

Supplementary Materials

Simple one-pot synthesis of shape-persistent macrocycles with alkoxy side chains based on imine dynamic covalent chemistry

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Experimental procedures

Scheme S1. Synthesis of 3,7-dimethyloctan-1-ol.

Scheme S2. Synthesis of 1-bromo-3,7-dimethyloctane.

Scheme S3. Synthesis of 1-bromo-2-(2-(2-methoxyethoxy)ethoxy)ethane.

Figure S1. ^1H -NMR spectrum of 3,7-dimethyloctan-1-ol.

Figure S2. ^{13}C -NMR spectrum of 3,7-dimethyloctan-1-ol.

Figure S3. ^1H -NMR spectrum of 1-bromo-3,7-dimethyloctane.

Figure S4. ^{13}C -NMR spectrum of 1-bromo-3,7-dimethyloctane.

Figure S5. ^1H -NMR spectrum of 1-bromo-2-(2-(2-methoxyethoxy)ethoxy)ethane.

Figure S6. ^{13}C -NMR spectrum of 1-bromo-2-(2-(2-methoxyethoxy)ethoxy)ethane.

Figure S7. ^1H -NMR spectrum of 2-octyloxy-5-nitrobenzaldehyde.

Figure S8. ^{13}C -NMR spectrum of 2-octyloxy-5-nitrobenzaldehyde.

Figure S9. ^1H -NMR spectrum of 2-(3,7-dimethyloctyloxy)-5-nitrobenzaldehyde.

Figure S10. ^{13}C -NMR spectrum of 2-(3,7-dimethyloctyloxy)-5-nitrobenzaldehyde.

Figure S11. ^{13}C -NMR(DEPT-135) spectrum of 2-(3,7-dimethyloctyloxy)-5-nitrobenzaldehyde.

Figure S12. H,H-cosy spectrum of 2-(3,7-dimethyloctyloxy)-5-nitrobenzaldehyde.

Figure S13. H,H-cosy spectrum of 2-(3,7-dimethyloctyloxy)-5-nitrobenzaldehyde (expanded).

Figure S14. C,H-cosy spectrum of 2-(3,7-dimethyloctyloxy)-5-nitrobenzaldehyde.

Figure S15. C,H-cosy spectrum of 2-(3,7-dimethyloctyloxy)-5-nitrobenzaldehyde. (expanded)

Figure S16. ^1H -NMR spectrum of 2-(2-(2-(2-methoxyethoxy)ethoxy)ethoxy)-5-nitrobenzaldehyde.

Figure S17. ^{13}C -NMR spectrum of 2-(2-(2-(2-methoxyethoxy)ethoxy)ethoxy)-5-nitrobenzaldehyde.

Figure S18. H,H-cosy spectrum of 2-(2-(2-(2-methoxyethoxy)ethoxy)ethoxy)-5-nitrobenzaldehyde.

Figure S19. H,H-cosy spectrum of 2-(2-(2-(2-methoxyethoxy)ethoxy)ethoxy)-5-nitrobenzaldehyde. (expanded)

Figure S20. C,H-cosy spectrum of 2-(2-(2-(2-methoxyethoxy)ethoxy)ethoxy)-5-nitrobenzaldehyde.

Figure S21. C,H-cosy spectrum of 2-(2-(2-(2-methoxyethoxy)ethoxy)ethoxy)-5-nitrobenzaldehyde. (expanded)

Figure S22. ^1H -NMR spectrum of 2-octyloxy-5-nitrobenzaldehyde diethyl acetal.

Figure S23. ^{13}C -NMR spectrum of 2-octyloxy-5-nitrobenzaldehyde diethyl acetal.

Figure S24. ^1H -NMR spectrum of 2-(3,7-dimethyloctyloxy)-5-nitrobenzaldehyde diethyl acetal.

Figure S25. ^{13}C -NMR spectrum of 2-(3,7-dimethyloctyloxy)-5-nitrobenzaldehyde diethyl acetal.

Figure S26. ^1H -NMR of 2-(2-(2-(2-methoxyethoxy)ethoxy)ethoxy)-5-nitrobenzaldehyde

diethylacetal.

Figure S27. ^{13}C -NMR of 2-(2-(2-(2-methoxyethoxy)ethoxy)ethoxy)-5-nitrobenzaldehyde diethylacetal.

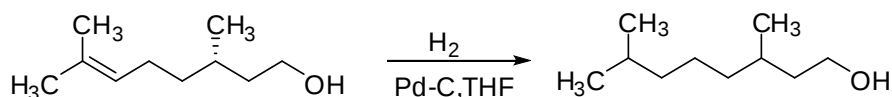
Figure S28. FT-IR spectrum of hexakis(2-octyloxy-1,5-phenyleneimine) macrocycle OcO-Cm6.

Experimental procedures

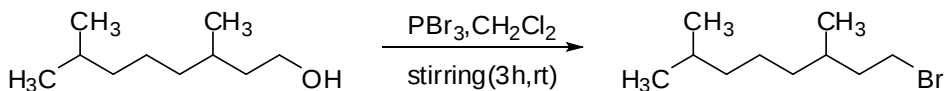
Synthesis of (S)-(-)-1-bromo-3,7-dimethyloctane

(-)- β -citronellol ((S)-(-)-3,7-dimethyl-6-octen-1-ol) (20.0 g, 0.128 mol), 5%Pd/C (1.50 g, 0.70 mmol as Pd), and tetrahydrofuran (solvent, 50 ml) were placed in a 100-mL glass-autoclave (TEM-V100, TAIATSU TECHNO Corp., Tokyo, Japan) equipped with a mechanical stirrer and a thermocouple. Hydrogen gas was supplied to the apparatus for 48 h at room temperature while maintaining a constant pressure of 1 MPa. The catalyst was filtered off through Celite® and the filtrate was dried with MgSO₄, then condensed to dryness by evaporation to give (S)-(-)-3,7-dimethyloctan-1-ol as a colorless liquid (yield 18.91g, 93%). (Scheme S1)

In a 200-mL pear-shaped flask were placed 3,7-dimethyloctan-1-ol (18.9 g, 0.119 mol), dichloromethane (100 ml), and PBr₃ (25 g, 0.092 mol) was added gradually to the solution. The mixture was stirred magnetically at room temperature for 3 h. Water (100 mL) was added dropwise in order to decompose the unreacted PBr₃. The product was extracted with dichloromethane (100 mL) three times and the combined extract was dried over MgSO₄. The filtrate was concentrated by evaporation, then was distilled under reduced pressure to give (S)-(-)-1-bromo-3,7-dimethyloctane as a colorless liquid (b.p. 58 °C/3 mmHg). Yield: 9.58 g (36%). (Scheme S2)



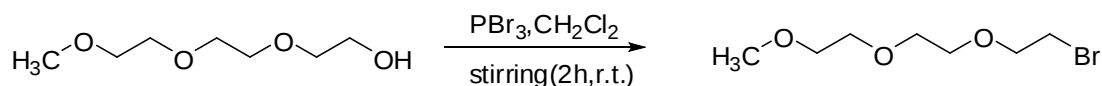
Scheme S1. Synthesis of 3,7-dimethyloctan-1-ol.



Scheme S2. Synthesis of 1-bromo-3,7-dimethyloctane.

Synthesis of 1-bromo-2-(2-(2-methoxyethoxy)ethoxy)ethane

Triethylene glycol monomethyl ether (2-(2-(2-methoxyethoxy)ethoxy)ethanol) (30.35 g, 0.185 mol) and dichloromethane (100 ml) were placed in a 200-mL pear-shaped flask. PBr₃ (25 g, 0.092 mol) was then gradually added to the solution. The mixture was magnetically stirred at room temperature for 3 hours. Following a similar procedure as mentioned above, 1-bromo-2-(2-(2-methoxyethoxy)ethoxy)ethane was obtained as a colorless liquid (b.p. 78 °C/4 mmHg). The yield was 19.06 g (45%).(Scheme S3)



Scheme S3. Synthesis of 1-bromo-2-(2-(2-methoxyethoxy)ethoxy)ethane.

