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**Supplementary data**

**to**

# Packing polymorphism, odd-even alternation and thermotropic phase transitions in *N*-, *O*-diacylethanolamines with varying *N*-acyl chains. A combined experimental and computational study

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Running Title: Packing polymorphism in mixed-chain diacylethanolamines

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## S1. RESULTS AND DISCUSSION

**S1.1. Synthesis and Characterization of *N*-acyl-*O*-palmitoylethanolamines and *N*-acyl-*O*-pentadecanoylethanolamines.** The homologous series of *N*-acyl-*O*-palmitoylethanolamines (Nn-O16s) and *N*-acyl-*O*-pentadecanoylethanolamines (Nn-O15s) synthesized in the present study were characterized by FTIR, $^{1}$H-NMR and $^{13}$C-NMR spectroscopies. A representative FTIR spectrum of *N*-myristoyl-*O*-palmitoylethanolamine (N14-O16) is given in Fig. S1. FTIR spectra of mixed chain DAEs (Nn-O16s and Nn-O15s) contained absorption bands due to the ester linkage at 1730-1742 $cm^{-1}$, amide linkage at 1638-1643 $cm^{-1}$ (amide-I) and 1544-1556 $cm^{-1}$ (amide-II). The C–H stretching bands were observed at 2909-2920 $cm^{-1}$ and 2843-2854 $cm^{-1}$. All DAEs with mixed acyl chains exhibited split bands corresponding to C–H bending (scissoring mode, 1462-1479 $cm^{-1}$) and rocking (712-728 $cm^{-1}$), which is characteristic of $O_{\perp}$ chain packing.[1] The N–H stretching bands were observed between 3293 and 3315 $cm^{-1}$. Since the chemical structures of all the compounds are similar, except for the acyl chain length, they gave similar spectra and the specific band positions corresponding to the individual Nn-O16s and Nn-O15s are listed in Tables S1 and S2, respectively. $^{1}$H-NMR spectra of Nn-O16s and Nn-O15s gave the following resonances: 0.87-0.90 δ (3H, t), 1.26-1.30 δ (nH, bs), 2.17-2.21 δ (2H, t), 2.32-2.34 δ (2H, t), 3.51-3.54 δ (2H, q), 4.17-4.19 δ (2H, t), 5.72-5.97 δ (1H, bs). The resonances are consistent with the structures of Nn-O16s and Nn-O15s and a representative spectrum of *N*-myristoyl-*O*-palmitoylethanolamine is given in Fig. S2. Since all the compounds are structurally rather similar, their $^{1}$H-NMR spectra were almost identical except for the value of integration in the peak corresponding to the polymethylene portion of the acyl chain, seen at 1.26-1.3δ. The details of key resonances corresponding to individual Nn-O16s and Nn-O15s investigated are listed in Table S3 and S4, respectively.

$^{13}$C-NMR spectral data for Nn-O16s and Nn-O15s are given in Table S5 and S6, respectively. A representative $^{13}$C-NMR spectrum of *N*-myristoyl-*O*-palmitoylethanolamine is given in Fig. S3. This spectrum shows a resonance at 14.10 δ corresponding to end methyl groups of *N*-myristoyl and *O*-palmitoyl chains. Methylene groups present in both the chains show resonances at 22.68, 24.93, 25.69, 31.92, 34.19, 36.73, 38.83, 63.07 δ and resonances between 29.16 to 29.68 δ (seven peaks with the peak at 29.48 δ being more intense than others) and two resonances at 173.28 and 173.98 δ corresponding to amide carbonyl and ester carbonyl carbons, respectively. These resonances are consistent with the structure of *N*-myristoyl-*O*-palmitoylethanolamine. All other mixed-chain DAEs (Nn-O16s and Nn-O15s) also show essentially identical spectra, except for the peak at ~29.48 δ whose intensity increased with increase in the chain length. These results, obtained from FTIR, $^{1}$H- and $^{13}$C-NMR spectroscopic measurements on Nn-O16s and Nn-O15s, are consistent with their structures and indicate that they are of high purity.

**S1.2. Analysis of crystal packing of N13-O16.** Packing arrangement of molecules in the crystal lattice of N13-O16, viewed along the *c*-axis and *b*-axis are shown in Fig. S6A and S6B, respectively. The packing of N13-O16 molecules in the crystal lattice is similar to that found for N12-O16 with the closest methyl-methyl distance between opposite layers and the same layer being 3.880 Å and 4.876 Å, respectively. The layer thickness (C1–C31 distance) in N13-O16 is 33.813 Å and the *all-trans N*- and *O*-acyl chains of the molecule are tilted by 35.65° and 34.91°, respectively, with respect to the layer normal to the respective methyl end planes, whereas the angle between *N*-tridecanoyl and *O*-palmitoyl chains is 109.9$^{o}$.

## REFERENCES

1. Di, L.; Small, D. M. Physical Behavior of the Hydrophobic Core of Membranes: Properties of 1-Stearoyl-2-Linoleoyl-sn-Glycerol. Biochemistry 1995, 34, 16672–16677.

**Table S1:** Assignment of resonances in the IR spectra of *N*-acyl-*O*-palmitoylethanolamines (Nn-O16s).

| Acyl chain length | Amide ($cm^{-1}$) | | | Ester ($cm^{-1}$) | | C-H ($cm^{-1}$) | | |
|---|---|---|---|---|---|---|---|---|
| | C=O Amide-1 | N-H (def) Amide-2 | N-H Stretch | C=O | C-O Stretch | C-H (Stretch) | C-H (Scissoring) | C-H (Rocking) |
| $C_8$ | ~1641 | ~1554 | ~3300 | ~1734 | ~1184 | ~2849-2916 | ~1471 | ~717 |
| $C_9$ | ~1643 | ~1556 | ~3302 | ~1736 | ~1182 | ~2851-2918 | ~1471 | ~719 |
| $C_{10}$ | ~1643 | ~1550 | ~3293 | ~1742 | ~1178 | ~2854-2920 | ~1468 | ~723 |
| $C_{11}$ | ~1641 | ~1556 | ~3304 | ~1736 | ~1182 | ~2851-2918 | ~1471 | ~719 |
| $C_{12}$ | ~1638 | ~1545 | ~3298 | ~1736 | ~1178 | ~2843-2915 | ~1468 | ~712 |
| $C_{13}$ | ~1641 | ~1556 | ~3304 | ~1736 | ~1180 | ~2851-2918 | ~1471 | ~ 719 |
| $C_{14}$ | ~1641 | ~1554 | ~3300 | ~1734 | ~1199 | ~2849-2916 | ~1471 | ~ 717 |
| $C_{15}$ | ~1643 | ~1554 | ~3315 | ~1734 | ~1184 | ~2849-2918 | ~1471 | ~719 |

**Table S2:** Assignment of resonances in the IR spectra of *N*-acyl-*O*-pentadecanoylethanolamines (Nn-O15s).

| Acyl chain length | Amide ($cm^{-1}$) | | | Ester ($cm^{-1}$) | | C-H ($cm^{-1}$) | | |
|---|---|---|---|---|---|---|---|---|
| | C=O Amide-1 | N-H (def) Amide-2 | N-H Stretch | C=O | C-O Stretch | C-H (Stretch) | C-H (Scissoring) | C-H (Rocking) |
| $C_8$ | ~1643 | ~1556 | ~3304 | ~1731 | ~1189 | ~2854-2920 | ~1479 | ~717 |
| $C_9$ | ~1638 | ~1550 | ~3298 | ~1731 | ~1183 | ~2849-2909 | ~1463 | ~712 |
| $C_{10}$ | ~1643 | ~1544 | ~3298 | ~1730 | ~1177 | ~2843-2909 | ~1462 | ~728 |
| $C_{11}$ | ~1638 | ~1550 | ~3304 | ~1731 | ~1183 | ~2843-2909 | ~1468 | ~723 |
| $C_{12}$ | ~1643 | ~1556 | ~3309 | ~1742 | ~1183 | ~2849-2920 | ~1468 | ~717 |
| $C_{13}$ | ~1638 | ~1556 | ~3315 | ~1731 | ~1190 | ~2849-2915 | ~1468 | ~728 |
| $C_{14}$ | ~1637 | ~1555 | ~3309 | ~1736 | ~1177 | ~2843-2920 | ~1467 | ~717 |

**Table S3:** $^{1}$H-NMR spectral data of *N*-acyl-*O*-palmitoylethanolamines (Nn-O16s).

| Acyl chain length | Amide moiety | | | Ester group | | Acyl chains | |
|---|---|---|---|---|---|---|---|
| | $CH_2$–CO | N–H | $CH_2$–NH | $CH_2$–O–CO | $CH_2$–CO | $CH_3$ | $(CH_2)_n$ |
| $C_8$ | 2.18, t | 5.74, s | 3.53, t | 4.17, t | 2.32, t | 0.88, t | 1.27, m |
| $C_9$ | 2.18, t | 5.73, s | 3.52, t | 4.17, t | 2.32, t | 0.88, t | 1.26, m |
| $C_{10}$ | 2.18, t | 5.74, s | 3.52, t | 4.17, t | 2.32, t | 0.88, t | 1.26, m |
| $C_{11}$ | 2.18, t | 5.73, s | 3.52, t | 4.17, t | 2.32, t | 0.88, t | 1.26, m |
| $C_{12}$ | 2.18, t | 5.72, s | 3.53, t | 4.17, t | 2.32, t | 0.88, t | 1.26, m |
| $C_{13}$ | 2.17, t | 5.74, s | 3.52, t | 4.17, t | 2.32, t | 0.87, t | 1.26, m |
| $C_{14}$ | 2.19, t | 5.82, s | 3.54, t | 4.18, t | 2.33, t | 0.89, t | 1.27, m |
| $C_{15}$ | 2.17, t | 5.73, s | 3.53, t | 4.17, t | 2.32, t | 0.88, t | 1.26, m |

**Table S4:** $^{1}$H-NMR spectral data of *N*-acyl-*O*-pentadecanoylethanolamines (Nn-O15s).

| Acyl chain length | Amide moiety | | | Ester group | | Acyl chains | |
|---|---|---|---|---|---|---|---|
| | $CH_2$–CO | N–H | $CH_2$–NH | $CH_2$–O–CO | $CH_2$–CO | $CH_3$ | $(CH_2)_n$ |
| $C_8$ | 2.21, t | 5.84, s | 3.54, t | 4.19, t | 2.34, t | 0.90, t | 1.30, m |
| $C_9$ | 2.19, t | 5.84, s | 3.54, t | 4.19, t | 2.34, t | 0.90, t | 1.28, m |
| $C_{10}$ | 2.18, t | 5.88, s | 3.52, t | 4.17, t | 2.32, t | 0.88, t | 1.29, m |
| $C_{11}$ | 2.19, t | 5.78, s | 3.53, t | 4.19, t | 2.34, t | 0.90, t | 1.30, m |
| $C_{12}$ | 2.19, t | 5.97, s | 3.51, t | 4.17, t | 2.32, t | 0.88, t | 1.29, m |
| $C_{13}$ | 2.19, t | 5.78, s | 3.53, t | 4.19, t | 2.34, t | 0.90, t | 1.27, m |
| $C_{14}$ | 2.20, t | 5.84, s | 3.53, t | 4.18, t | 2.33, t | 0.89, t | 1.27, m |

**Table S5:** $^{13}$C-NMR spectral data of *N*-acyl-*O*-palmitoylethanolamines (Nn-O16s).

| Acyl chain length | $CH_3$-$CH_2$-$(CH_2)_n$ | $CH_2$-$(CH_2)_n$ | $(CH_2)_n$ | $CH_2$-COOR | COO-$CH_2$-$CH_2$-NH | COO-$CH_2$-$CH_2$-NH | HN-CO-$CH_2$ | R-COO | NH-C=O |
|---|---|---|---|---|---|---|---|---|---|
| 8 | 14.10 | 22.66 | 24.94-31.93 | 34.20 | 63.11 | 38.85 | 36.76 | 174.04 | 173.30 |
| 9 | 14.07 | 22.65 | 24.92-31.91 | 34.18 | 63.05 | 38.81 | 36.70 | 173.97 | 173.32 |
| 10 | 14.09 | 22.66 | 24.92-31.91 | 34.18 | 62.99 | 38.92 | 36.62 | 173.99 | 173.54 |
| 11 | 14.08 | 22.66 | 24.92-31.91 | 34.17 | 63.02 | 38.82 | 36.68 | 173.95 | 173.37 |
| 12 | 14.08 | 22.67 | 24.92-31.91 | 34.17 | 63.03 | 38.82 | 36.69 | 173.96 | 173.35 |
| 13 | 14.07 | 22.66 | 24.91-31.90 | 34.16 | 62.99 | 38.81 | 36.66 | 173.93 | 173.39 |
| 14 | 14.10 | 22.68 | 24.93-31.92 | 34.19 | 63.07 | 38.83 | 36.73 | 173.98 | 173.28 |
| 15 | 14.11 | 22.69 | 24.92-31.92 | 34.18 | 63.02 | 38.85 | 36.67 | 173.99 | 173.45 |

**Table S6:** $^{13}$C-NMR spectral data of *N*-acyl-*O*-pentadecanoylethanolamines (Nn-O15s).

| Acyl chain length | $CH_3$-$CH_2$-$(CH_2)_n$ | -$CH_2$-$(CH_2)_n$- | -$(CH_2)_n$- | -$CH_2$-COOR | (COO)-$CH_2$-$CH_2$-NH | (COO)-$CH_2$-$CH_2$-NH | HN-CO-$CH_2$ | -$CH_2$-COO | NH-C=O |
|---|---|---|---|---|---|---|---|---|---|
| 8 | 14.09 | 22.65 | 24.93-31.92 | 34.20 | 63.08 | 38.91 | 36.70 | 174.06 | 173.43 |
| 9 | 14.10 | 22.66 | 24.92-31.92 | 34.18 | 63.05 | 38.81 | 36.71 | 174.00 | 173.36 |
| 10 | 14.10 | 22.67 | 24.92-31.91 | 34.18 | 63.05 | 38.80 | 36.71 | 173.98 | 173.33 |
| 11 | 14.12 | 22.69 | 24.93-31.92 | 34.19 | 63.03 | 38.89 | 36.67 | 174.03 | 173.49 |
| 12 | 14.09 | 22.67 | 24.91-31.91 | 34.17 | 63.01 | 38.82 | 36.67 | 173.97 | 173.43 |
| 13 | 14.12 | 22.69 | 24.93-31.93 | 34.19 | 63.07 | 38.85 | 36.73 | 174.02 | 173.37 |
| 14 | 14.11 | 22.69 | 24.93-31.92 | 34.19 | 63.07 | 38.84 | 36.73 | 174.01 | 173.35 |

