSi surface for 2h.

CD calibration of Br-MBA

To determinate the concentration of the **R-Br-MBA** pure salt in excess after the immersion for two hours of **Psi-SalCav**, we performed a CD spectra of **R-Br-MBA** solution at different concentrations (Figure S3), then we reported the CD values vs solution concentrations, obtaining a strait line (Figure S4). From equation $y = a + bx$, using $a = 0,07618$ and $b = 0,0503$ we calculate the corresponding value of concentration for CD signal of 0,2410, which is the value of CD signal of the racemate solution after two hours immersion of **Psi-SalCav**, getting as a result 3,28 μM .

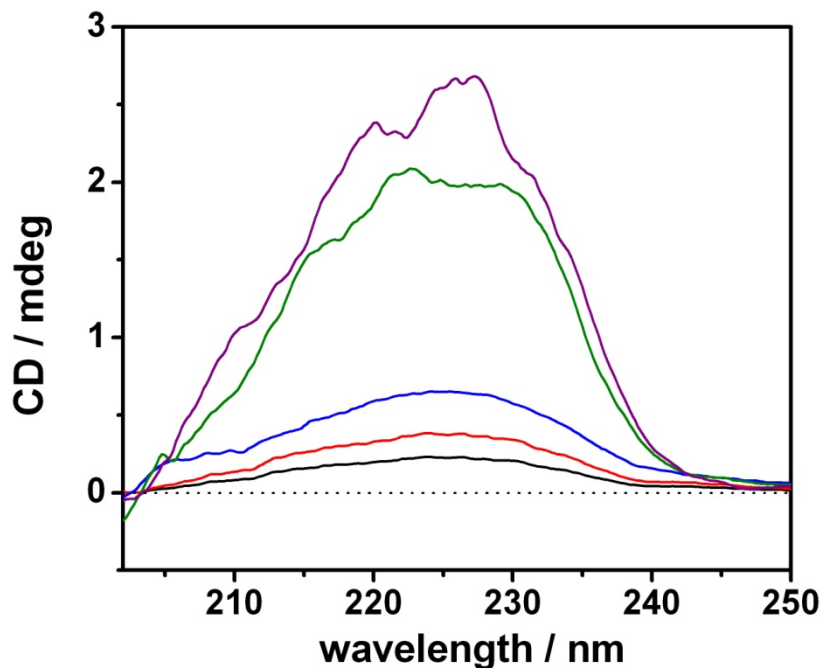


Figure S4: CD spectra of **R-BrMBA** salt at different concentration: 3 μM (balck curve), 5 μM (red curve), 10 μM (blue curve), 40 μM (green curve), 50 μM (purple curve).

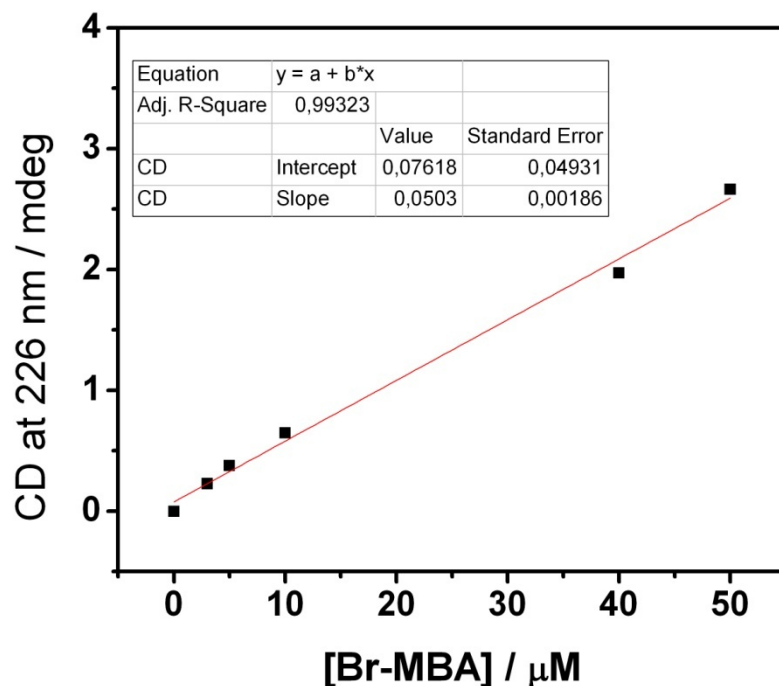


Figure S5: Graphic reporting CD signal at 226 nm vs concentration of **R-Br-MBA** salt. Inset shows the fitting equation used