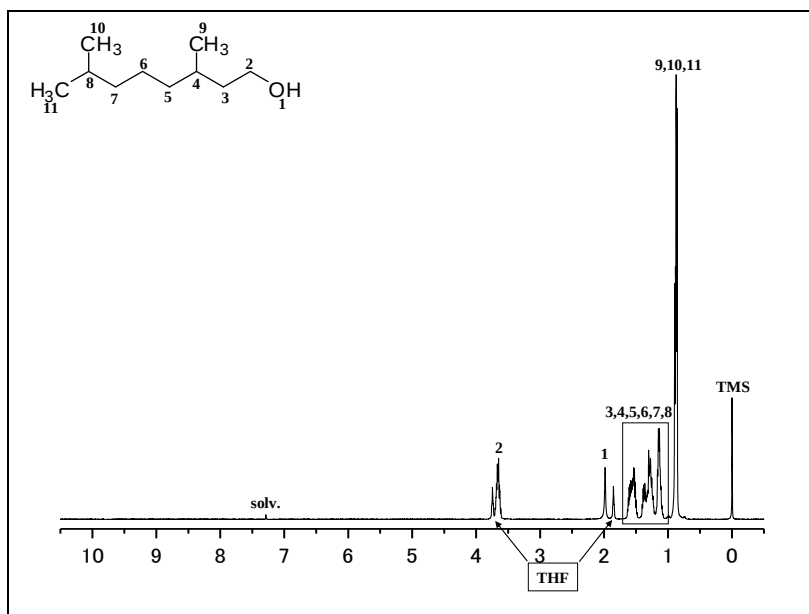


Figure S1. ^1H -NMR spectrum of 3,7-dimethyloctan-1-ol; solvent: CDCl_3 .

^1H -NMR (δ , ppm): 0.87(d, $J=6.7\text{Hz}$, 6H), 0.89(d, $J=6.4\text{Hz}$, 3H), 1.08-1.16(m, 3H), 1.20-1.40(m, 4H), 1.47-1.63(m, 3H), 1.98(s, 1H), 3.61-3.70(m, 2H).

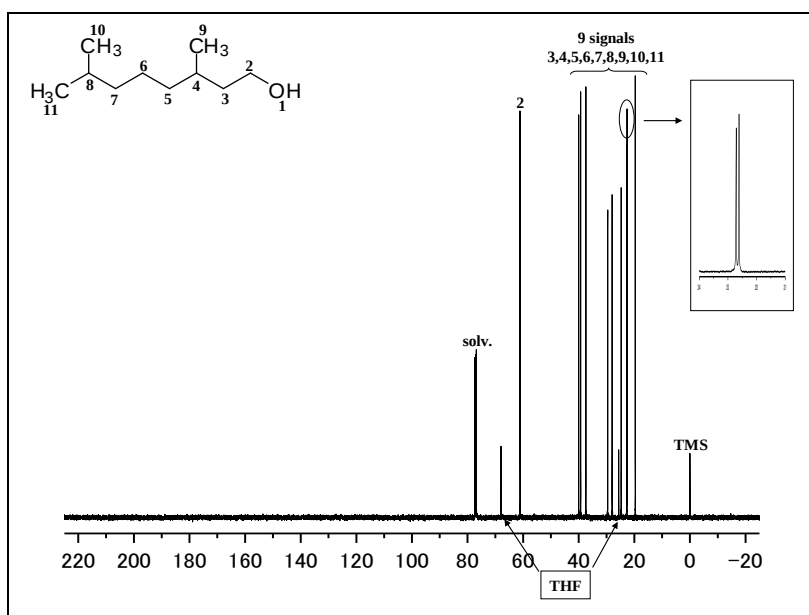


Figure S2. ^{13}C -NMR spectrum of 3,7-dimethyloctan-1-ol; solvent: CDCl_3 .

^{13}C -NMR (δ , ppm): 19.66, 22.61, 22.71, 24.71, 27.99, 29.57, 37.44, 39.31, 40.02, 61.11.

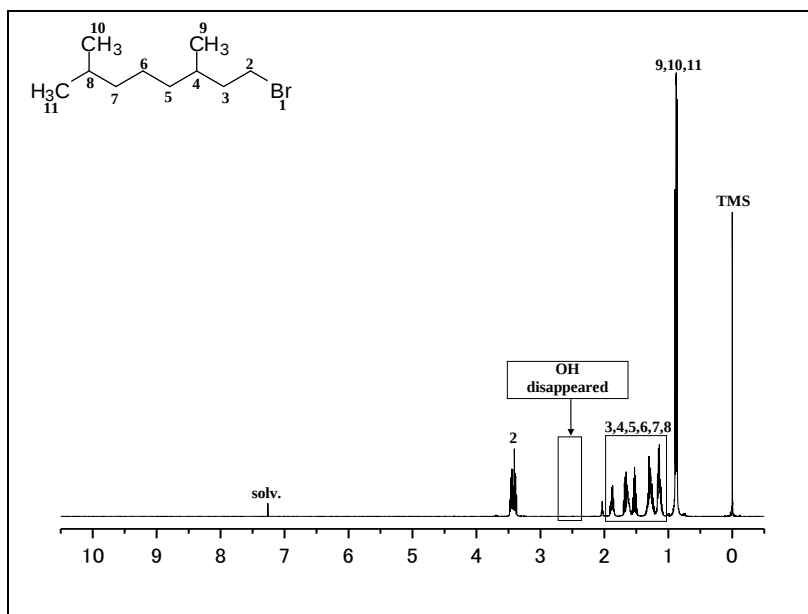


Figure S3. ^1H -NMR spectrum of 1-bromo-3,7-dimethyloctane; solvent: CDCl_3 .

^1H -NMR (δ , ppm): 0.87(d, $J=6.7\text{Hz}$, 6H), 0.89(d, $J=6.4\text{Hz}$, 3H), 1.10-1.16(m, 3H), 1.22-1.33(m, 3H), 1.48-1.56(m, 1H), 1.16-1.70(m, 2H), 1.85-1.91(m, 1H), 3.37-3.48(m, 2H).

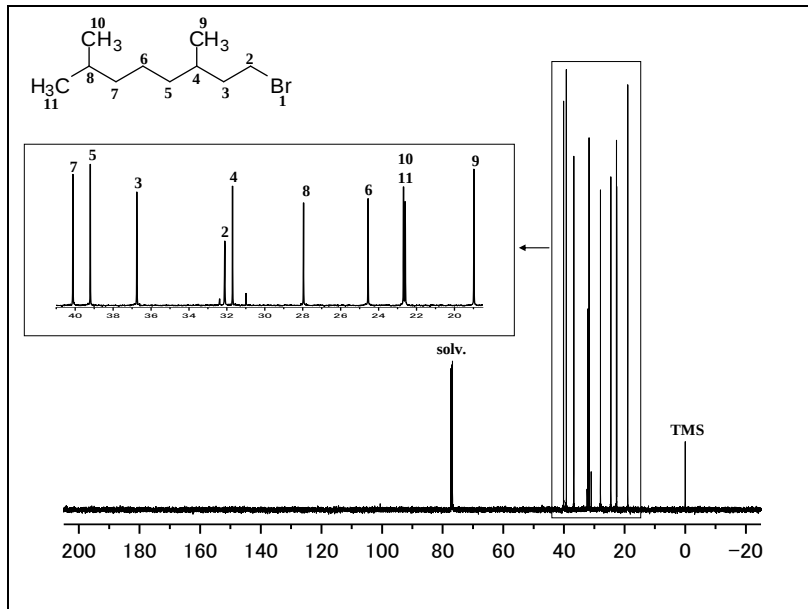


Figure S4. ^{13}C -NMR spectrum of 1-bromo-3,7-dimethyloctane; solvent: CDCl_3 .

^{13}C -NMR (δ , ppm): 18.91, 22.59, 22.68, 24.55, 27.95, 31.70, 32.11, 36.75, 39.20, 40.12.

