Supplementary Information

Poly(methyl methacrylate)s with pendant calixpyrroles: Polymeric extractants for halide anion salts

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Mono-hydroxyl functionalized calix[4]pyrrole (2)

In a 25 mL round bottom flask, the respective calix[4]pyrrole ethyl ester\(^1\) (500 mg, 1.027 mmol) was first dissolved in 10 mL THF and placed under an atmosphere of Ar. After adding NaBH\(_4\) (233 mg, 6.165 mmol) in a single portion, the resulting mixture was heated to reflux for 15 min. To the hot mixture, 10 mL of dry MeOH was added dropwise over the course of 15 min. After 24 h of additional heating at reflux, the reaction was cooled to ambient temperature and quenched with 20 mL of an aqueous solution saturated with ammonium chloride. The organic components were then extracted with CH\(_2\)Cl\(_2\) (3 x 20 mL) and dried over Na\(_2\)SO\(_4\). The crude product was then purified by column chromatography (silica gel; eluent: 80:20 CH\(_2\)Cl\(_2\):hexanes gradually changing to 10:90 MeOH:CH\(_2\)Cl\(_2\)) which, after removal of residual solvent, afforded 343 mg of 2 as a yellow solid (75% yield). \(R_f = 0.15\) (80:20 CH\(_2\)Cl\(_2\):hexanes); \(^1\)H NMR (500 MHz, CDCl\(_3\)): 1.42 (s, 3H, \textit{meso}-CH\(_3\)), 1.51-1.55 (m, 18H, \textit{meso}-CH\(_3\)), 1.94 (t, 1H, \(J = 5\) Hz, OH), 3.85 (d, 2H, \(J = 5\)Hz, \textit{meso}-CH\(_2\)), 5.90-5.96 (m, 8H, pyrrole CH), 7.11 (br s, 2H, NH), 7.57 (br s, 2H, NH); \(^{13}\)C NMR (100 MHz, CDCl\(_3\)): 24.76, 28.33, 29.45, 41.19, 69.83, 102.65, 102.91, 103.06, 103.37, 134.36, 138.21, 138.46, 138.82; HRMS (CI) calcd for C\(_{28}\)H\(_{37}\)N\(_4\)O \([\text{M+H}^+\]): 445.2967, found: 445.2966. This compound was further characterized by single crystal X-ray diffraction analysis.

Methacrylate functionalized calix[4]pyrrole (3)

A 25 mL round bottom flask was charged with 250 mg (0.56 mmol) of alcohol 2, triethylamine (97.5 µL, 0.7 mmol) and 10 mL of dry, degassed THF. After cooling the flask to 0 °C using an ice bath, methacryloyl chloride (60 µL, 0.62 mmol) was added dropwise via syringe. The reaction was then allowed to warm to ambient temperature over the course of 24 h. After 50 mL of water was added, the mixture was extracted with CH\(_2\)Cl\(_2\) (3 x 20 mL). The organic layer was then dried over Na\(_2\)SO\(_4\) and filtered. The crude product was then purified by column chromatography (silica gel; eluent: CH\(_2\)Cl\(_2\)) which, after removal of residual solvent, afforded 236 mg of 3 as a white powder (82% yield). \(R_f = 0.80\) (CH\(_2\)Cl\(_2\)); \(^1\)H NMR (500 MHz, CD\(_2\)Cl\(_2\)): 1.45-1.52 (m, 18H, \textit{meso}-CH\(_3\) protons), 1.87 (dd, 3H, CH\(_3\)), 4.34 (s, 2H, CH\(_2\)), 5.55 (m, 1H, CH), 5.84-5.92 (m, 8H, pyrrole CH), 5.97 (m, 1H, CH), 7.03 (br s, 2H, NH), 7.11 (br s, 2H, NH); \(^{13}\)C NMR (100 MHz, CDCl\(_3\)): 18.40, 28.92, 29.27, 33.34, 39.43, 70.59, 102.74, 102.88, 103.08, 104.18, 133.18, 138.31, 138.51, 138.86, 191.65; HRMS (CI) calcd for C\(_{32}\)H\(_{41}\)N\(_4\)O\(_2\) \([\text{M+H}^+\]): 513.3230, found: 513.3232. This compound was further characterized by single crystal X-ray diffraction analysis.