**Table S7.** Average values of transition temperatures ($T_t$), transition enthalpies ($\Delta H_t$), and transition entropies ($\Delta S_t$) of *N*-acyl-*O*-palmitoylethanolamines (Nn-O16s) and *N*-acyl-*O*-pentadecanoylethanolamines (Nn-O15s) in the dry state. The standard deviations indicated correspond to at least 3 independent measurements.

| **Acyl chain length** | **Nn-O16s** | | | **Nn-O15s** | | |
|---|---|---|---|---|---|---|
| | $T_t$ (°C) | $\Delta H_t$ (kcal.mol$^{-1}$) | $\Delta S_t$ (cal.mol$^{-1}$.K$^{-1}$) | $T_t$ (°C) | $\Delta H_t$ (kcal.mol$^{-1}$) | $\Delta S_t$ (cal.mol$^{-1}$.K$^{-1}$) |
| 8 | 75.8 (±0.1) | 17.87 (±0.29) | 51.2 (±0.8) | 72.9 (±0.1) | 13.69 (±0.12) | 39.6 (±0.3) |
| 9 | 76.7 (±0.1) | 15.81 (±0.21) | 45.2 (±0.6) | 74.3 (±0.1) | 14.81 (±0.16) | 42.7 (±0.5) |
| 10 | 78.8 (±0.1) | 20.35 (±0.17) | 57.9 (±0.5) | 75.5 (±0.1) | 16.58 (±0.13) | 47.6 (±0.4) |
| 11 | 79.2 (±0.1) | 19.29 (±0.42) | 54.8 (±1.2) | 77.3 (±0.1) | 16.72 (±0.13) | 47.7 (±0.4) |
| 12 | 82.3 (±0.1) | 23.32 (±0.14) | 65.6 (±0.4) | 78.8 (±0.1) | 19.54 (±0.38) | 55.6 (±1.1) |
| 13 | 83.1 (±0.1) | 22.96 (±0.22) | 64.5 (±0.6) | 80.2 (±0.1) | 21.74 (±0.13) | 61.6 (±0.4) |
| 14 | 86.6 (±0.1) | 24.76 (±0.37) | 68.8 (±1.0) | 82.4 (±0.2) | 22.72 (±0.16) | 63.9 (±0.5) |
| 15 | 86.0 (±0.1) | 24.23 (±0.27) | 68.0 (±1.1) | - | - | - |

**Table S8:** Fractional atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters ($Å^2 \times 10^3$) for the *N*-lauroyl-*O*-palmitoylethanolamine (N12-O16). U(eq) is defined as one third of the trace of the orthogonalized $U_{ij}$ tensor [$U(eq) = \frac{1}{3} \sum_i \sum_j U_{ij} a_{i*} a_{j*} a_i a_j \cos(ai, aj)$].

| Atom | x | y | z | U(eq) |
|---|---|---|---|---|
| C(1) | 4801(1) | 4406(13) | 1416(6) | 85(2) |
| C(2) | 4697(1) | 5552(11) | 2700(6) | 67(1) |
| C(3) | 4498(1) | 4404(9) | 2819(5) | 53(1) |
| C(4) | 4391(1) | 5557(9) | 4088(5) | 53(1) |
| C(5) | 4193(1) | 4413(9) | 4249(5) | 51(1) |
| C(6) | 4089(1) | 5583(9) | 5518(5) | 47(1) |
| C(7) | 3890(1) | 4435(9) | 5667(5) | 47(1) |
| C(8) | 3790(1) | 5605(8) | 6977(4) | 42(1) |
| C(9) | 3588(1) | 4554(8) | 7145(4) | 40(1) |
| C(10) | 3499(1) | 5692(8) | 8505(4) | 36(1) |
| C(11) | 3298(1) | 4607(8) | 8704(4) | 39(1) |
| C(12) | 3154(1) | 5644(7) | 7515(4) | 32(1) |
| C(13) | 2907(1) | 4476(10) | 5599(6) | 62(1) |
| C(14) | 2727(1) | 5079(15) | 6145(7) | 105(2) |
| C(15) | 2446(1) | 4717(11) | 4572(6) | 62(1) |
| C(16) | 2326(1) | 5878(9) | 3316(5) | 51(1) |
| C(17) | 2134(1) | 4607(9) | 3043(5) | 53(1) |
| C(18) | 2020(1) | 5766(9) | 1697(5) | 51(1) |
| C(19) | 1825(1) | 4486(9) | 1398(5) | 52(1) |
| C(20) | 1717(1) | 5653(9) | 22(5) | 49(1) |
| C(21) | 1521(1) | 4431(9) | -300(5) | 50(1) |
| C(22) | 1415(1) | 5593(9) | -1677(5) | 47(1) |
| C(23) | 1216(1) | 4401(9) | -1983(5) | 49(1) |

| | | | | |
|---|---|---|---|---|
| C(24) | 1114(1) | 5594(9) | -3373(5) | 48(1) |
| C(25) | 914(1) | 4420(9) | -3693(5) | 50(1) |
| C(26) | 809(1) | 5588(9) | -5062(5) | 51(1) |
| C(27) | 608(1) | 4410(10) | -5373(5) | 56(1) |
| C(28) | 505(1) | 5571(10) | -6746(5) | 60(1) |
| C(29) | 303(1) | 4414(12) | -7045(6) | 75(2) |
| C(30) | 200(1) | 5555(13) | -8428(7) | 90(2) |
| N(1) | 3049(1) | 3782(7) | 6792(4) | 44(1) |
| O(1) | 3138(1) | 8080(5) | 7238(4) | 57(1) |
| O(2) | 2601(1) | 5937(11) | 4872(6) | 127(2) |
| O(3) | 2402(1) | 2898(13) | 5267(7) | 186(3) |

**Table S9:** Selected bond distances (Å) and bond angles (degrees) for *N*-lauroyl-*O*-palmitoylethanolamine (N12-O16).

| **Bond distances (Å)** | | **Bond angle (degree)** | |
|---|---|---|---|
| C(2)-C(1) | 1.485(7) | C(1)-C(2)-C(3) | 113.1(4) |
| C(3)-C(2) | 1.489(6) | C(2)-C(3)-C(4) | 114.0(4) |
| C(3)-C(4) | 1.491(6) | C(5)-C(4)-C(3) | 115.2(4) |
| C(5)-C(4) | 1.484(5) | C(6)-C(5)-C(4) | 114.3(4) |
| C(5)-C(6) | 1.481(6) | C(5)-C(6)-C(7) | 114.0(3) |
| C(6)-C(7) | 1.497(5) | C(6)-C(7)-C(8) | 112.8(3) |
| C(8)-C(7) | 1.494(6) | C(9)-C(8)-C(7) | 114.4(3) |
| C(9)-C(8) | 1.496(5) | C(10)-C(9)-C(8) | 112.3(3) |
| C(9)-C(10) | 1.492(5) | C(9)-C(10)-C(11) | 112.8(3) |
| C(11)-C(10) | 1.502(5) | C(12)-C(11)-C(10) | 112.4(3) |
| C(11)-C(12) | 1.501(5) | C(12)-N(1)-C(13) | 122.7(4) |
| N(1)-C(12) | 1.309(5) | O(1)-C(12)-N(1) | 121.9(4) |
| N(1)-C(13) | 1.449(5) | O(1)-C(12)-C(11) | 121.5(3) |
| O(1)-C(12) | 1.211(4) | N(1)-C(12)-C(11) | 116.6(3) |
| C(13)-C(14) | 1.387(7) | C(13)-C(14)-O(2 | 107.2(5) |
| O(2)-C(14) | 1.452(6) | O(2)-C(15)-C(16) | 115.4(4) |
| C(15)-O(2) | 1.241(5) | O(3)-C(15)-O(2) | 120.5(5) |
| C(15)-O(3) | 1.128(6) | O(3)-C(15)-C(16) | 124.0(5) |
| C(16)-C(15) | 1.472(6) | C(15)-O(2)-C(14) | 120.4(5) |
| C(17)-C(16) | 1.472(5) | C(15)-C(16)-C(17) | 115.8(4) |
| C(18)-C(17) | 1.508(5) | C(16)-C(17)-C(18) | 113.8(4) |
| C(19)-C(18) | 1.496(5) | C(19)-C(18)-C(17) | 114.5(4) |
| C(19)-C(20) | 1.512(5) | C(18)-C(19)-C(20) | 113.1(4) |
| C(21)-C(20) | 1.496(5) | C(21)-C(20)-C(19) | 114.4(4) |
| C(21)-C(22) | 1.504(5) | C(20)-C(21)-C(22) | 113.9(3) |
| C(23)-C(22) | 1.502(5) | C(23)-C(22)-C(21) | 113.9(3) |
| C(24)-C(23) | 1.512(5) | C(22)-C(23)-C(24) | 112.9(4) |
| C(24)-C(25) | 1.505(5) | C(25)-C(24)-C(23) | 113.5(4) |

| | | | |
|---|---|---|---|
| C(26)-C(25) | 1.497(5) | C(26)-C(25)-C(24) | 114.3(4) |
| C(26)-C(27) | 1.512(5) | C(25)-C(26)-C(27) | 114.0(4) |
| C(27)-C(28) | 1.495(6) | C(28)-C(27)-C(26) | 113.8(4) |
| C(28)-C(29) | 1.515(6) | C(27)-C(28)-C(29) | 113.7(4) |
| C(29)-C(30) | 1.498(6) | C(30)-C(29)-C(28) | 113.8(5) |

**Table S10:** Selected torsion angles (degrees) for *N*-lauroyl-*O*-palmitoylethanolamine (N12-O16).

| | |
|---|---|
| C(1) C(2) C(3) C(4) | -179.17 |
| C(2) C(3) C(4) C(5) | -178.99 |
| C(3) C(4) C(5) C(6) | 179.87 |
| C(4) C(5) C(6) C(7) | 179.55 |
| C(5) C(6) C(7) C(8) | 178.68 |
| C(6) C(7) C(8) C(9) | 178.77 |
| C(7) C(8) C(9) C(10) | 177.53 |
| C(8) C(9) C(10) C(11) | -178.84 |
| C(9) C(10) C(11) C(12) | -68.61 |
| C(10) C(11) C(12) O(1) | -51.85 |
| C(10) C(11) C(12) N(1) | 127.85 |
| O(1) C(12) N(1) C(13) | 0.76 |
| C(11) C(12) N(1) C(13) | -178.94 |
| C(14) C(13) N(1) C(12) | -87.35 |
| N(1) C(13) C(14) O(2) | 175.79 |
| C(13) C(14) O(2) C(15) | 123.29 |
| O(3) C(15) O(2) C(14) | -1.38 |
| C(16) C(15) O(2) C(14) | 176.36 |
| O(2) C(15) C(16) C(17) | -174.52 |
| O(3) C(15) C(16) C(17) | 3.13 |
| C(15) C(16) C(17) C(18) | -176.99 |
| C(16) C(17) C(18) C(19) | 179.70 |
| C(17) C(18) C(19) C(20) | -178.75 |
| C(18) C(19) C(20) C(21) | -179.50 |
| C(19) C(20) C(21) C(22) | -179.61 |
| C(20) C(21) C(22) C(23) | -178.97 |
| C(21) C(22) C(23) C(24) | -179.84 |
| C(22) C(23) C(24) C(25) | -179.94 |
| C(23) C(24) C(25) C(26) | 179.68 |

| | |
|---|---|
| C(24) C(25) C(26) C(27) | -179.71 |
| C(25) C(26) C(27) C(28) | -179.66 |
| C(26) C(27) C(28) C(29) | -179.30 |
| C(27) C(28) C(29) C(30) | -179.50 |

**Table S11:** Fractional atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters ($Å^2 \times 10^3$) for the *N*-tridecanoyl-*O*-palmitoylethanolamine (N13-O16). U(eq) is defined as one third of the trace of the orthogonalized $U_{ij}$ tensor [$U(eq) = \frac{1}{3} \sum_i \sum_j U_{ij} a_{i*} a_{j*} a_i a_j \cos(ai, aj)$].

| Atom | x | y | z | U(eq) |
|---|---|---|---|---|
| C(1) | 100(1) | 7088(9) | 4622(5) | 39(1) |
| C(2) | 198(1) | 8215(8) | 4375(4) | 27(1) |
| C(3) | 245(1) | 7015(7) | 2990(4) | 22(1) |
| C(4) | 343(1) | 8131(7) | 2746(4) | 19(1) |
| C(5) | 392(1) | 6916(7) | 1369(3) | 18(1) |
| C(6) | 488(1) | 8096(7) | 1118(3) | 17(1) |
| C(7) | 536(1) | 6883(7) | -263(3) | 18(1) |
| C(8) | 633(1) | 8079(7) | -518(3) | 17(1) |
| C(9) | 681(1) | 6878(7) | -1913(3) | 18(1) |
| C(10) | 779(1) | 8025(7) | -2175(3) | 18(1) |
| C(11) | 823(1) | 6878(6) | -3622(3) | 17(1) |
| C(12) | 921(1) | 8006(7) | -3890(3) | 18(1) |
| C(13) | 991(1) | 7020(6) | -2691(3) | 16(1) |
| C(14) | 1113(1) | 8245(7) | -836(4) | 22(1) |
| C(15) | 1198(1) | 6990(8) | -1506(4) | 29(1) |
| C(16) | 1333(1) | 7677(7) | 116(4) | 20(1) |
| C(17) | 1388(1) | 6513(7) | 1433(3) | 18(1) |
| C(18) | 1483(1) | 7893(7) | 1682(3) | 18(1) |
| C(19) | 1535(1) | 6720(7) | 3072(3) | 17(1) |
| C(20) | 1630(1) | 8024(6) | 3349(3) | 17(1) |
| C(21) | 1681(1) | 6875(6) | 4755(3) | 16(1) |
| C(22) | 1777(1) | 8099(7) | 5069(3) | 17(1) |
| C(23) | 1826(1) | 6906(6) | 6476(3) | 17(1) |
| C(24) | 1923(1) | 8118(6) | 6795(3) | 16(1) |
| C(25) | 1971(1) | 6899(6) | 8199(3) | 14(1) |

| | | | | |
|---|---|---|---|---|
| C(26) | 2068(1) | 8106(6) | 8523(3) | 16(1) |
| C(27) | 2117(1) | 6888(7) | 9925(3) | 17(1) |
| C(28) | 2214(1) | 8099(7) | 10250(3) | 17(1) |
| C(29) | 2263(1) | 6888(7) | 11655(3) | 17(1) |
| C(30) | 2360(1) | 8077(7) | 11962(4) | 22(1) |
| C(31) | 2407(1) | 6906(7) | 13386(4) | 24(1) |
| N(1) | 1044(1) | 8936(6) | -2020(3) | 18(1) |
| O(1) | 998(1) | 4569(4) | -2378(3) | 21(1) |
| O(2) | 1260(1) | 6062(6) | -274(3) | 32(1) |
| O(3) | 1346(1) | 9792(7) | -501(4) | 61(1) |