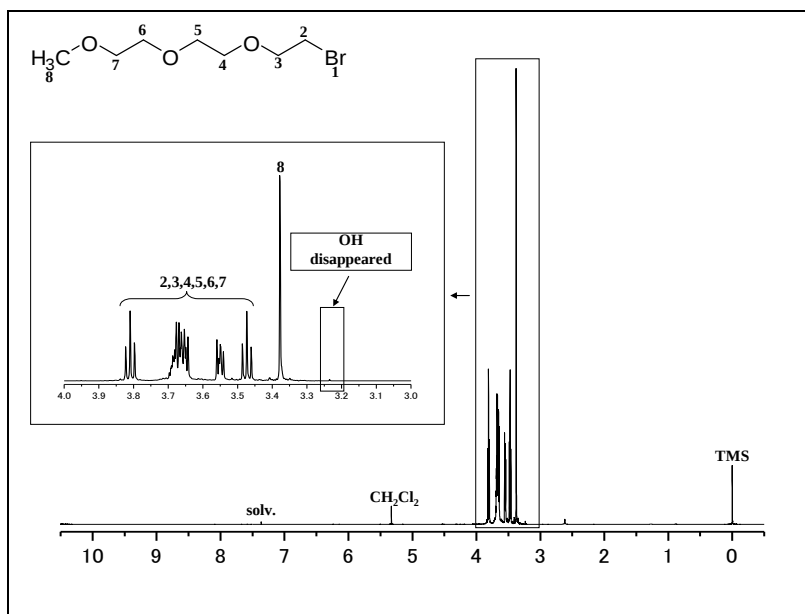


Figure S5. ¹H-NMR spectrum of 1-bromo-2-(2-(2-methoxyethoxy)ethoxy)ethane; solvent: CDCl₃.

¹H-NMR (δ, ppm): 3.37(s,3H), 3.47(t,J=6.4Hz,2H), 3.54(t,J=4.5Hz,2H), 3.64–3.69(m,6H), 3.80(t,J=6.1Hz,2H).

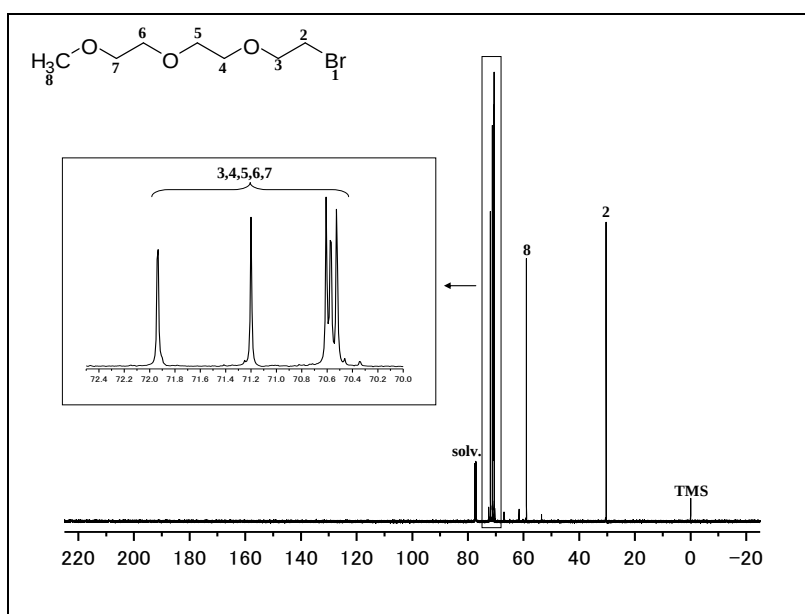


Figure S6. ¹³C-NMR spectrum of 1-bromo-2-(2-(2-methoxyethoxy)ethoxy)ethane; solvent: CDCl₃.

¹³C-NMR (δ, ppm): 30.32, 58.96, 70.52, 70.57, 70.60, 71.20, 71.93.

2-Octyloxy-5-nitrobenzaldehyde

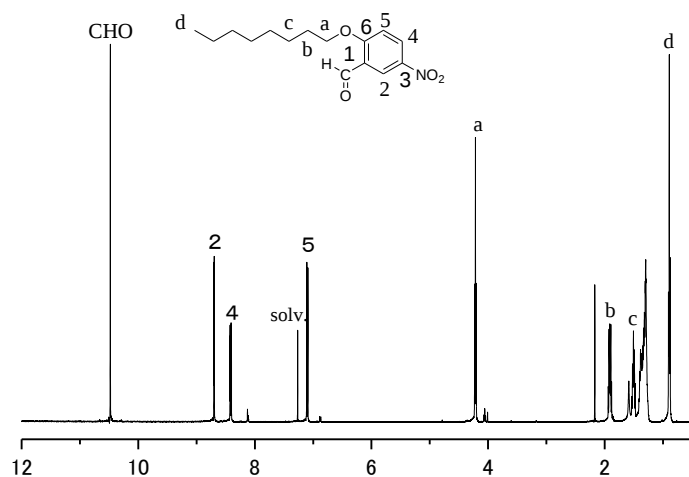


Figure S7. ^1H -NMR spectrum of 2-octyloxy-5-nitrobenzaldehyde; solvent: CDCl_3 .
 ^1H -NMR (δ , ppm): 0.89(t, $J=6.1\text{ Hz}$, 3H, H-d), 1.30(m, 8H), 1.51(quin, $J=7.7\text{ Hz}$, 2H, H-c), 1.91(quin, $J=6.7\text{ Hz}$, 2H, H-b), 4.22(t, $J=6.4\text{ Hz}$, 2H, H-a), 7.10(d, $J=9.2$, 1H, H-5), 8.41(quar, $J=6.1\text{ Hz}$, 1H, H-4), 8.69(d, $J=2.8\text{ Hz}$, 1H, H-2), 10.48(s, 1H, CHO).

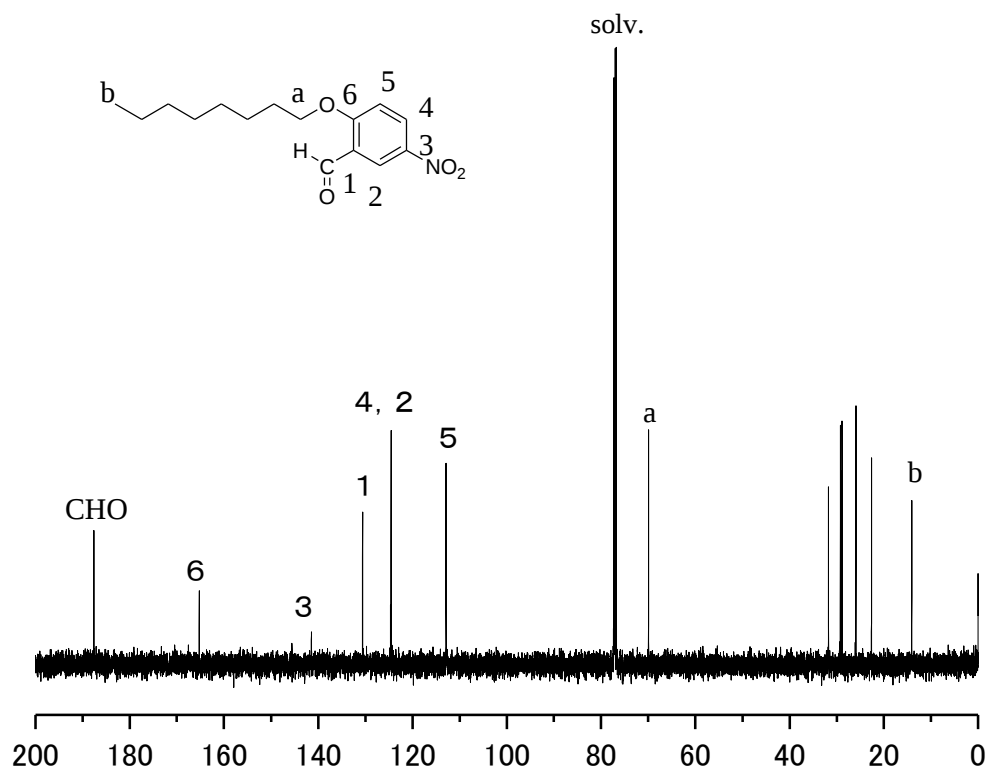


Figure S8. ^{13}C -NMR spectrum of 2-octyloxy-5-nitrobenzaldehyde; solvent: CDCl_3 .
 ^{13}C -NMR (δ , ppm): 14.1(C-b), 28.9, 29.16, 29.23, 31.8, 69.9(C-a), 112.9(C-5), 124.5(C-2), 124.7(C-4), 130.6(C-1), 141.5(C-3), 165.3(C-6), 187.6(CHO).