UV spectra of Br-MBA solution after extraction

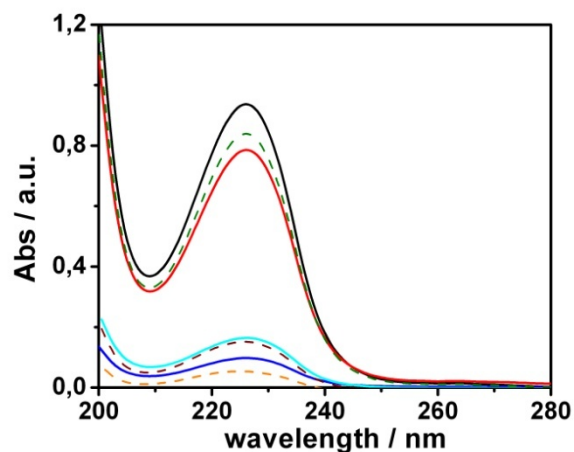


Figure S6: UV spectra of: a) **Br-MBA** salt racemic solution 30 μM (black curve, Abs λ_{max} 0.91); b) **R-Br-MBA** enantiomer 3 μM (blue curve); c) subtraction of spectra *a* minus *b* (dashed green curve, Abs λ_{max} 0.84); d) **Br-MBA** salt racemic solution after two hours dipping of modified substrate (red curve, Abs λ_{max} 0.79); e) subtraction of spectra *c* minus *d* (dashed orange curve); f) desorbed solution (cyan curve); g) sum of spectra *e* plus *b* (dashed brown curve).

Reversibility experiments

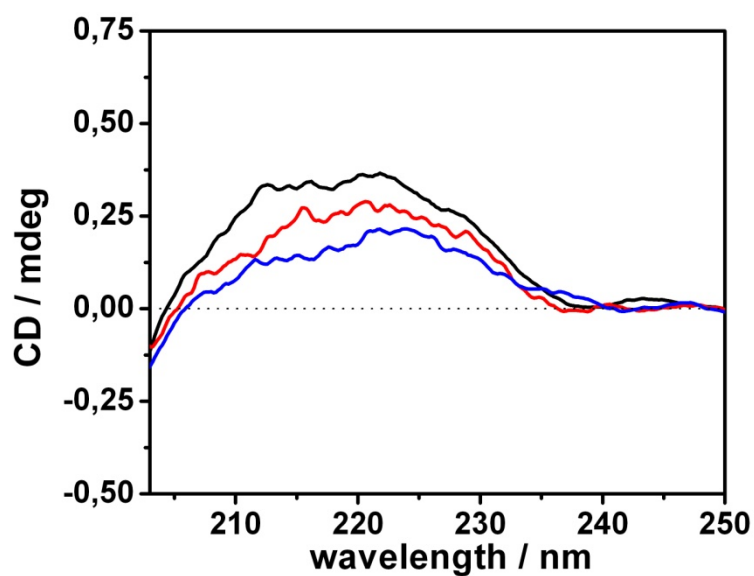


Figure S7: CD spectra of three solutions of **Br-MBA** after 2 hours immersion of **PSi-SalCav** surface.

[¹] a) I. L. Swift, *Surf. Interface Anal.* **1982**, *4*, 47–51; b) D. Briggs, G. Beamson, *Anal. Chem.* **1992**, *64*, 1729–1736.

[²] C. Chartier, S. Bastide, C. Lèvy-Clément, *Electrochim. Acta* **2008**, *53*, 5509–5516.

[³] Z. Huang, N. Geyer, P. Werner, J. de Boor, U. Gösele, *Adv. Mater.* **2011**, *23*, 285–308.