**Table S12:** Selected bond distances (Å) and bond angles (degrees) for *N*-tridecanoyl-*O*-palmitoylethanolamine (N13-O16).

| **Bond distances (Å)** | | **Bond angle (degree)** | |
|---|---|---|---|
| C(1)-C(2) | 1.520(5) | C(3)-C(2)-C(1) | 113.7(3) |
| C(2)-C(3) | 1.518(4) | C(2)-C(3)-C(4) | 113.8(3) |
| C(3)-C(4) | 1.523(4) | C(5)-C(4)-C(3) | 114.0(3) |
| C(4)-C(5) | 1.520(4) | C(4)-C(5)-C(6) | 113.5(3) |
| C(5)-C(6) | 1.521(4) | C(7)-C(6)-C(5) | 113.3(3) |
| C(6)-C(7) | 1.520(4) | C(6)-C(7)-C(8) | 113.2(3) |
| C(7)-C(8) | 1.529(4) | C(7)-C(8)-C(9) | 113.4(3) |
| C(8)-C(9) | 1.529(4) | C(10)-C(9)-C(8) | 114.1(3) |
| C(9)-C(10) | 1.526(4) | C(9)-C(10)-C(11) | 112.6(3) |
| C(10)-C(11) | 1.531(4) | C(12)-C(11)-C(10) | 113.0(3) |
| C(11)-C(12) | 1.527(4) | C(13)-C(12)-C(11) | 112.4(2) |
| C(12)-C(13) | 1.520(4) | O(1)-C(13)-N(1) | 122.7(3) |
| O(1)-C(13) | 1.230(4) | O(1)-C(13)-C(12) | 120.8(3) |
| N(1)-C(13) | 1.331(4) | N(1)-C(13)-C(12) | 116.5(3) |
| N(1)-C(14) | 1.457(4) | N(1)-C(14)-C(15) | 111.5(3) |
| C(14)-C(15) | 1.498(5) | O(2)-C(15)-C(14) | 109.3(3) |
| O(2)-C(16) | 1.342(4) | O(3)-C(16)-O(2) | 122.0(3) |
| O(2)-C(15) | 1.454(4) | O(3)-C(16)-C(17) | 126.3(3) |
| O(3)-C(16) | 1.181(4) | O(2)-C(16)-C(17) | 111.7(3) |
| C(16)-C(17) | 1.498(4) | C(16)-C(17)-C(18) | 113.5(3) |
| C(17)-C(18) | 1.523(4) | C(17)-C(18)-C(19) | 111.7(3) |
| C(18)-C(19) | 1.527(4) | C(20)-C(19)-C(18) | 113.3(3) |
| C(19)-C(20) | 1.523(4) | C(21)-C(20)-C(19) | 112.7(2) |
| C(20)-C(21) | 1.519(4) | C(20)-C(21)-C(22) | 114.6(3) |
| C(21)-C(22) | 1.523(4) | C(23)-C(22)-C(21) | 113.4(3) |
| C(22)-C(23) | 1.518(4) | C(22)-C(23)-C(24) | 113.6(3) |
| C(23)-C(24) | 1.531(4) | C(25)-C(24)-C(23) | 113.4(2) |
| C(24)-C(25) | 1.521(4) | C(24)-C(25)-C(26) | 113.6(2) |

| | | | |
|---|---|---|---|
| C(25)-C(26) | 1.531(4) | C(27)-C(26)-C(25) | 113.7(2) |
| C(26)-C(27) | 1.520(4) | C(26)-C(27)-C(28) | 113.7(3) |
| C(27)-C(28) | 1.529(4) | C(29)-C(28)-C(27) | 113.7(3) |
| C(28)-C(29) | 1.521(4) | C(28)-C(29)-C(30) | 113.5(3) |
| C(29)-C(30) | 1.524(4) | C(31)-C(30)-C(29) | 113.2(3) |
| C(30)-C(31) | 1.517(4) | | |

**Table S13:** Selected torsion angles (degrees) for *N*-tridecanoyl-*O*-palmitoylethanolamine (N13-O16).

| | |
|---|---|
| C(1) C(2) C(3) C(4) | -179.67 |
| C(2) C(3) C(4) C(5) | 179.46 |
| C(3) C(4) C(5) C(6) | 178.62 |
| C(4) C(5) C(6) C(7) | -179.81 |
| C(5) C(6) C(7) C(8) | 179.80 |
| C(6) C(7) C(8) C(9) | -179.54 |
| C(7) C(8) C(9) C(10) | -179.32 |
| C(8) C(9) C(10) C(11) | -177.31 |
| C(9) C(10) C(11) C(12) | -179.79 |
| C(10) C(11) C(12) C(13) | 67.84 |
| C(11) C(12) C(13) O(1) | 50.37 |
| C(11) C(12) C(13) N(1) | -129.94 |
| N(1) C(14) C(15) O(2) | -173.74 |
| C(16) O(2) C(15) C(14) | -99.76 |
| C(15) O(2) C(16) O(3) | 0.48 |
| C(15) O(2) C(16) C(17) | 177.86 |
| C(14) N(1) C(13) O(1) | -1.34 |
| C(14) N(1) C(13) C(12) | 178.97 |
| C(13) N(1) C(14) C(15) | 76.32 |
| O(2) C(16) C(17) C(18) | 166.66 |
| O(3) C(16) C(17) C(18) | -16.10 |
| C(16) C(17) C(18) C(19) | 177.74 |
| C(17) C(18) C(19) C(20) | 179.31 |
| C(18) C(19) C(20) C(21) | 178.85 |
| C(19) C(20) C(21) C(22) | 179.42 |
| C(20) C(21) C(22) C(23) | -179.79 |
| C(21) C(22) C(23) C(24) | 179.75 |
| C(22) C(23) C(24) C(25) | -179.58 |

| | |
|---|---|
| C(23) C(24) C(25) C(26) | -180.00 |
| C(24) C(25) C(26) C(27) | -179.95 |
| C(25) C(26) C(27) C(28) | -179.87 |
| C(26) C(27) C(28) C(29) | 179.85 |
| C(27) C(28) C(29) C(30) | 179.26 |
| C(28) C(29) C(30) C(31) | 178.69 |

**Table S14:** Fractional atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters ($Å^2 \times 10^3$) for the *N*-myristoyl-*O*-palmitoylethanolamine (N14-O16). U(eq) is defined as one third of the trace of the orthogonalized $U_{ij}$ tensor [$U(eq) = \frac{1}{3} \sum_i \sum_j U_{ij} a_{i*} a_{j*} a_i a_j \cos(ai, aj)$].

| Atom | x | y | z | U(eq) |
|---|---|---|---|---|
| C(1) | 7644(3) | 6915(5) | 5701(1) | 27(1) |
| C(2) | 6233(3) | 8096(5) | 5793(1) | 20(1) |
| C(3) | 5945(3) | 6886(5) | 5984(1) | 17(1) |
| C(4) | 4562(3) | 8102(4) | 6080(1) | 16(1) |
| C(5) | 4275(3) | 6882(4) | 6270(1) | 16(1) |
| C(6) | 2886(3) | 8096(4) | 6366(1) | 15(1) |
| C(7) | 2595(3) | 6878(4) | 6555(1) | 15(1) |
| C(8) | 1203(3) | 8109(5) | 6651(1) | 15(1) |
| C(9) | 906(3) | 6891(5) | 6841(1) | 16(1) |
| C(10) | -490(3) | 8127(4) | 6936(1) | 15(1) |
| C(11) | -799(3) | 6964(4) | 7127(1) | 15(1) |
| C(12) | -2251(3) | 8138(5) | 7214(1) | 15(1) |
| C(13) | -2565(3) | 7017(4) | 7405(1) | 14(1) |
| C(14) | -1397(2) | 8002(4) | 7545(1) | 11(1) |
| C(15) | 433(3) | 6732(5) | 7784(1) | 21(1) |
| C(16) | -261(3) | 7978(6) | 7954(1) | 29(1) |
| C(17) | 1310(3) | 7319(5) | 8218(1) | 20(1) |
| C(18) | 2606(3) | 8511(5) | 8326(1) | 15(1) |
| C(19) | 2826(3) | 7113(5) | 8512(1) | 19(1) |
| C(20) | 4204(3) | 8298(5) | 8615(1) | 16(1) |
| C(21) | 4452(3) | 6988(5) | 8802(1) | 16(1) |
| C(22) | 5846(3) | 8144(5) | 8901(1) | 16(1) |
| C(23) | 6120(3) | 6897(5) | 9091(1) | 15(1) |
| C(24) | 7517(3) | 8091(5) | 9187(1) | 15(1) |
| C(25) | 7795(3) | 6873(5) | 9379(1) | 16(1) |

| | | | | |
|---|---|---|---|---|
| C(26) | 9186(3) | 8097(5) | 9473(1) | 16(1) |
| C(27) | 9471(3) | 6895(5) | 9665(1) | 15(1) |
| C(28) | 10856(3) | 8107(5) | 9760(1) | 15(1) |
| C(29) | 11139(3) | 6902(5) | 9951(1) | 15(1) |
| C(30) | 12535(3) | 8107(5) | 10048(1) | 17(1) |
| C(31) | 12801(3) | 6909(5) | 10238(1) | 20(1) |
| C(32) | 14223(3) | 8096(5) | 10332(1) | 23(1) |
| N(1) | -734(2) | 6073(4) | 7649(1) | 15(1) |
| O(1) | -1082(2) | 10442(3) | 7561(1) | 22(1) |
| O(2) | 952(2) | 8907(4) | 8075(1) | 34(1) |
| O(3) | 674(3) | 5228(6) | 8248(1) | 66(1) |

**Table S15:** Selected bond distances (Å) and bond angles (degrees) for *N*-myristoyl-*O*-palmitoylethanolamine (N14-O16).

| **Bond distances (Å)** | | **Bond angle (degree)** | |
|---|---|---|---|
| C(1)-C(2) | 1.520(3) | C(1)-C(2)-C(3) | 112.7(2) |
| C(3)-C(2) | 1.529(3) | C(4)-C(3)-C(2) | 113.4(2) |
| C(3)-C(4) | 1.520(3) | C(3)-C(4)-C(5) | 113.29(19) |
| C(5)-C(4) | 1.526(3) | C(6)-C(5)-C(4) | 113.36(19) |
| C(5)-C(6) | 1.525(3) | C(7)-C(6)-C(5) | 113.47(19) |
| C(7)-C(6) | 1.519(3) | C(6)-C(7)-C(8) | 113.05(19) |
| C(7)-C(8) | 1.528(3) | C(9)-C(8)-C(7) | 113.24(19) |
| C(9)-C(8) | 1.527(3) | C(8)-C(9)-C(10) | 113.07(19) |
| C(9)-C(10) | 1.530(3) | C(11)-C(10)-C(9) | 114.00(19) |
| C(10)-C(11) | 1.525(3) | C(10)-C(11)-C(12) | 112.58(19) |
| C(11)-C(12) | 1.533(3) | C(13)-C(12)-C(11) | 113.19(19) |
| C(12)-C(13) | 1.518(3) | C(12)-C(13)-C(14) | 111.96(18) |
| C(13)-C(14) | 1.520(3) | O(1)-C(14)-N(1) | 122.0(2) |
| O(1)-C(14) | 1.228(3) | O(1)-C(14)-C(13) | 121.41(19) |
| N(1)-C(14) | 1.339(3) | N(1)-C(14)-C(13) | 116.59(19) |
| C(15)-N(1) | 1.458(3) | N(1)-C(15)-C(16) | 111.15(19) |
| C(16)-C(15) | 1.506(3) | O(2)-C(16)-C(15) | 108.9(2) |
| O(2)-C(16) | 1.449(3) | C(17)-O(2)-C(16) | 117.5(2) |
| C(17)-O(2) | 1.337(3) | O(2)-C(17)-C(18) | 111.2(2) |
| O(3)-C(17) | 1.182(3) | O(3)-C(17)-O(2) | 121.9(2) |
| C(18)-C(17) | 1.499(3) | O(3)-C(17)-C(18) | 126.8(2) |
| C(19)-C(18) | 1.527(3) | C(17)-C(18)-C(19) | 112.7(2) |
| C(20)-C(19) | 1.534(3) | C(18)-C(19)-C(20) | 111.3(2) |
| C(21)-C(20) | 1.520(3) | C(21)-C(20)-C(19) | 113.03(19) |
| C(21)-C(22) | 1.524(3) | C(20)-C(21)-C(22) | 112.3(2) |
| C(23)-C(22) | 1.532(3) | C(21)-C(22)-C(23) | 113.7(2) |
| C(23)-C(24) | 1.526(3) | C(24)-C(23)-C(22) | 112.9(2) |
| C(25)-C(24) | 1.530(3) | C(23)-C(24)-C(25) | 113.3(2) |

| | | | |
|---|---|---|---|
| C(25)-C(26) | 1.524(3) | C(26)-C(25)-C(24) | 112.7(2) |
| C(26)-C(27) | 1.530(3) | C(25)-C(26)-C(27) | 113.03(19) |
| C(27)-C(28) | 1.518(3) | C(28)-C(27)-C(26) | 113.27(19) |
| C(29)-C(28) | 1.530(3) | C(27)-C(28)-C(29) | 113.2(2) |
| C(29)-C(30) | 1.530(3) | C(30)-C(29)-C(28) | 113.6(2) |
| C(31)-C(30) | 1.519(3) | C(31)-C(30)-C(29) | 113.2(2) |
| C(31)-C(32) | 1.536(3) | C(30)-C(31)-C(32) | 112.7(2) |