2-(3,7-Dimethyloctyloxy)-5-nitrobenzaldehyde

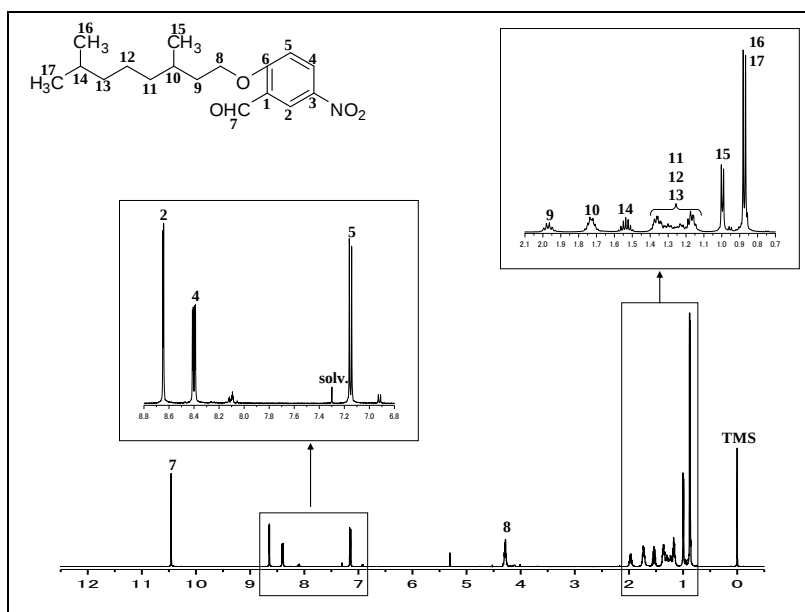


Figure S9. ^1H -NMR spectrum of 2-(3,7-dimethyloctyloxy)-5-nitrobenzaldehyde; solvent: CDCl_3 .

^1H -NMR (δ , ppm): 0.87(d, $J=6.7\text{Hz}$, 6H), 1.00(d, $J=6.1\text{Hz}$, 3H), 1.14–1.39(m, 6H), 1.49–1.57(m, 1H), 1.93–1.99(m, 2H), 4.25–4.32(m, 2H), 7.15(d, $J=9.1\text{Hz}$, 1H), 8.40(d, $J=9.4\text{Hz}$, 1H), 8.64(d, $J=2.7\text{Hz}$, 1H), 10.45(s, 1H).

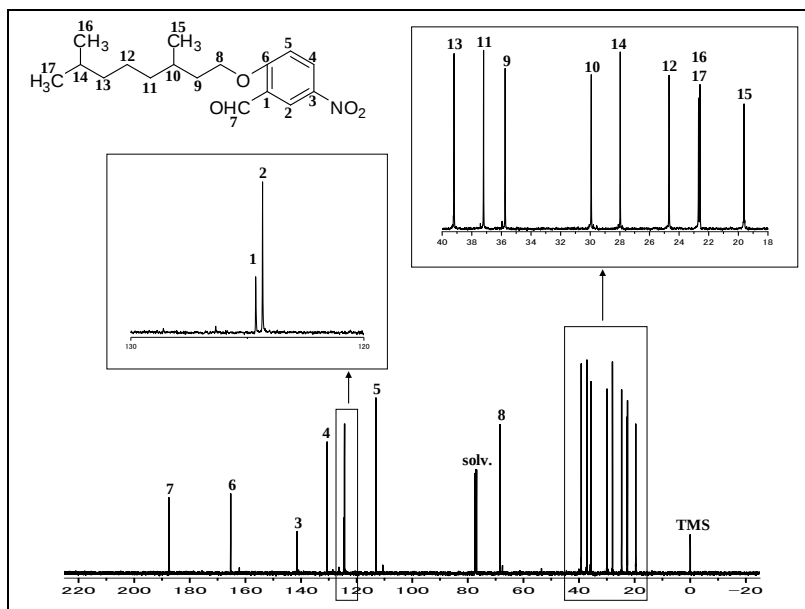


Figure S10. ^{13}C -NMR spectrum of 2-(3,7-dimethyloctyloxy)-5-nitrobenzaldehyde; solvent: CDCl_3 .

^{13}C -NMR (δ , ppm): 19.6, 22.6, 22.7, 24.7, 28.0, 29.9, 35.7, 37.2, 39.2, 68.4, 113.1, 124.3, 124.6, 130.6, 141.4, 165.3, 187.5.

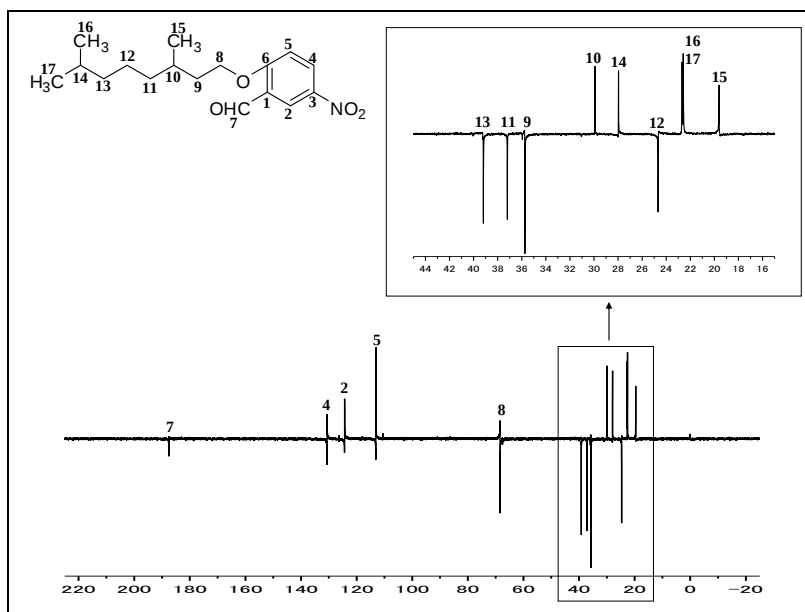


Figure S11. ^{13}C -NMR (DEPT-135) spectrum of 2-(3,7-dimethyloctyloxy)-5-nitrobenzaldehyde; solvent: CDCl_3 .

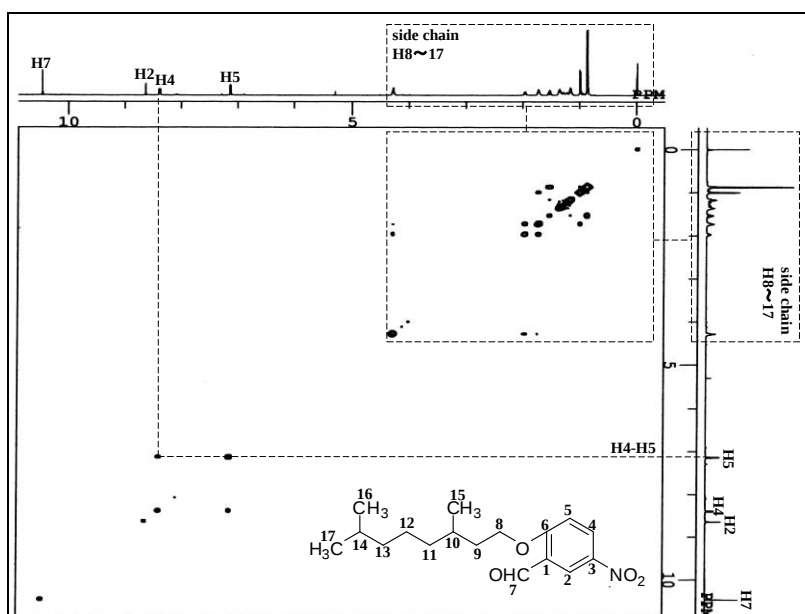


Figure S12. ^1H , ^1H -cosy spectrum of 2-(3,7-dimethyloctyloxy)-5-nitrobenzaldehyde; solvent: CDCl_3 .