**Homopolymer (5)**

Homopolymer 5 was prepared by dissolving monomer 3 in THF (0.3 M) followed by treatment with 1 mol% of azoisobutyronitrile (AIBN). After stirring at 70 °C for 17 h under an nitrogen atmosphere, the resulting viscous solution was added dropwise into an excess of methanol that rapidly stirred. This caused precipitation of polymer 5, which was subsequently isolated via filtration in 66% yield as a yellow solid. Using gel permeation chromatography, the polymer was found to have a number-average molecular weight ($M_n$) of 23,600 Da (relative to PMMA standards) and a polydispersity index (PDI) of 2.3. $^1$H NMR (500 MHz, CD$_2$Cl$_2$): 0.34-0.95 (br s, 2H, polymer backbone CH$_2$), 1.25-1.85 (br m, 24H, meso-CH$_3$ and polymer backbone CH$_3$), 4.15 (br s, 2H, meso-CH$_2$), 5.89 (br s, 8H, pyrrole CH), 7.12 (br s, 4H, NH).

**Copolymer (6)**

Using the conventional free radical polymerization conditions described above, a 77% yield of copolymer 6 was obtained as a white solid from a 1:10 mixture of 3 and MMA. Using GPC, 6 was found to possess a $M_n$ of 85,500 Da and a PDI of 2.1 (relative to PMMA standards). $^1$H NMR (500 MHz, CD$_2$Cl$_2$): 0.82 (br s, 30H, polymer backbone CH$_2$), 0.99 (br s, 13.21H, polymer backbone CH$_2$), 1.52-1.55 (br m, 29.13H, calixpyrrole meso-CH$_3$), 1.80-1.88 (br m, 25.76H, MMA CH$_3$), 3.58 (br s, 43.57H, MMA CH$_3$), 4.11 (br s, 2H, calixpyrrole meso-CH$_2$), 5.89-5.95 (br m, 8H, pyrrole CH), 7.11 (br s, 4H, NH).
$^1$H NMR Spectrum of Calix[4]pyrrole 2
\(^{13}\text{C}\) NMR Spectrum of Calix[4]pyrrole 2
$^1$H NMR Spectrum of Calix[4]pyrrole 3
$^{13}$C NMR Spectrum of Calix[4]pyrrole 3
$^1$H NMR Spectrum of Polymer 5
$^1$H NMR Spectrum of Copolymer 6
$^1$H NMR Spectrum of (a) in Figure 3
$^1$H NMR Spectrum of (b) in Figure 3
$^1$H NMR Spectrum of (d) in Figure 3
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$^1$H NMR Spectrum of (b) in Figure 4
$^1$H NMR Spectrum of (d) in Figure 4
Figure S1. Thermogravigram of a PMMA homopolymer taken under an atmosphere of nitrogen at a scan rate = 10 °C/min.
Figure S2. Thermogravigram of a polymer 5 taken under an atmosphere of nitrogen at a scan rate = 10 °C/min.
Figure S3. Thermogravigram of copolymer 6 taken under an atmosphere of nitrogen at a scan rate = 10 °C/min.
Figure S4. Thermogravigram of a PMMA homopolymer (control), after being exposed to TBAF as described in the text, taken under an atmosphere of nitrogen at a scan rate = 10 °C/min.
Figure S5. Thermogravigram of a PMMA homopolymer (control), after being exposed to TBACl as described in the text, taken under an atmosphere of nitrogen at a scan rate = 10 °C/min.
Figure S6. Thermogravigram of copolymer 5, after being exposed to TBACL as described in the text, taken under an atmosphere of nitrogen at a scan rate = 10 °C/min.
Figure S7. Thermogravigram of copolymer 5, after being exposed to TBAF as described in the text, taken under an atmosphere of nitrogen at a scan rate = 10 °C/min.
**X-ray Experimental for C_{28}H_{36}N_{4}O – 1/3 CH_{2}Cl_{2} (2)**

Crystals grew as pale yellow lathes by colorless laths by vapor diffusion of hexanes into a dichloromethane solution of the calixpyrrole. The data crystal was a long lathe that had approximate dimensions; 0.34 x 0.13 x 0.04 mm. The data were collected on a Nonius Kappa CCD diffractometer using a graphite monochromator with MoKα radiation (λ = 0.71073Å). A total of 341 frames of data were collected using ω-scans with a scan range of 1.2° and a counting time of 198 seconds per frame. The data were collected at 153 K using an Oxford Cryostream low temperature device. Data reduction were performed using DENZO-SMN. The structure was solved by direct methods using SIR97 and refined by full-matrix least-squares on F^2 with anisotropic displacement parameters for the non-H atoms using SHELXL-97. The hydrogen atoms on carbon were calculated in ideal positions with isotropic displacement parameters set to 1.2xUeq of the attached atom (1.5xUeq for methyl hydrogen atoms).