**Table S16:** Selected torsion angles (degrees) for *N*-myristoyl-*O*-palmitoylethanolamine (N14-O16).

| | |
|---|---|
| C(1) C(2) C(3) C(4) | -178.41 |
| C(2) C(3) C(4) C(5) | -179.78 |
| C(3) C(4) C(5) C(6) | 179.90 |
| C(4) C(5) C(6) C(7) | -179.81 |
| C(5) C(6) C(7) C(8) | -179.94 |
| C(6) C(7) C(8) C(9) | 179.97 |
| C(7) C(8) C(9) C(10) | 179.92 |
| C(8) C(9) C(10) C(11) | 179.33 |
| C(9) C(10) C(11) C(12) | 177.02 |
| C(10) C(11) C(12) C(13) | 179.50 |
| C(11) C(12) C(13) C(14) | -68.26 |
| C(12) C(13) C(14) O(1) | -51.00 |
| C(12) C(13) C(14) N(1) | 129.05 |
| O(1) C(14) N(1) C(15) | 1.59 |
| C(13) C(14) N(1) C(15) | -178.47 |
| C(16) C(15) N(1) C(14) | -76.24 |
| N(1) C(15) C(16) O(2) | 172.91 |
| C(16) O(2) C(17) O(3) | -0.20 |
| C(16) O(2) C(17) C(18) | -178.50 |
| C(17) O(2) C(16) C(15) | 101.14 |
| O(2) C(17) C(18) C(19) | -167.66 |
| O(3) C(17) C(18) C(19) | 14.14 |
| C(17) C(18) C(19) C(20) | -177.49 |
| C(18) C(19) C(20) C(21) | -179.23 |
| C(19) C(20) C(21) C(22) | -178.69 |
| C(20) C(21) C(22) C(23) | -179.23 |
| C(21) C(22) C(23) C(24) | 179.78 |
| C(22) C(23) C(24) C(25) | -179.60 |
| C(23) C(24) C(25) C(26) | 179.63 |

| | |
|---|---|
| C(24) C(25) C(26) C(27) | -179.89 |
| C(25) C(26) C(27) C(28) | -179.98 |
| C(26) C(27) C(28) C(29) | -180.00 |
| C(27) C(28) C(29) C(30) | -179.89 |
| C(28) C(29) C(30) C(31) | -179.70 |
| C(29) C(30) C(31) C(32) | -178.90 |

**Table S17:** Fractional atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters ($Å^2 \times 10^3$) for the *N*-lauroyl-*O*-pentadecanoylethanolamine (N12-O15). U(eq) is defined as one third of the trace of the orthogonalized $U_{ij}$ tensor [$U(eq) = \frac{1}{3} \sum_i \sum_j U_{ij} a_{i*} a_{j*} a_i a_j \cos(ai, aj)$].

| Atom | x | y | z | U(eq) |
|---|---|---|---|---|
| C(1) | 2401(1) | 3089(7) | 3395(4) | 29(1) |
| C(2) | 2351(1) | 1918(7) | 1962(4) | 26(1) |
| C(3) | 2248(1) | 3113(6) | 1660(4) | 22(1) |
| C(4) | 2196(1) | 1906(6) | 242(4) | 22(1) |
| C(5) | 2094(1) | 3112(6) | -66(4) | 20(1) |
| C(6) | 2042(1) | 1895(6) | -1465(4) | 22(1) |
| C(7) | 1940(1) | 3101(6) | -1800(4) | 22(1) |
| C(8) | 1888(1) | 1890(6) | -3219(4) | 22(1) |
| C(9) | 1785(1) | 3028(6) | -3534(4) | 21(1) |
| C(10) | 1739(1) | 1870(6) | -5001(4) | 22(1) |
| C(11) | 1635(1) | 2999(6) | -5346(4) | 21(1) |
| C(12) | 1560(1) | 2022(6) | -4185(3) | 20(1) |
| C(13) | 1431(1) | 3258(6) | -2402(4) | 26(1) |
| C(14) | 1339(1) | 1978(8) | -3120(4) | 34(1) |
| C(15) | 1197(1) | 2687(7) | -1581(4) | 24(1) |
| C(16) | 1138(1) | 1517(6) | -292(4) | 24(1) |
| C(17) | 1038(1) | 2893(6) | -100(4) | 24(1) |
| C(18) | 982(1) | 1730(6) | 1260(4) | 24(1) |
| C(19) | 881(1) | 3026(6) | 1477(4) | 24(1) |
| C(20) | 828(1) | 1871(6) | 2856(4) | 23(1) |
| C(21) | 726(1) | 3110(6) | 3104(4) | 23(1) |
| C(22) | 673(1) | 1908(6) | 4470(4) | 25(1) |
| C(23) | 571(1) | 3123(6) | 4728(4) | 23(1) |

| | | | | |
|---|---|---|---|---|
| C(24) | 519(1) | 1922(6) | 6107(4) | 22(1) |
| C(25) | 416(1) | 3107(6) | 6359(4) | 25(1) |
| C(26) | 364(1) | 1879(6) | 7736(4) | 24(1) |
| C(27) | 261(1) | 3003(6) | 7978(4) | 27(1) |
| C(28) | 211(1) | 1783(7) | 9355(4) | 32(1) |
| C(29) | 107(1) | 2912(9) | 9615(5) | 47(1) |
| N(1) | 1504(1) | 3931(5) | -3546(3) | 23(1) |
| O(1) | 1552(1) | -439(4) | -3872(3) | 26(1) |
| O(2) | 1275(1) | 1076(5) | -1922(3) | 38(1) |
| O(3) | 1183(1) | 4794(7) | -2229(4) | 67(1) |

**Table S18:** Selected bond distances (Å) and bond angles (degrees) for *N*-lauroyl-*O*-pentadecanoylethanolamine (N12-O15).

| **Bond distances (Å)** | | **Bond angle (degree)** | |
|---|---|---|---|
| C(2)-C(1) | 1.521(4) | C(1)-C(2)-C(3) | 112.7(3) |
| C(2)-C(3) | 1.528(4) | C(4)-C(3)-C(2) | 113.1(3) |
| C(4)-C(3) | 1.527(4) | C(5)-C(4)-C(3) | 113.1(3) |
| C(4)-C(5) | 1.527(4) | C(6)-C(5)-C(4) | 113.1(3) |
| C(6)-C(5) | 1.516(4) | C(5)-C(6)-C(7) | 113.8(3) |
| C(6)-C(7) | 1.527(4) | C(8)-C(7)-C(6) | 113.5(3) |
| C(8)-C(7) | 1.525(4) | C(9)-C(8)-C(7) | 113.8(3) |
| C(8)-C(9) | 1.521(4) | C(8)-C(9)-C(10) | 112.1(2) |
| C(10)-C(9) | 1.524(4) | C(9)-C(10)-C(11) | 113.0(2) |
| C(10)-C(11) | 1.534(4) | C(12)-C(11)-C(10) | 112.0(2) |
| C(11)-C(12) | 1.523(4) | O(1)-C(12)-C(11) | 120.9(3) |
| O(1)-C(12) | 1.237(4) | N(1)-C(12)-C(11) | 117.0(3) |
| N(1)-C(12) | 1.335(4) | O(1)-C(12)-N(1) | 122.1(3) |
| N(1)-C(13) | 1.456(4) | O(2)-C(14)-C(13) | 109.2(3) |
| C(13)-C(14) | 1.512(5) | N(1)-C(13)-C(14) | 111.7(3) |
| O(2)-C(14) | 1.446(4) | C(15)-O(2)-C(14) | 117.8(3) |
| O(2)-C(15) | 1.347(4) | O(3)-C(15)-O(2) | 121.3(3) |
| O(3)-C(15) | 1.188(4) | C(15)-C(16)-C(17) | 113.8(3) |
| C(16)-C(15) | 1.509(4) | C(16)-C(17)-C(18) | 112.2(3) |
| C(16)-C(17) | 1.521(4) | C(19)-C(18)-C(17) | 113.8(3) |
| C(18)-C(17) | 1.532(4) | C(18)-C(19)-C(20) | 112.9(3) |
| C(18)-C(19) | 1.520(4) | (21)-C(20)-C(19) | 114.4(3) |
| C(20)-C(19) | 1.529(4) | C(22)-C(21)-C(20) | 113.5(3) |
| C(20)-C(21) | 1.527(4) | C(21)-C(22)-C(23) | 114.1(3) |
| C(22)-C(21) | 1.521(4) | C(24)-C(23)-C(22) | 113.7(3) |
| C(22)-C(23) | 1.528(4) | C(23)-C(24)-C(25) | 113.9(3) |
| C(24)-C(23) | 1.526(4) | C(26)-C(25)-C(24) | 113.5(3) |

| | | | |
|---|---|---|---|
| C(24)-C(25) | 1.527(4) | C(27)-C(26)-C(25) | 113.9(3) |
| C(25)-C(26) | 1.527(4) | C(28)-C(27)-C(26) | 113.4(3) |
| C(26)-C(27) | 1.522(4) | C(27)-C(28)-C(29) | 113.8(3) |
| C(27)-C(28) | 1.515(5) | | |
| C(28)-C(29) | 1.526(5) | | |

**Table S19:** Selected torsion angles (degrees) for *N*-lauroyl-*O*-pentadecanoylethanolamine (N12-O15).

| | |
|---|---|
| C(1) C(2) C(3) C(4) | -178.79 |
| C(2) C(3) C(4) C(5) | -179.65 |
| C(3) C(4) C(5) C(6) | -179.49 |
| C(4) C(5) C(6) C(7) | -179.38 |
| C(5) C(6) C(7) C(8) | 179.37 |
| C(6) C(7) C(8) C(9) | 178.44 |
| C(7) C(8) C(9) C(10) | 177.25 |
| C(8) C(9) C(10) C(11) | -179.74 |
| C(9) C(10) C(11) C(12) | -67.70 |
| C(10) C(11) C(12) O(1) | -50.91 |
| C(10) C(11) C(12) N(1) | 129.77 |
| N(1) C(13) C(14) O(2) | 173.61 |
| C(15) O(2) C(14) C(13) | 100.19 |
| C(14) O(2) C(15) O(3) | -0.69 |
| C(14) O(2) C(15) C(16) | -178.82 |
| C(13) N(1) C(12) O(1) | 1.75 |
| C(13) N(1) C(12) C(11) | -178.94 |
| C(12) N(1) C(13) C(14) | -76.26 |
| O(2) C(15) C(16) C(17) | -167.05 |
| O(3) C(15) C(16) C(17) | 14.95 |
| C(15) C(16) C(17) C(18) | -177.64 |
| C(16) C(17) C(18) C(19) | -179.19 |
| C(17) C(18) C(19) C(20) | -178.96 |
| C(18) C(19) C(20) C(21) | -179.55 |
| C(19) C(20) C(21) C(22) | 179.30 |
| C(20) C(21) C(22) C(23) | -179.80 |
| C(21) C(22) C(23) C(24) | -179.56 |
| C(22) C(23) C(24) C(25) | -179.34 |
| C(23) C(24) C(25) C(26) | 179.66 |

| | |
|---|---|
| C(24) C(25) C(26) C(27) | -178.80 |
| C(25) C(26) C(27) C(28) | -179.57 |
| C(26) C(27) C(28) C(29) | 179.57 |

**Table S20:** Fractional atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters ($Å^2 \times 10^3$) for the *N*-myristoyl-*O*-pentadecanoylethanolamine (N14-O15). U(eq) is defined as one third of the trace of the orthogonalized $U_{ij}$ tensor [$U(eq) = \frac{1}{3} \sum_i \sum_j U_{ij} a_{i*} a_{j*} a_i a_j \cos(ai, aj)$].

| Atom | x | y | z | U(eq) |
|---|---|---|---|---|
| C(1) | 2407(1) | 6907(5) | 1536(2) | 27(1) |
| C(2) | 2360(1) | 8084(4) | 2933(2) | 23(1) |
| C(3) | 2263(1) | 6891(4) | 3171(2) | 20(1) |
| C(4) | 2214(1) | 8096(4) | 4545(2) | 19(1) |
| C(5) | 2117(1) | 6884(4) | 4788(2) | 19(1) |
| C(6) | 2068(1) | 8099(4) | 6162(2) | 19(1) |
| C(7) | 1972(1) | 6887(4) | 6411(2) | 19(1) |
| C(8) | 1923(1) | 8103(4) | 7787(2) | 18(1) |
| C(9) | 1827(1) | 6902(4) | 8038(2) | 18(1) |
| C(10) | 1779(1) | 8117(4) | 9424(2) | 19(1) |
| C(11) | 1682(1) | 6973(4) | 9680(2) | 18(1) |
| C(12) | 1637(1) | 8131(4) | 11114(2) | 18(1) |
| C(13) | 1540(1) | 6990(4) | 11395(2) | 18(1) |
| C(14) | 1470(1) | 7979(4) | 10196(2) | 17(1) |
| C(15) | 1348(1) | 6747(4) | 8322(2) | 23(1) |
| C(16) | 1262(1) | 8031(5) | 8996(3) | 29(1) |
| C(17) | 1128(1) | 7317(4) | 7365(2) | 23(1) |
| C(18) | 1072(1) | 8493(4) | 6045(2) | 21(1) |
| C(19) | 977(1) | 7101(4) | 5789(2) | 21(1) |
| C(20) | 925(1) | 8279(4) | 4399(2) | 20(1) |
| C(21) | 830(1) | 6972(4) | 4104(2) | 20(1) |
| C(22) | 779(1) | 8136(4) | 2694(2) | 19(1) |
| C(23) | 683(1) | 6888(4) | 2381(2) | 19(1) |

| | | | | |
|---|---|---|---|---|
| C(24) | 634(1) | 8085(4) | 966(2) | 19(1) |
| C(25) | 537(1) | 6868(4) | 646(2) | 20(1) |
| C(26) | 488(1) | 8087(4) | -763(2) | 19(1) |
| C(27) | 392(1) | 6891(4) | -1086(2) | 20(1) |
| C(28) | 343(1) | 8133(4) | -2490(2) | 21(1) |
| C(29) | 245(1) | 6991(4) | -2811(2) | 23(1) |
| C(30) | 197(1) | 8225(5) | -4225(3) | 29(1) |
| C(31) | 101(1) | 7087(6) | -4547(3) | 39(1) |
| N(1) | 1416(1) | 6070(3) | 9516(2) | 20(1) |
| O(1) | 1462(1) | 10442(3) | 9875(2) | 24(1) |
| O(2) | 1200(1) | 8943(4) | 7756(2) | 33(1) |
| O(3) | 1114(1) | 5200(5) | 7975(3) | 62(1) |