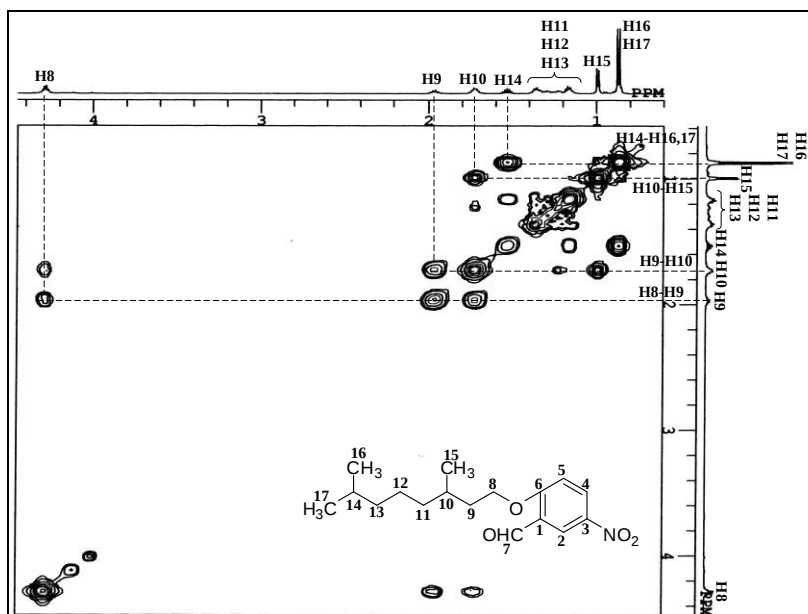


Figure S13. ^1H , ^1H -cosy spectrum of 2-(3,7-dimethyloctyloxy)-5-nitrobenzaldehyde; solvent: CDCl_3 . (expanded)

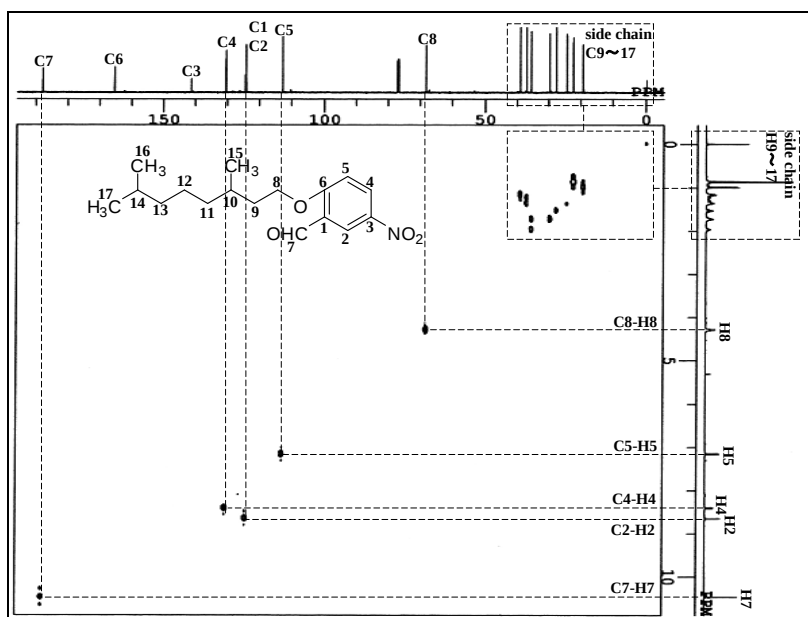


Figure S14. ^{13}C , ^1H -cosy spectrum of 2-(3,7-dimethyloctyloxy)-5-nitrobenzaldehyde; solvent: CDCl_3 .

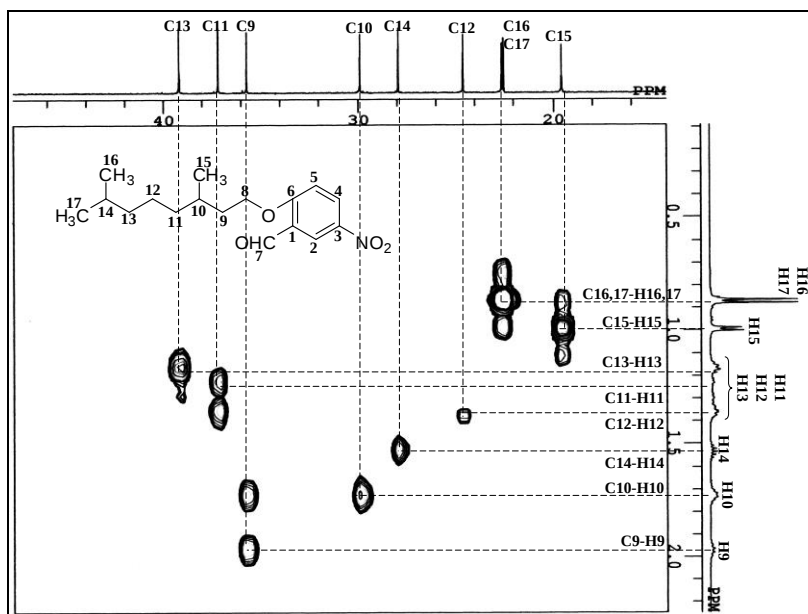


Figure S15. C,H-cosy spectrum of 2-(3,7-dimethyloctyloxy)-5-nitrobenzaldehyde; solvent: CDCl₃. (expanded)

2-(2-(2-(2-methoxyethoxy)ethoxy)ethoxy)-5-nitrobenzaldehyde

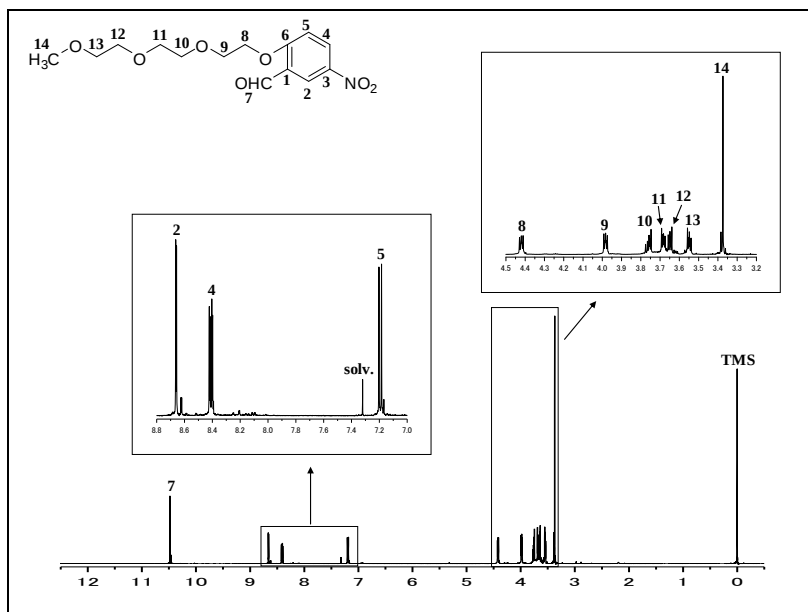


Figure S16. ¹H-NMR spectrum of 2-(2-(2-(2-methoxyethoxy)ethoxy)ethoxy)-5-nitrobenzaldehyde; solvent: CDCl₃.

^1H -NMR(δ , ppm): 3.37(s,3H), 3.53–3.55(m,2H), 3.63–3.69(m,4H), 3.74–3.77(m,2H), 3.98(t, J =4.5, 2H), 4.42(t, J =4.5 Hz, 2H), 7.19(d, J =9.4 Hz, 1H), 8.41(d, J =6.4 Hz, 1H), 8.66(d, J =2.7 Hz, 1H), 10.48(s, 1H).