The hydroxyl group was disordered in two of the three calixpyrrole molecules. In one calixpyrrole, the hydroxyl group was disordered over two different methyl groups. In the second calixpyrrole, the disorder amounted to a conformational difference on the same methyl group.

The disorder was modeled in the same way for both groups. The site occupancy factor for one oxygen atom was assigned the variable x. The site occupancy factor for the alternate oxygen atom was assigned to (1-x). A common isotropic displacement parameter was refined for both oxygen atoms while refining the site occupancy factor. The C-O bond lengths and the C-C-O bond angles were restrained to be equivalent throughout the refinement.

The function, Σw(|F_o|^2 - |F_c|^2)^2, was minimized, where w = 1/[(σ(F_o))^2 + (0.0546*P)^2 + (1.9114*P)] and P = (|F_o|^2 + 2|F_c|^2)/3. R_w(F^2) refined to 0.234, with R(F) equal to 0.0833 and a goodness of fit, S = 1.05. Definitions used for calculating R(F), R_w(F^2) and the goodness of fit, S, are given below. The data were corrected for secondary extinction effects. The correction takes the form: F_corr = kF_c/[1 + (4.0(4)x10^-6)* F_c^2 λ^3/(sin2θ)]^0.25 where k is the overall scale factor. Neutral atom scattering factors and values used to calculate the linear absorption
coefficient are from the International Tables for X-ray Crystallography (1992). All figures were generated using SHELXTL/PC.7

Figure S8. Diagram of 2. Displacement ellipsoids were drawn at the 50% probability level.
X-ray Experimental for C_{32}H_{40}N_{4}O_{2} - CH_{2}Cl_{2} (3)

Crystals grew as colorless prisms by slow evaporation from dichloromethane. The data crystal was cut from a larger crystal and had approximate dimensions; 0.30 x 0.26 x 0.14 mm. The data were collected on a Nonius Kappa CCD diffractometer using a graphite monochromator with MoKα radiation (λ = 0.71073Å). A total of 242 frames of data were collected using ω-scans with a scan range of 2° and a counting time of 74 seconds per frame.

The data were collected at 153 K using an Oxford Cryostream low temperature device. Data reduction were performed using DENZO-SMN.2 The structure was solved by direct methods using SIR973 and refined by full-matrix least-squares on F^2 with anisotropic displacement parameters for the non-H atoms using SHELXL-97.4 The hydrogen atoms were calculated in ideal positions with isotropic displacement parameters set to 1.2xUeq of the attached atom (1.5xUeq for methyl hydrogen atoms).

The function, Σw(|Fo|^2 - |Fc|^2)^2, was minimized, where w = 1/[(σ(Fo))^2 + (0.0483*P)^2 + (1.4744*P)] and P = (|Fo|^2 + 2|Fc|^2)/3. Rw(F^2) refined to 0.150, with R(F) equal to 0.0574 and a goodness of fit, S, = 1.08. Definitions used for calculating R(F), Rw(F^2) and the goodness of fit, S, are given below.5 The data were corrected for secondary extinction effects. The correction takes the form: Fcorr = kFc/[1 + (4.4(14)x10^-6)* Fc^2 λ^3/(sin2θ)]0.25 where k is the overall scale factor.

Neutral atom scattering factors and values used to calculate the linear absorption coefficient are from the International Tables for X-ray Crystallography (1992).6 All figures were generated using SHELXTL/PC.7
**Figure S9.** Diagram of 3. Displacement ellipsoids were drawn at the 50% probability level.

**References**


5) $R_w(F^2) = \frac{\sum w(|F_o|^2 - |F_c|^2)^2}{\sum w(|F_o|)^2}^{1/2}$ where w is the weight given each reflection. $R(F) = \Sigma (|F_o| - |F_c|)/\Sigma |F_o|$ for reflections with $F_o > 4(\sigma(F_o))$. $S = \frac{\sum w(|F_o|^2 - |F_c|^2)^2}{(n - p)}^{1/2}$, where n is the number of reflections and p is the number of refined parameters.