**Table S21:** Selected bond distances (Å) and bond angles (degrees) for *N*-myristoyl-*O*-pentadecanoylethanolamine (N14-O15).

| Bond distances (Å) | | Bond angle (degree) | |
|---|---|---|---|
| C(1)-C(2) | 1.526(3) | C(1)-C(2)-C(3) | 113.03(17) |
| C(2)-C(3) | 1.531(3) | C(4)-C(3)-C(2) | 113.70(16) |
| C(3)-C(4) | 1.529(3) | C(3)-C(4)-C(5) | 113.59(16) |
| C(4)-C(5) | 1.532(3) | C(6)-C(5)-C(4) | 113.52(16) |
| C(5)-C(6) | 1.532(3) | C(5)-C(6)-C(7) | 113.69(16) |
| C(6)-C(7) | 1.533(3) | C(8)-C(7)-C(6) | 113.42(16) |
| C(7)-C(8) | 1.529(3) | C(7)-C(8)-C(9) | 113.59(16) |
| C(8)-C(9) | 1.530(3) | C(8)-C(9)-C(10) | 113.32(16) |
| C(9)-C(10) | 1.532(3) | C(11)-C(10)-C(9) | 114.13(16) |
| C(10)-C(11) | 1.531(3) | C(12)-C(11)-C(10) | 112.84(16) |
| C(11)-C(12) | 1.530(3) | C(11)-C(12)-C(13) | 113.56(16) |
| C(12)-C(13) | 1.538(3) | C(14)-C(13)-C(12) | 111.71(15) |
| C(13)-C(14) | 1.517(3) | O(1)-C(14)-N(1) | 121.89(18) |
| N(1)-C(14) | 1.341(3) | O(1)-C(14)-C(13) | 121.28(18) |
| O(1)-C(14) | 1.241(2) | N(1)-C(14)-C(13) | 116.82(16) |
| N(1)-C(15) | 1.459(3) | N(1)-C(15)-C(16) | 111.27(17) |
| O(2)-C(16) | 1.452(3) | O(2)-C(16)-C(15) | 108.98(18) |
| O(2)-C(17) | 1.353(3) | O(3)-C(17)-O(2) | 122.3(2) |
| O(3)-C(17) | 1.182(3) | O(3)-C(17)-C(18) | 126.1(2) |
| C(17)-C(18) | 1.507(3) | O(2)-C(17)-C(18) | 111.53(18) |
| C(18)-C(19) | 1.531(3) | C(17)-C(18)-C(19) | 113.56(17) |
| C(19)-C(20) | 1.529(3) | C(20)-C(19)-C(18) | 111.65(16) |
| C(20)-C(21) | 1.530(3) | C(19)-C(20)-C(21) | 113.65(16) |
| C(21)-C(22) | 1.528(3) | C(22)-C(21)-C(20) | 112.90(16) |
| C(22)-C(23) | 1.536(3) | C(21)-C(22)-C(23) | 114.08(16) |
| C(23)-C(24) | 1.529(3) | C(24)-C(23)-C(22) | 113.22(16) |
| C(24)-C(25) | 1.530(3) | C(23)-C(24)-C(25) | 113.72(16) |

| | | | |
|---|---|---|---|
| C(25)-C(26) | 1.528(3) | C(26)-C(25)-C(24) | 113.39(16) |
| C(26)-C(27) | 1.531(3) | C(25)-C(26)-C(27) | 113.71(16) |
| C(27)-C(28) | 1.526(3) | C(28)-C(27)-C(26) | 113.32(16) |
| C(28)-C(29) | 1.533(3) | C(27)-C(28)-C(29) | 113.91(17) |
| C(29)-C(30) | 1.526(3) | C(30)-C(29)-C(28) | 113.49(18) |
| C(30)-C(31) | 1.524(3) | C(31)-C(30)-C(29) | 113.5(2) |

**Table S22:** Selected torsion angles (degrees) for *N*-myristoyl-*O*-pentadecanoylethanolamine (N14-O15).

| | |
|---|---|
| C(1) C(2) C(3) C(4) | -178.70 |
| C(2) C(3) C(4) C(5) | -179.59 |
| C(3) C(4) C(5) C(6) | -179.85 |
| C(4) C(5) C(6) C(7) | -179.91 |
| C(5) C(6) C(7) C(8) | 179.86 |
| C(6) C(7) C(8) C(9) | 179.94 |
| C(7) C(8) C(9) C(10) | 179.65 |
| C(8) C(9) C(10) C(11) | 179.12 |
| C(9) C(10) C(11) C(12) | 177.38 |
| C(10) C(11) C(12) C(13) | -179.65 |
| C(11) C(12) C(13) C(14) | -68.55 |
| C(12) C(13) C(14) O(1) | -50.58 |
| C(12) C(13) C(14) N(1) | 129.98 |
| N(1) C(15) C(16) O(2) | 173.64 |
| C(17) O(2) C(16) C(15) | 99.92 |
| C(16) O(2) C(17) O(3) | -1.40 |
| C(16) O(2) C(17) C(18) | -178.75 |
| C(15) N(1) C(14) O(1) | 1.88 |
| C(15) N(1) C(14) C(13) | -178.69 |
| C(14) N(1) C(15) C(16) | -76.44 |
| O(2) C(17) C(18) C(19) | -166.92 |
| O(3) C(17) C(18) C(19) | 15.86 |
| C(17) C(18) C(19) C(20) | -177.58 |
| C(18) C(19) C(20) C(21) | -179.48 |
| C(19) C(20) C(21) C(22) | -178.93 |
| C(20) C(21) C(22) C(23) | -179.24 |
| C(21) C(22) C(23) C(24) | 179.90 |
| C(22) C(23) C(24) C(25) | -179.71 |
| C(23) C(24) C(25) C(26) | 179.65 |

| | |
|---|---|
| C(24) C(25) C(26) C(27) | -179.68 |
| C(25) C(26) C(27) C(28) | 179.67 |
| C(26) C(27) C(28) C(29) | -179.00 |
| C(27) C(28) C(29) C(30) | -179.43 |
| C(28) C(29) C(30) C(31) | 179.90 |

**Table S23:** The unit cell parameters of simulated and experimental (***in brackets***) systems at 100K; unit cell lengths (a, b and c) and angles (α, β and γ) are reported in Å and degrees, respectively.

| **System** (Total atoms in each polymorph) | **Supercell size** | **a, b, c (Å)** | **α, β and γ (degrees)** |
|---|---|---|---|
| **N14-O16** (79200) | α (10×10×2) | 9.51, 4.72, 72.95 ***(8.78, 4.88, 72.68)*** | 90.02, 89.97, 89.92 ***(90, 90, 90)*** |
| | β (1×10×10) | ***145.82, 4.76, 8.72*** | ***93.2, 91.6, 90.1*** |
| **N13-O16** (76800) | α (10×10×2) | 7.43, 4.8, 83.0 | 91.7, 94.8, 90.1 |
| | β (1×10×10) | 144.07, 4.73, 8.65 ***(143.4, 4.88, 8.73)*** | 89.99, 91.8, 89.97 ***(90.0, 91.14, 90.0)*** |
| **N12-O16** (74400) | α (10×10×2) | 9.51, 4.72, 68.77 | 90.03, 89.99, 89.89 |
| | β (2×10×10) | 68.95, 4.74, 8.67 ***(68.97, 4.85, 8.91)*** | 89.94, 92.91, 89.97 ***(90.0, 92.79, 90.0)*** |
| **N14-O15** (76800) | α (10×10×2) | 8.64, 4.74, 72.10 | 90.96, 88.39, 86.86 |
| | β (1×10×10) | 143.93, 4.74, 8.66 ***(144.31, 4.89, 8.75)*** | 90.05, 91.75, 90.05 ***(90.0, 91.44, 90.0)*** |
| **N12-O15** (72000) | α (10×10×2) | 8.60, 4.73, 68.28 | 89.09, 90.73, 90.00 |
| | β (1×10×10) | 135.93, 4.77, 8.63 ***(135.24, 4.88, 8.74)*** | 89.95, 94.71, 90.00 ***(90.0, 91,27, 90.0)*** |
| **N11-O16** (72000) | α (10×10×2) | 8.7, 4.8, 67.8 | 90.04, 90.03, 89.97 |
| | β (1×10×10) | 134.00, 4.77, 8.72 | 90.05, 91.4, 89.98 |