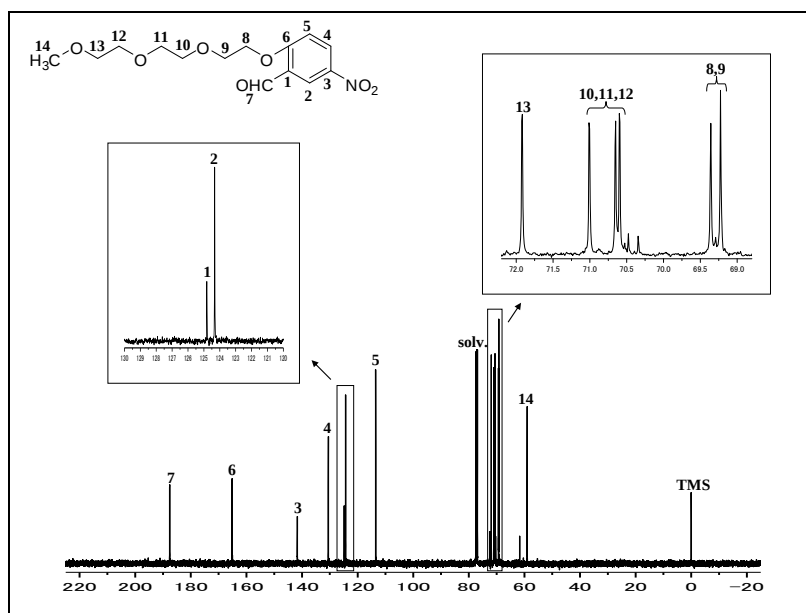


Figure S17. ^{13}C -NMR spectrum of 2-(2-(2-(2-methoxyethoxy)ethoxy)ethoxy)-5-nitrobenzaldehyde; solvent: CDCl_3 , internal standard: TMS.

^{13}C -NMR (δ , ppm): 59.0, 69.2, 69.4, 70.6, 70.6, 71.0, 71.9, 113.5, 124.3, 124.8, 130.5, 141.7, 165.1, 187.6.

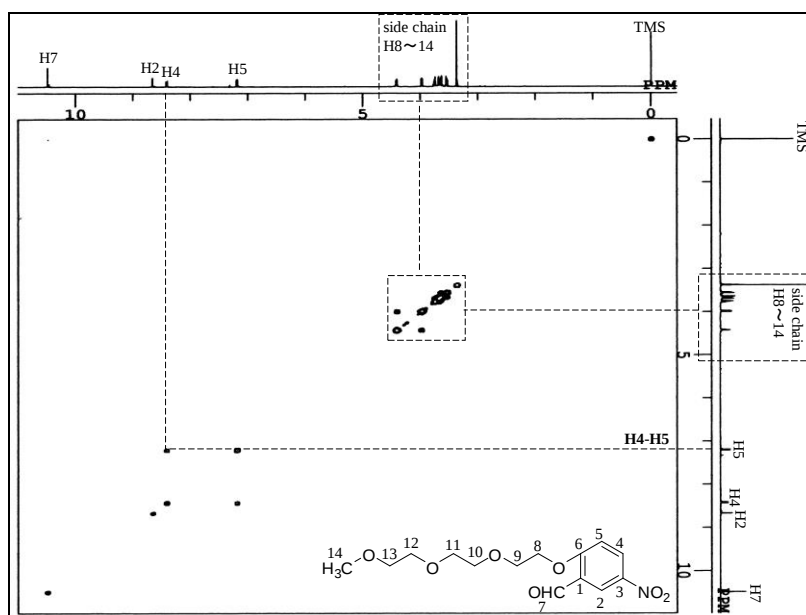


Figure S18. H,H-cosy spectrum of 2-(2-(2-(2-methoxyethoxy)ethoxy)ethoxy)-5-nitrobenzaldehyde; solvent: CDCl_3 .

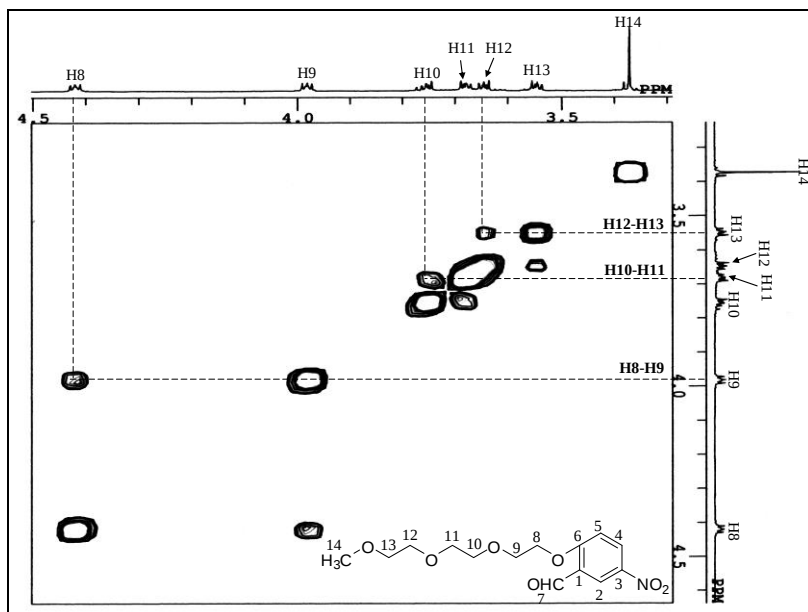


Figure S19. ^1H - ^1H -cosy spectrum of 2-(2-(2-(2-methoxyethoxy)ethoxy)ethoxy)-5-nitrobenzaldehyde; solvent: CDCl_3 . (expanded)

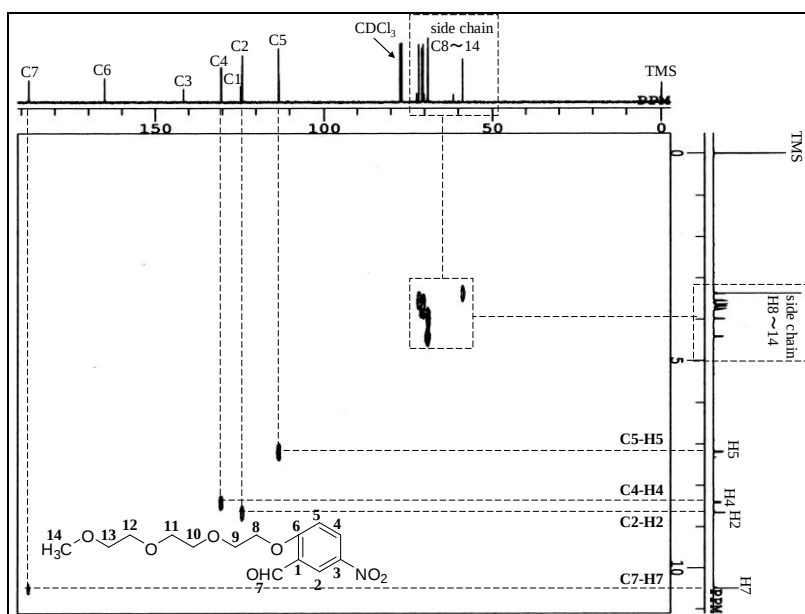


Figure S20. ^{13}C - ^1H -cosy spectrum of 2-(2-(2-(2-methoxyethoxy)ethoxy)ethoxy)-5-nitrobenzaldehyde; solvent: CDCl_3 .

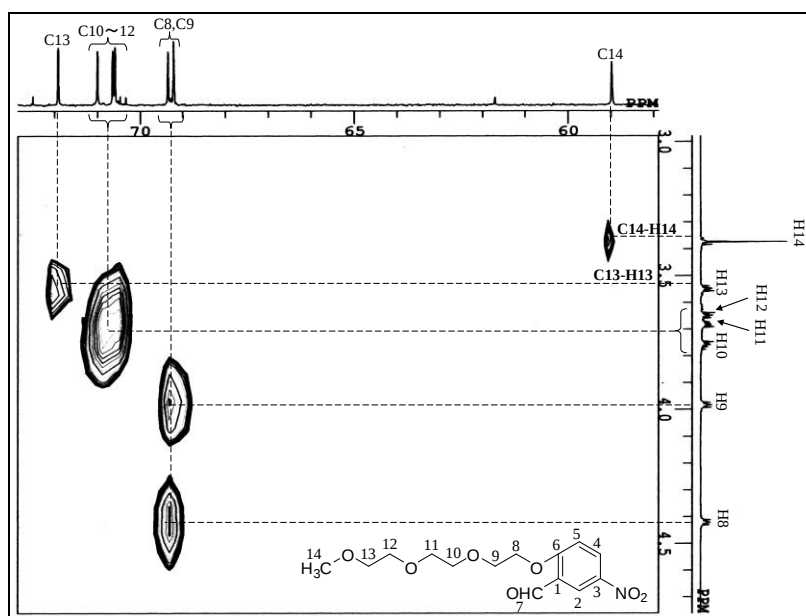


Figure S21. C,H-cosy spectrum of 2-(2-(2-(2-methoxyethoxy)ethoxy)ethoxy)-5-nitrobenzaldehyde; solvent: CDCl₃. (expanded)