## Supporting Figures:

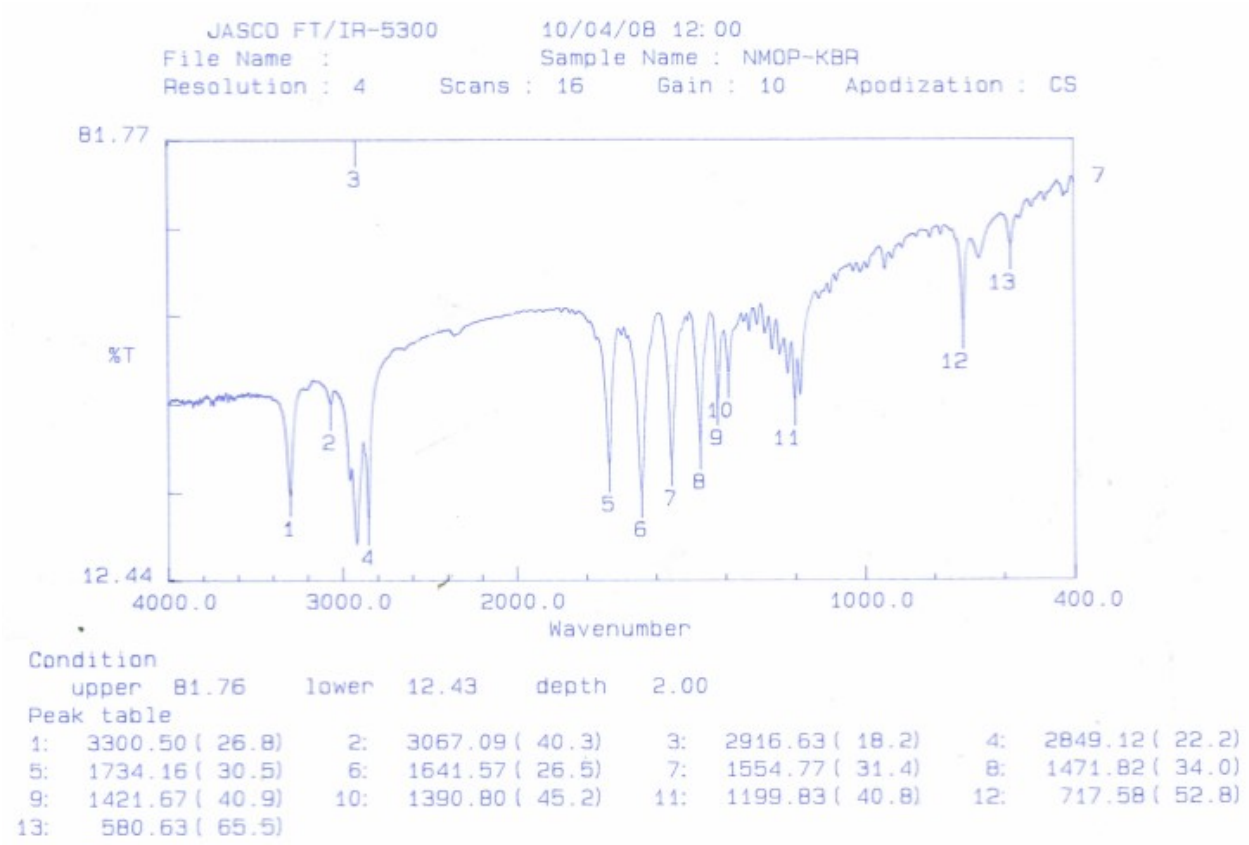


**Fig. S1.** FT-IR spectrum of *N*-myristoyl-*O*-palmitoylethanolamine (N14-O16s) using KBr pellet at room temperature.

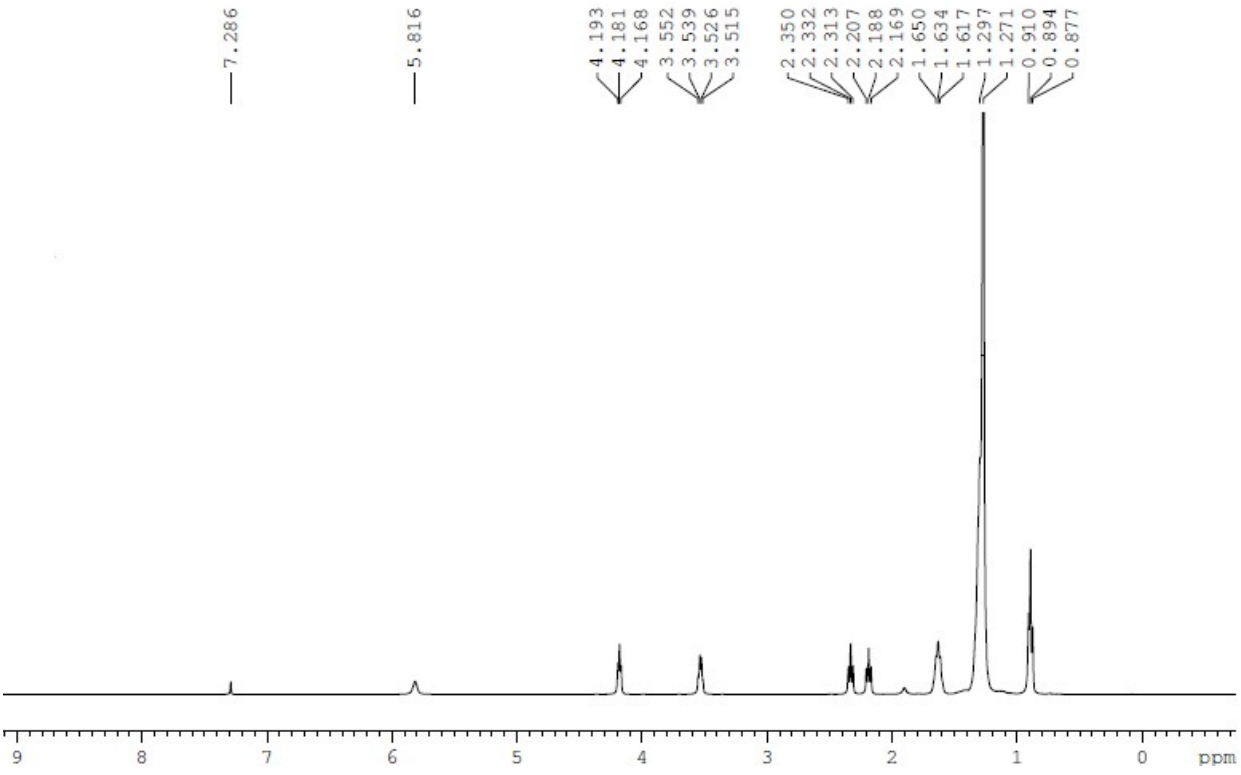


**Fig. S2.** $^{1}$H-NMR spectrum of *N*-myristoyl-*O*-palmitoylethanolamine (N14-O16s) in $CDCl_3$ (solvent) at room temperature.

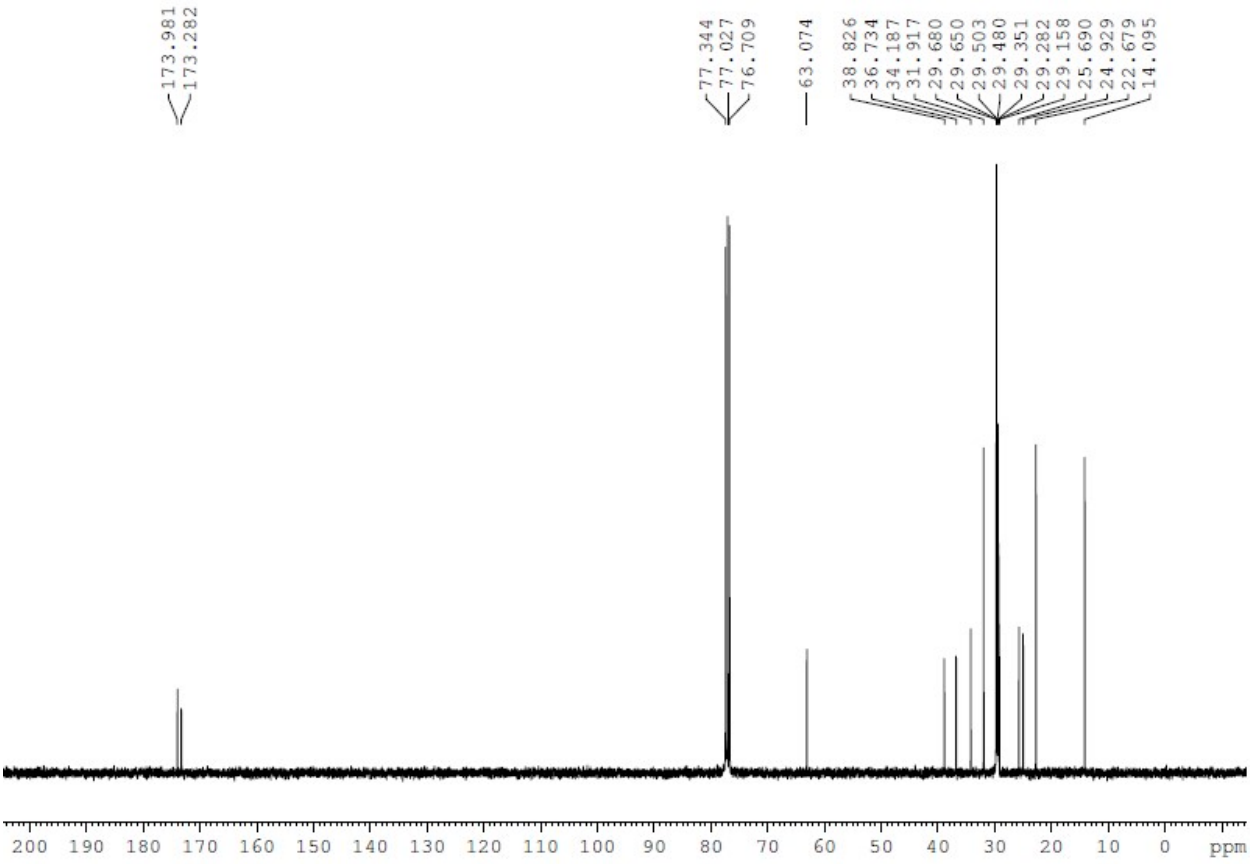


**Fig. S3.** $^{13}$C-NMR spectrum of *N*-myristoyl-*O*-palmitoyl-ethanolamine (N14-O16s) in $CDCl_3$ (solvent) at room temperature.

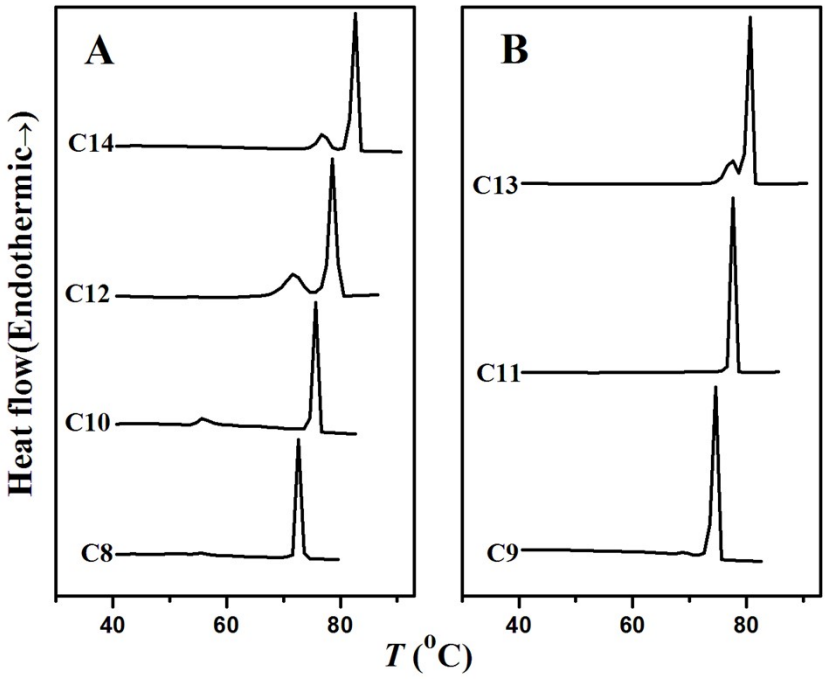


**Fig. S4.** DSC heating thermograms of dry DAEs with fixed *O*-pentadecanoyl chains and different *N*-acyl chains (C=8-14). A) Thermograms of DAEs with even number of C-atoms in the *N*-acyl chains. B) Thermograms of DAEs with odd number of C-atoms in the *N*-acyl chains. The number of C-atoms in the *N*-acyl chain is indicated against each thermogram.

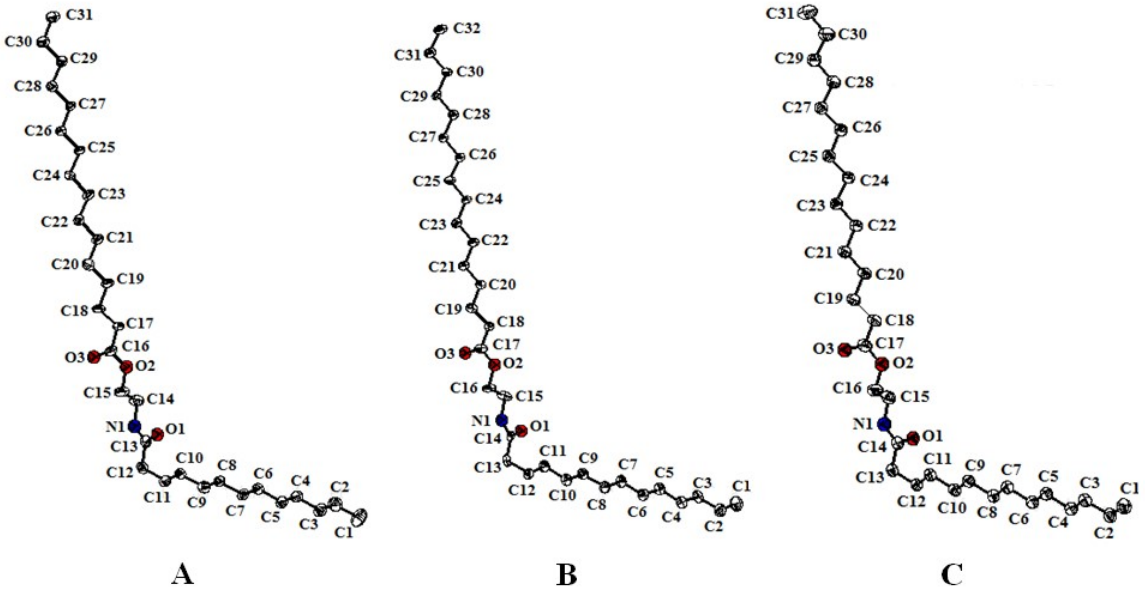


**Fig. S5.** ORTEP diagrams of DAEs. (A) *N*-tridecanoyl-*O*-palmitoylethanolamine (N13-O16), (B) *N*-myristoyl-*O*-palmitoylethanolamine (N14-O16), and (C) *N*-myristoyl-*O*-pentadecanoyl-ethanolamine (N14-O15).

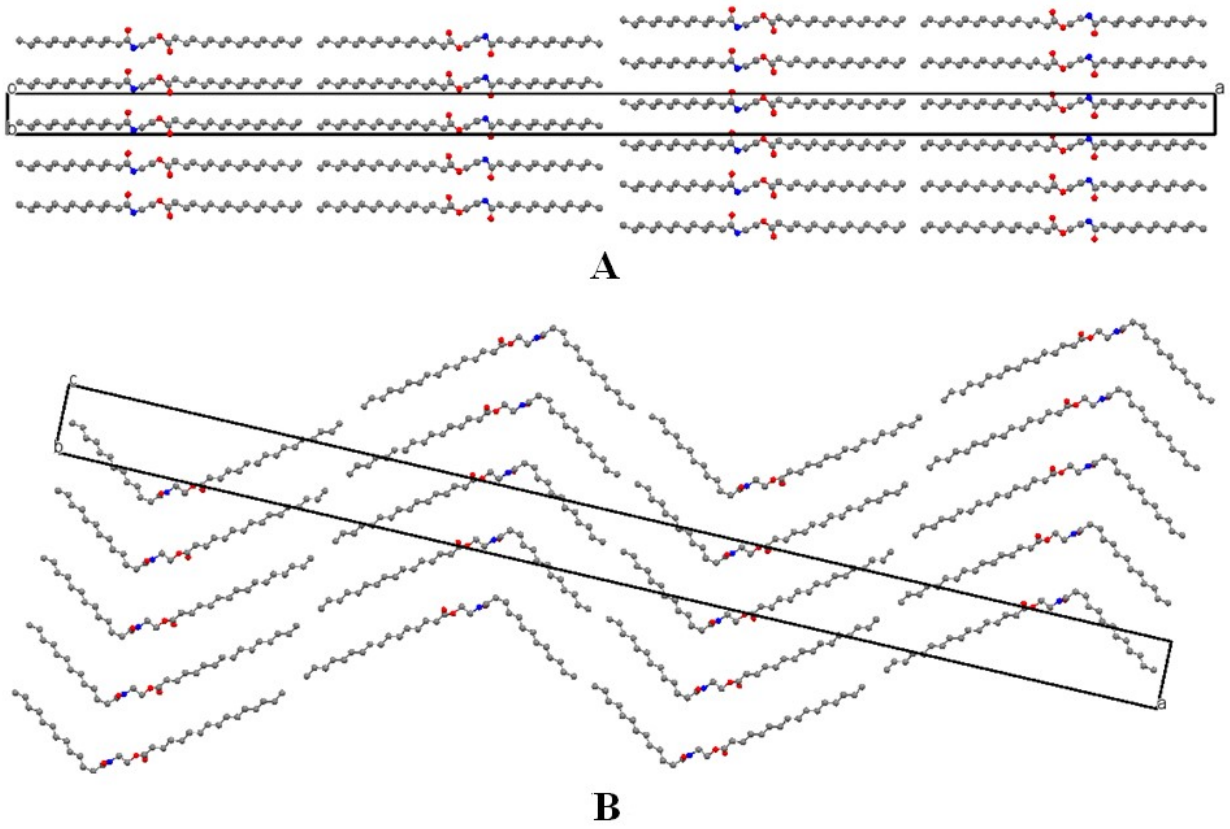


**Fig. S6.** Packing diagrams of N13-O16. (A) A view down the *c*-axis. (B) A view down the *b*-axis. Length of hydrophobic region is also indicated. The crystal lattice of N13-O16 has two different types of hydrophobic regions, one shorter in length and other longer.