2-Octyloxy-5-nitrobenzaldehyde diethyl acetal

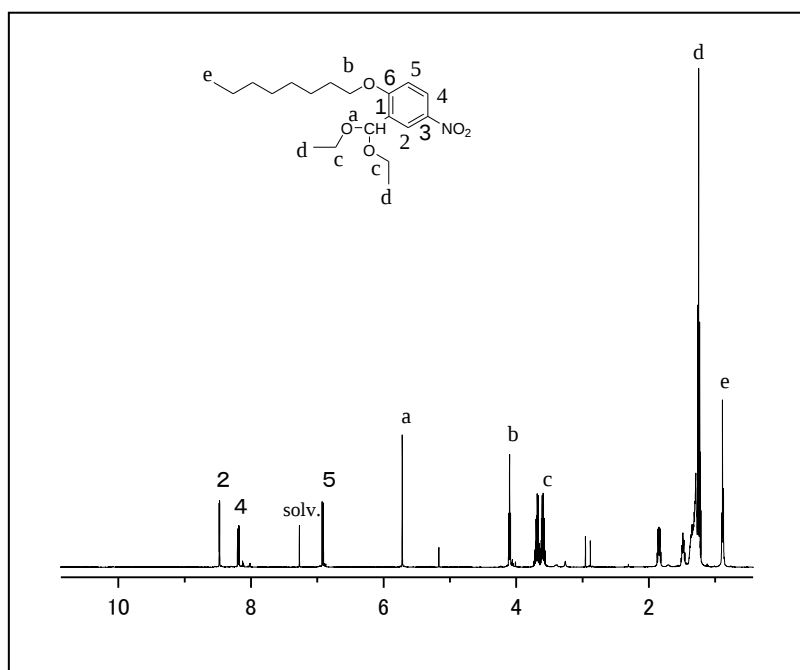


Figure S22. ¹H-NMR spectrum of 2-octyloxy-5-nitrobenzaldehyde diethyl acetal; solvent: CDCl₃.

¹H-NMR (δ, ppm): 0.89(t, J=6.7Hz, 3H, H-e), 1.25(t, J=7.0Hz, 6H, H-d), 1.29(m, 8H), 1.49(quin, J=7.6Hz, 2H), 1.85(quin, J=7.0Hz, 2H), 3.63(m, 4H, H-c), 4.10(t, J=6.4Hz, 2H, H-b), 5.72(s, 1H, -CH-(acetal)), 6.91(d, J=8.9Hz, 1H, H-5), 8.18(quar, J=6.1Hz, 1H, H-4), 8.47(d, J=2.8Hz, 1H, H-2)

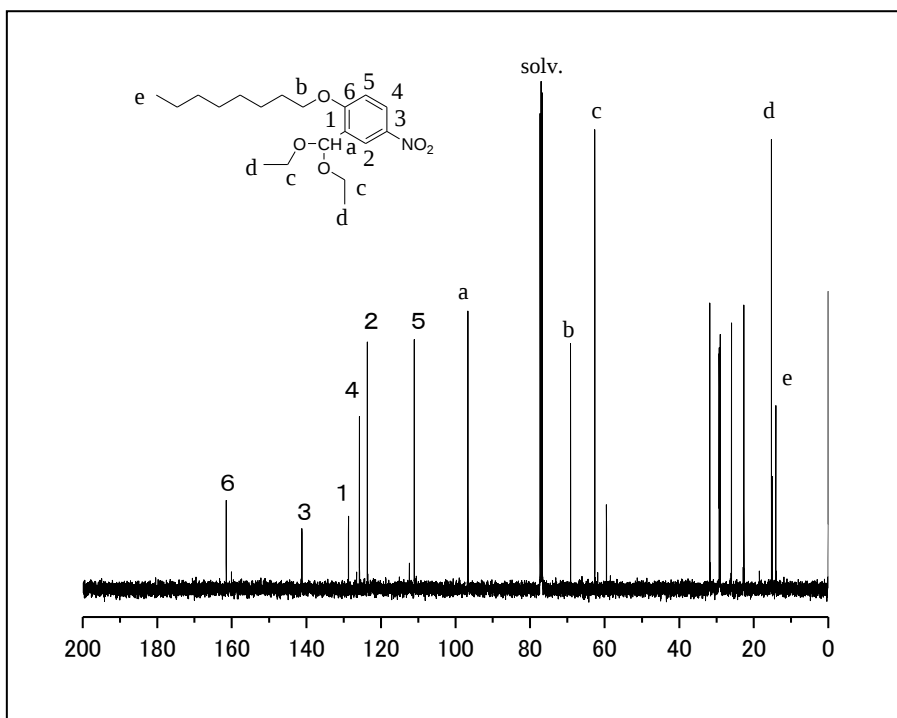


Figure S23. ^{13}C -NMR spectrum of 2-octyloxy-5-nitrobenzaldehyde diethyl acetal; solvent: CDCl_3 .

^{13}C -NMR (δ , ppm): 14.1(C-e), 15.2(C-d), 29.0, 29.2, 29.3, 31.8, 62.6(C-c), 69.1(C-b), 96.7(C-a), 111.1(C-5), 123.6(C-2), 125.8(C-4), 128.7(C-1), 141.2(C-3), 161.5(C-6).

2-(3,7-Dimethyloctyloxy)-5-nitrobenzaldehyde diethyl acetal

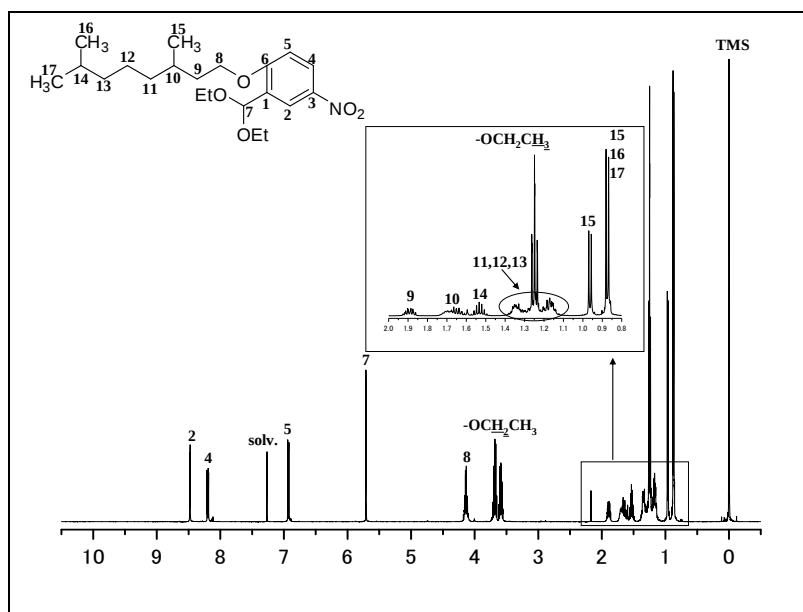


Figure S24. ^1H -NMR spectrum of 2-(3,7-dimethyloctyloxy)-5-nitrobenzaldehyde diethyl acetal; solvent: CDCl_3 .

^1H -NMR (δ , ppm): 0.87(d, $J=6.7\text{Hz}$, 6H), 0.96(d, $J=6.4\text{Hz}$, 3H), 1.14–1.36(m, 6H), 1.24(t, $J=7.0\text{Hz}$, 6H), 1.49–1.73(m, 3H), 1.86–1.92(m, 1H), 3.56–3.71(m, 4H), 4.11–4.15(m, 2H), 6.93(d, $J=9.1\text{Hz}$, 1H), 8.19(d, $J=9.1\text{Hz}$, 1H), 8.48(d, $J=2.7\text{Hz}$, 1H).