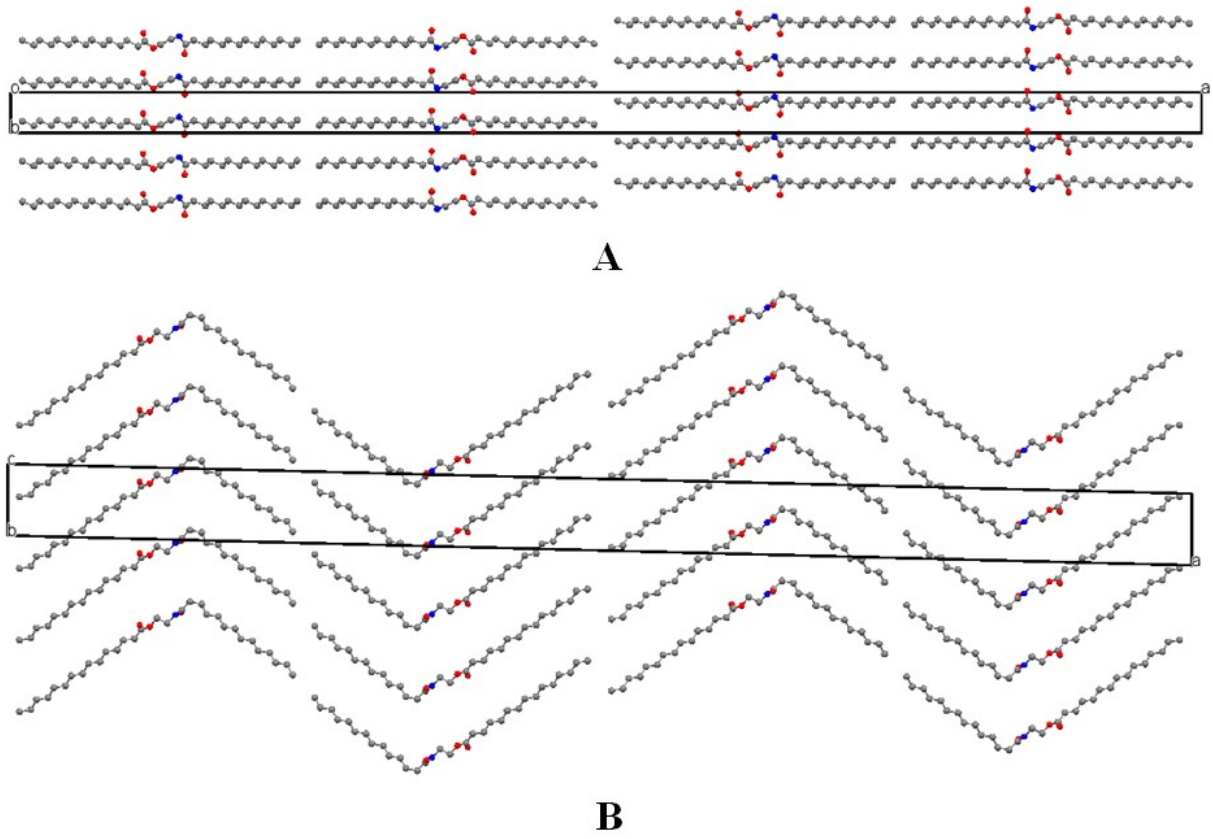


**Fig. S7**. Packing diagrams of N14-O15. (A) A view down the *c*-axis. (B) A view down the *b*-axis. Length of hydrophobic region is also indicated. The crystal lattice of N14-O15 has two different types of hydrophobic regions, one shorter in length and other longer.

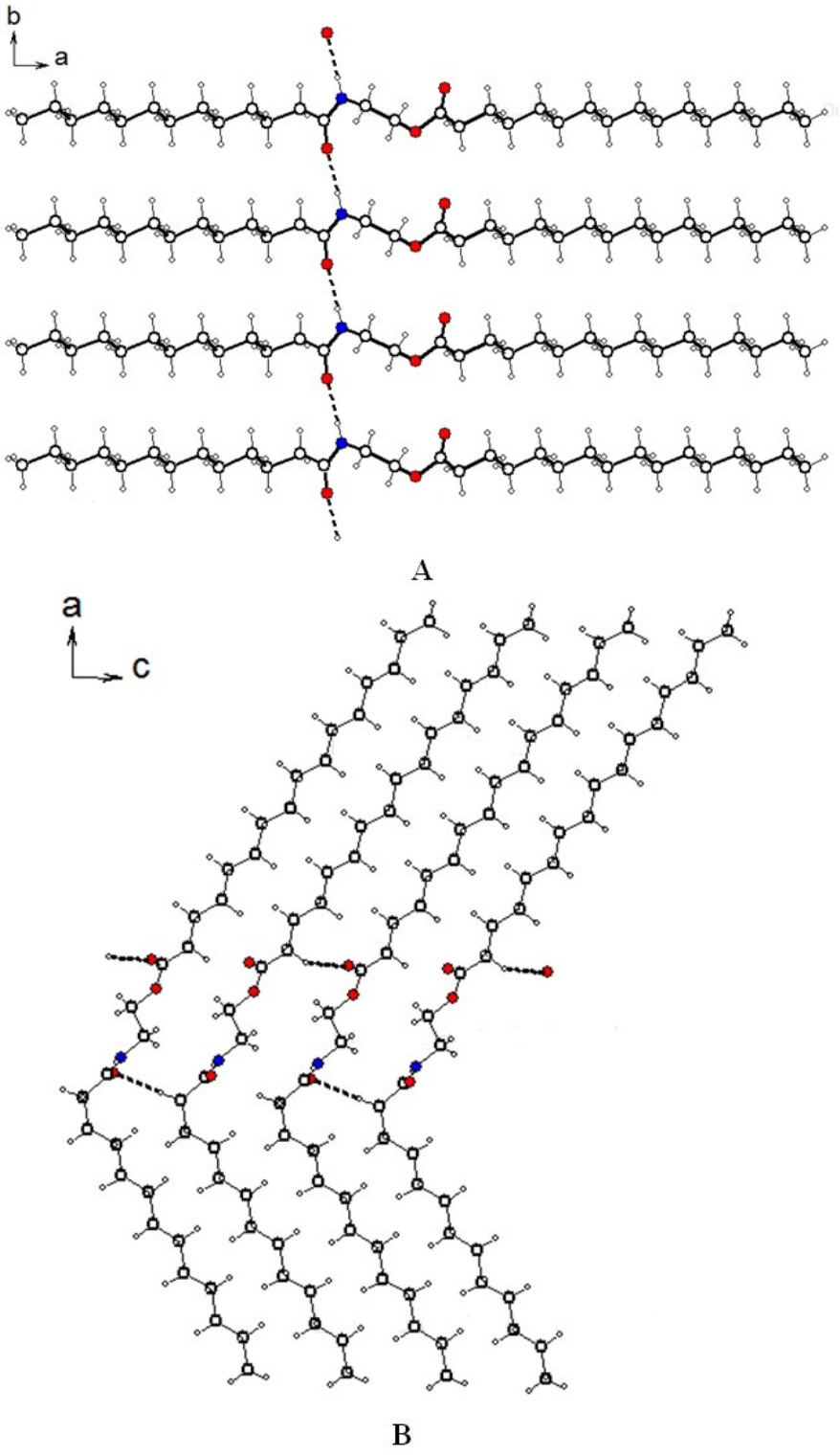


**Fig. S8.** A view of hydrogen bonding pattern in the crystal lattice of N13-O16 along the *c*-axis displaying N–H···O type hydrogen bonding interactions (A), and along *b*-axis displaying C–H···O type hydrogen bonding interactions (B).

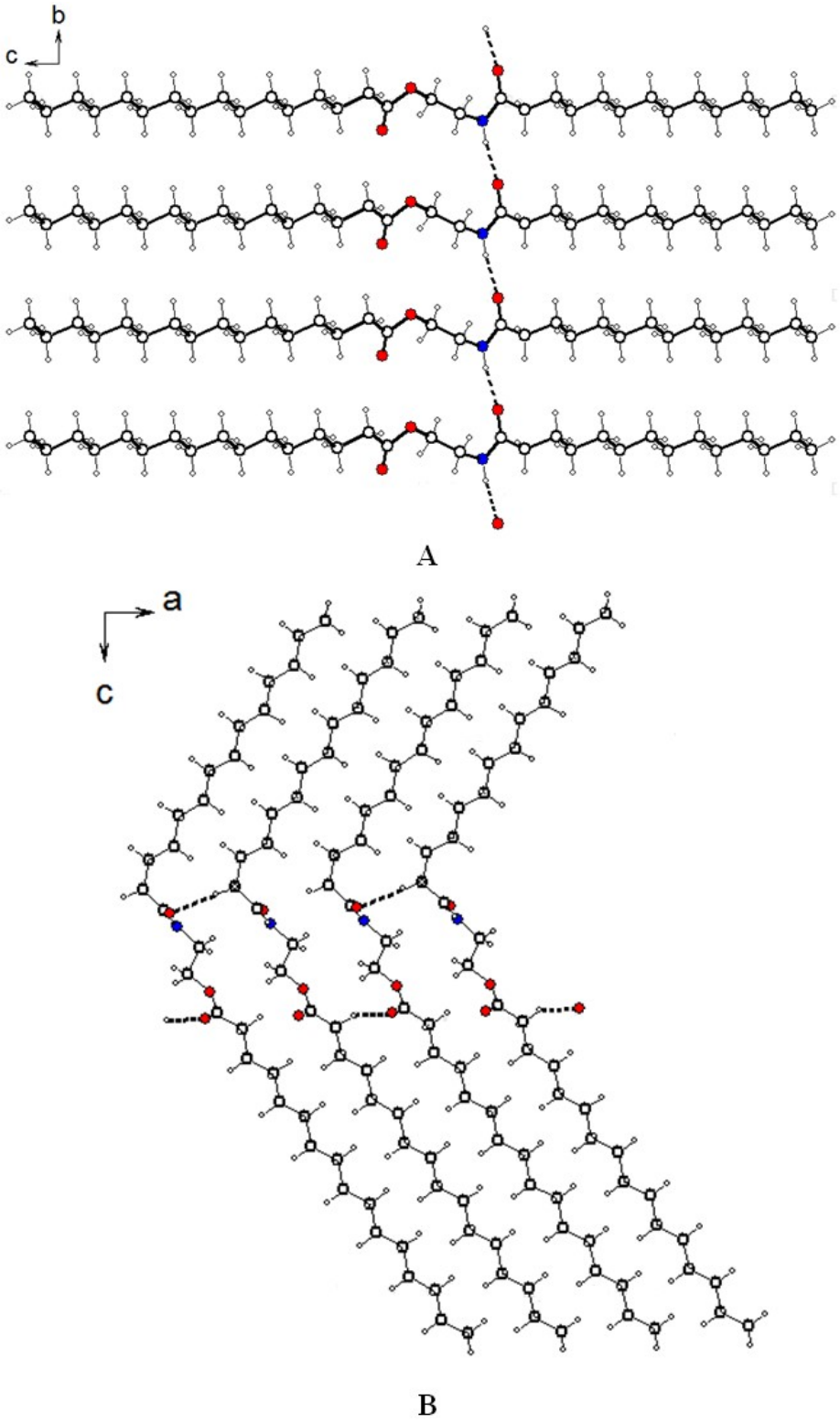


**Fig. S9.** A view of hydrogen bonding pattern in the crystal lattice of N14-O16 along the *a*-axis displaying N–H···O type hydrogen bonding interactions (A), and along *b*-axis displaying C–H···O type hydrogen bonding interactions (B).

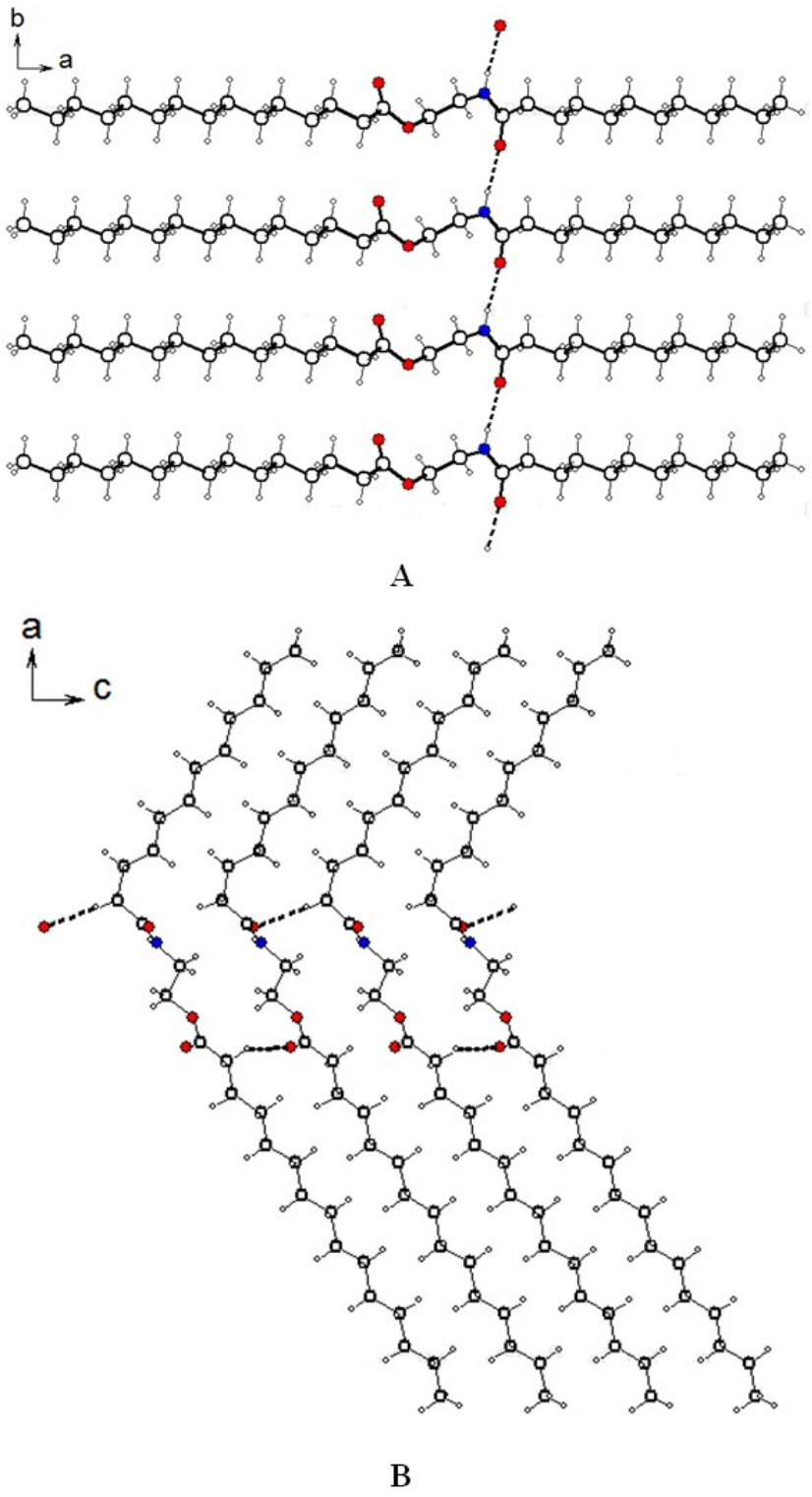


**Fig. S10.** A view of hydrogen bonding pattern in the crystal lattice of N12-O15 along the *c*-axis displaying N–H···O type hydrogen bonding interactions (A), and along *b*-axis displaying C–H···O type hydrogen bonding interactions (B).