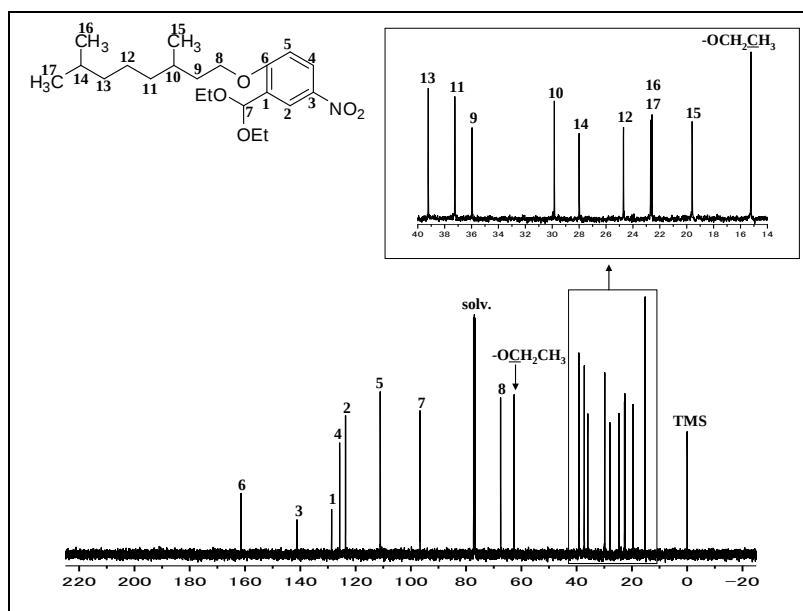


Figure S25. ^{13}C -NMR spectrum of 2-(3,7-dimethyloctyloxy)-5-nitrobenzaldehyde diethyl acetal; solvent: CDCl_3 .

^{13}C -NMR (δ , ppm): 15.2, 19.6, 22.6, 22.7, 24.7, 278.0, 29.8, 36.0, 37.2, 39.2, 62.6, 67.5, 96.7, 111.0, 123.6, 125.8, 128.7, 141.2, 161.4.

2-(2-(2-(2-methoxyethoxy)ethoxy)ethoxy)-5-nitrobenzaldehyde diethyl acetal

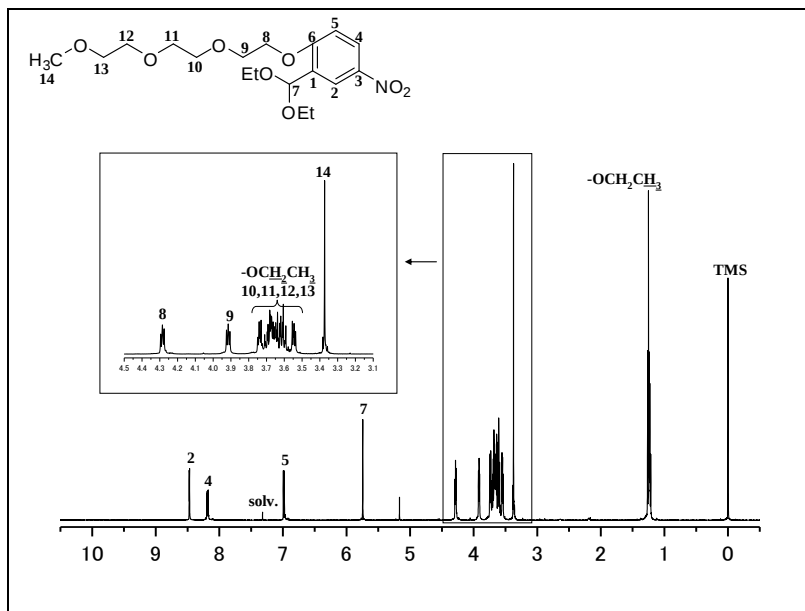


Figure S26. ^1H -NMR of 2-(2-(2-(2-methoxyethoxy)ethoxy)ethoxy)-5-nitrobenzaldehyde diethylacetal; solvent: CDCl_3 .

^1H -NMR (δ , ppm): 1.21(t, $J=7.0\text{Hz}$, 6H), 3.37(s, 3H), 3.53–3.55(m, 2H), 3.59–3.71(m, 8H), 3.73–3.74(m, 2H), 3.91(t, $J=4.8\text{Hz}$, 2H), 4.28(t, $J=4.5\text{Hz}$, 2H), 5.74(s, 1H), 6.98(d, $J=9.1\text{Hz}$, 1H), 8.10(d, $J=6.1\text{Hz}$, 1H), 8.47(d, $J=3.0\text{Hz}$, 1H).

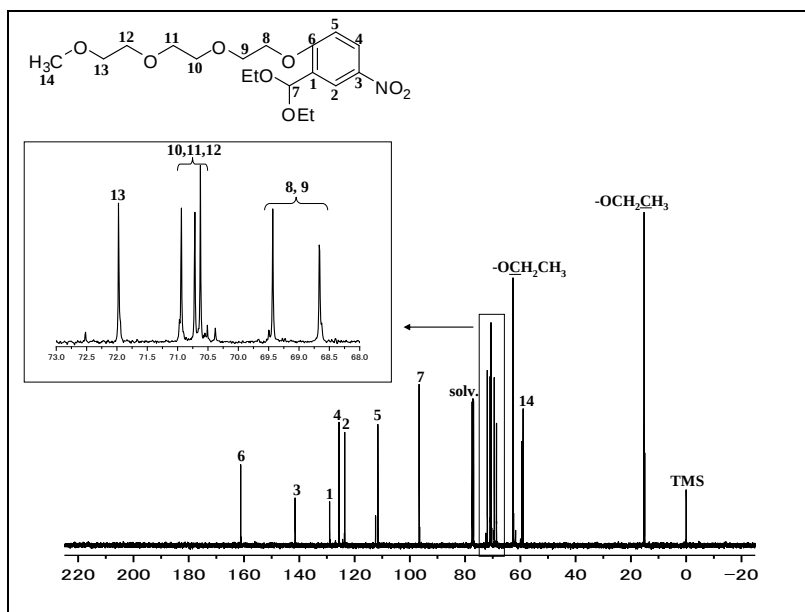


Figure S27. ^{13}C -NMR of 2-(2-(2-(2-methoxyethoxy)ethoxy)ethoxy)-5-nitrobenzaldehyde diethylacetal; solvent: CDCl_3 .

^{13}C -NMR (δ , ppm): 15.2, 59.0, 62.7, 68.7, 69.4, 70.6, 70.7, 70.9, 72.0, 96.6, 111.6, 123.6, 125.6, 129.1, 141.5, 161.2.

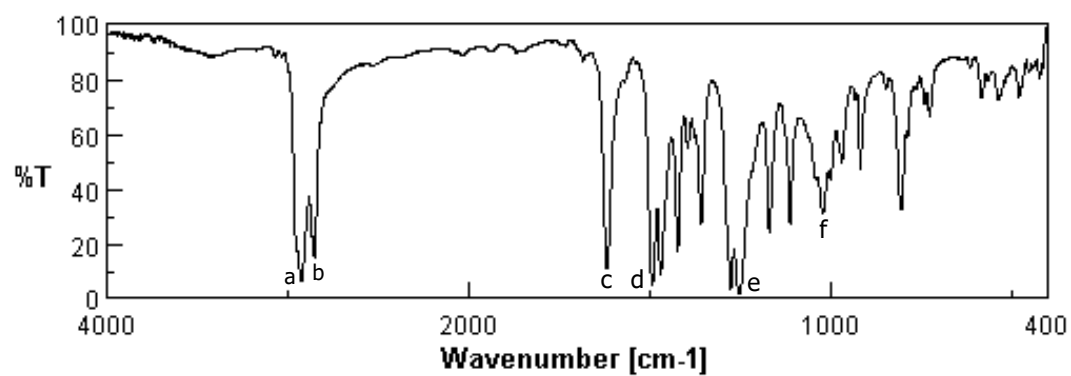


Figure S28. FT-IR spectrum of hexakis(2-octyloxy-1,5-phenyleneimine) macrocycle OcO-Cm6.

FT-IR(KBr, cm^{-1}): 2925 ($\nu\text{C-H,CH}_3$), 2852 ($\nu\text{C-H,CH}_2$), 1618 ($\nu\text{C=N}$), 1492, 1253, 1021.