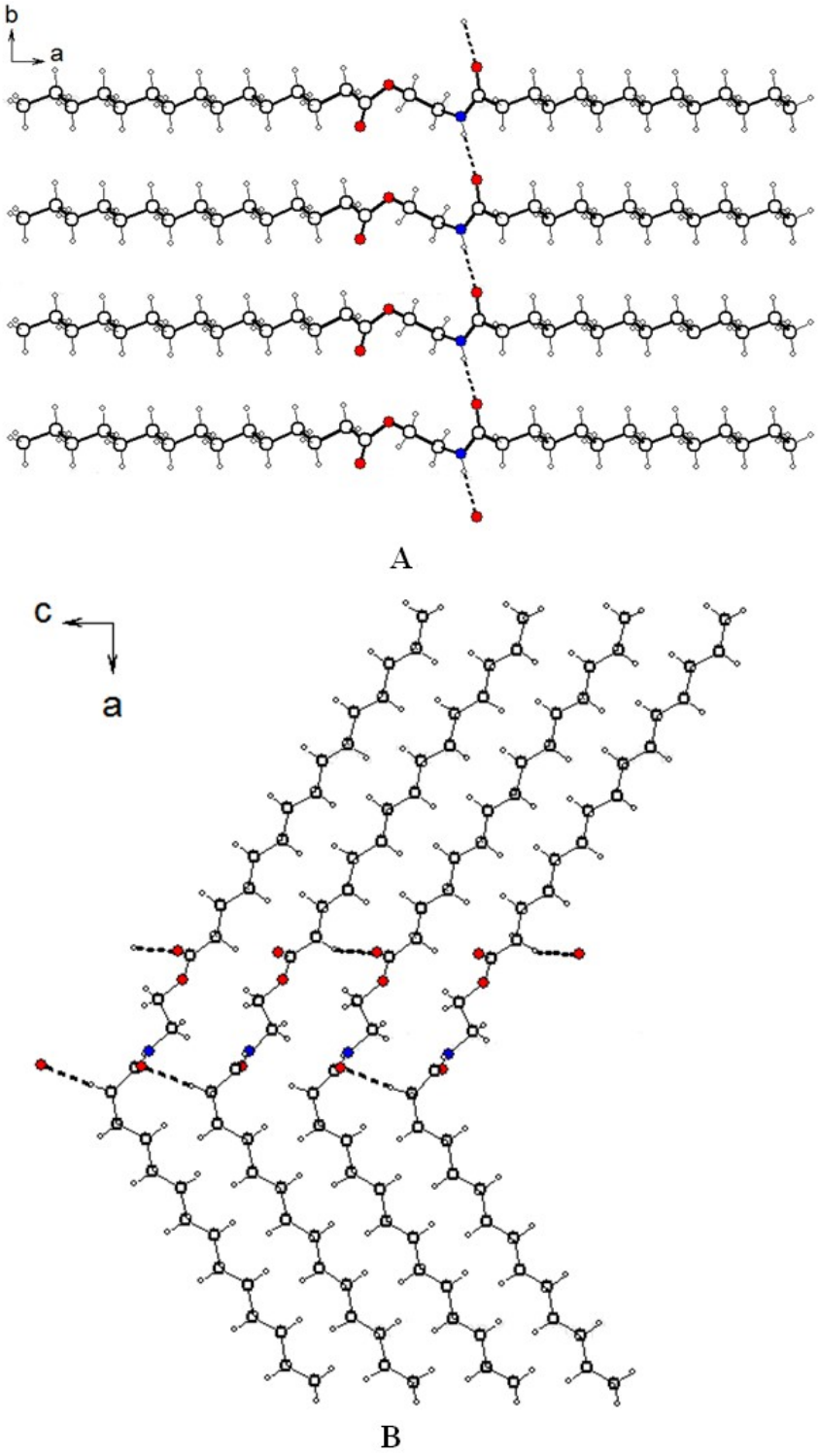


**Fig. S11.** A view of hydrogen bonding pattern in the crystal lattice of N14-O15 along the *c*-axis displaying N–H···O type hydrogen bonding interactions (A), and along *b*-axis displaying C–H···O type hydrogen bonding interactions (B).

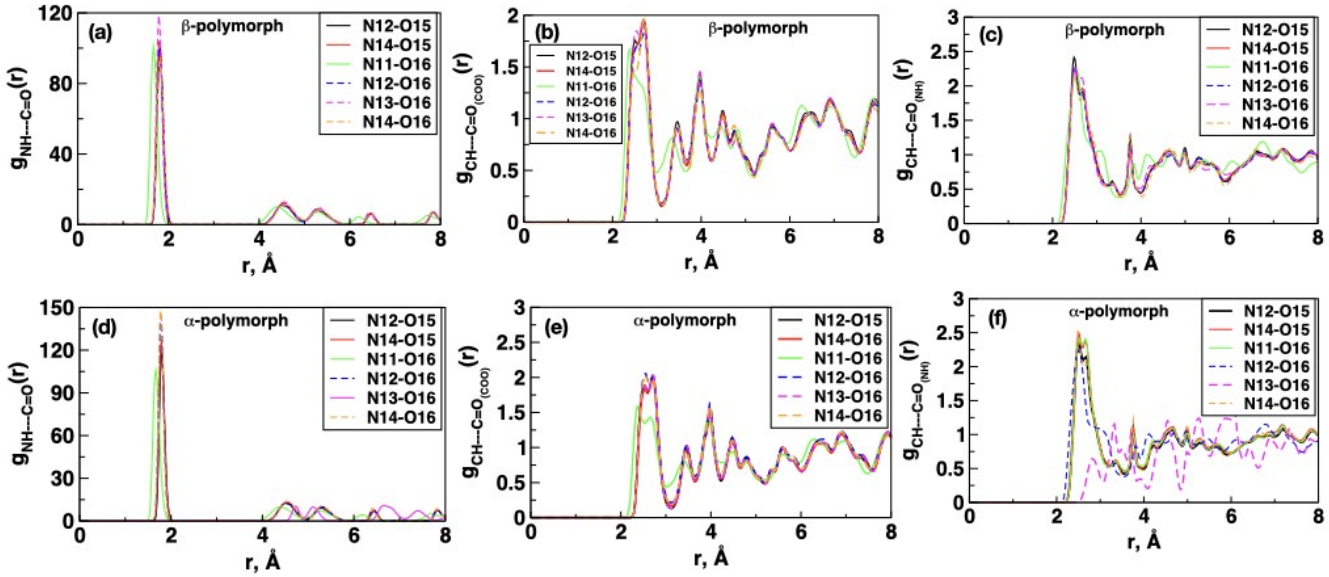


**Fig. S12.** Radial distribution function plot for N-H···O (a-b), C-H···O (amide oxygen) (c-d) and C-H···O (carboxyl oxygen) (e-f) in α and β polymorphs of N14-O16, N12-O15, N12-O16, N14-O15 and N13-O16.

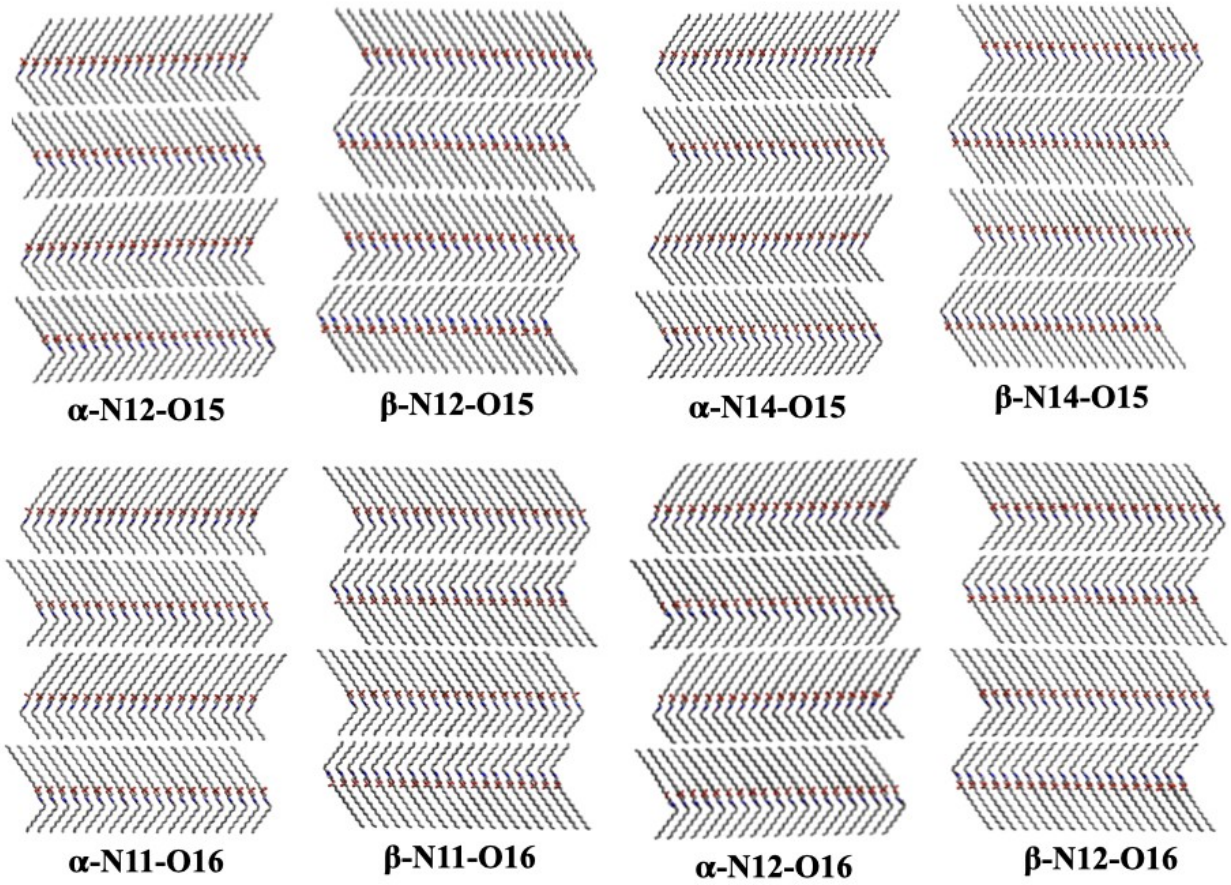


Fig S13a. VMD snapshots of simulated structures of α and β polymorphs of N12-O15, N14-O15, N11-O16 and N12-O16 at 100K.

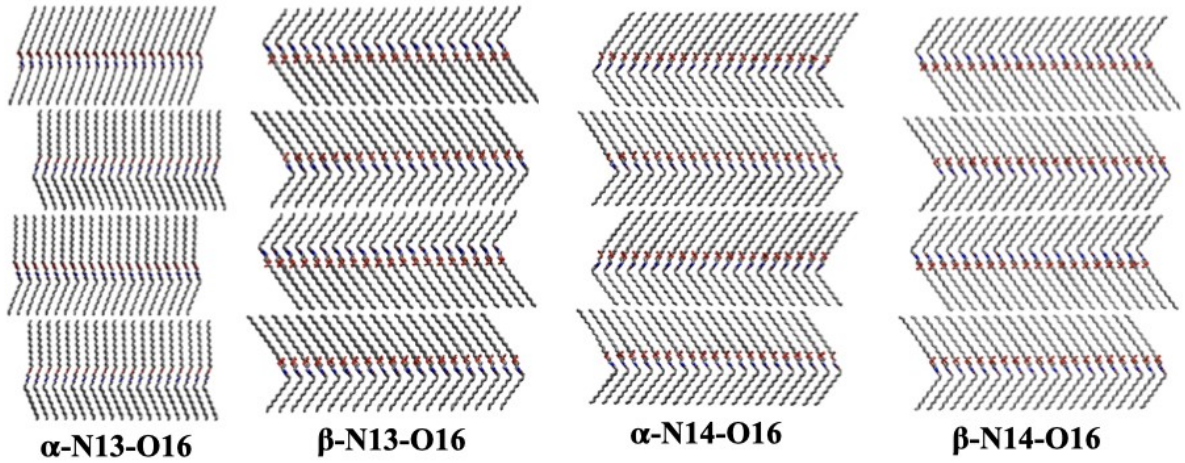


**Fig S13b.** VMD snapshots of simulated structures of α and β polymorphs of N13-O16 and N14-O16 at 100K.