Complementary Amphiphilic Ribonucleotides Confined into Nanostructured Environments

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**Figure S1.** MS/MS spectrum (Collisional Energy: 35%) and product ion assignments for the [M-H]⁻ ion of the tri-alkylated derivative of UMP (m/z 876.5), detected after 118 days in reaction mixtures involving only UMP. Square brackets indicate that R or R’ groups can be linked (through the starred carbon atom) either to the Uracyl N₃ atom or to one of the two OH groups arising from tautomerization of -NH-C=O to -N=C-OH. The product ion compatible with contemporary alkylation of both ribose OH groups was excluded from regioisomeric ions having m/z 691.3, since no further MS/MS signal confirmed that possibility. See Ref. 5 for further details on fragments already observed in the MS/MS spectrum of bi-alkylated UMP.

**Figure S2.** MS/MS spectrum (Collisional Energy: 35%) and product ion assignments for the [M-H]⁻ ion of the tri-alkylated derivative of AMP (m/z 899.3), detected after 118 days in reaction mixtures involving only AMP. Note that:
1) the ion with m/z 579.2 has the same structure proposed in Figure S1 (R corresponds to R₁ in this case);
2) double alkylation on the NH₂ group, hypothesized for the fragment ion with m/z 687.3, is the only reasonable possibility for double alkylation on the adenine ring and was observed for the tri-alkylated AMP derivative but never for the bi-alkylated one (see Ref. 5). In this case the linkage between a hydroxy-dodecyl moiety and the adenine N₁ atom (compatible also with fragments at m/z 502.5 and 332.4), is likely formed during fragmentation, as a result of hydroxy-dodecyl migration from an alkylated OH on ribose to the adenine N₁ atom, concomitant with ribose detachment;
3) alternative structures for fragment ions at m/z 634.5, 502.5 and 332.4, having two hydroxyl-dodecyl groups on the adenine NH₂ cannot be excluded, although they are less likely than those reported;
4) only in the case of adenine NH₂ group the nucleophilic attack can occur also to the more hindered carbon atom of the DE epoxidic ring (thus leading to a linkage with a R₂ group). See Ref. 5 for further details on this aspect and on fragmentations already observed in the MS/MS spectrum of bi-alkylated AMP (e.g. the presence of a CH₃ group on an alkylation site, involving the loss of n-undecanal from a previously linked R₁ group).
Figure S1

[Diagram showing mass spectrum with peaks at 876.5, 579.4, 335.2, 263.3, and 295.4 m/z.]

[Chemical structures labeled with m/z values: 876.5, 579.4, 335.2, 295.4, and 263.3.]

[M-H]⁻ ion for bi-alkylated UMP (11 possible regioisomers)
Figure S2

[Supplementary Material for PCCP
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**Figure S2**

![Mass spectrum with annotations](image)

- **m/z 899.3**
  - [M-H]⁻ ion for bi-alkylated AMP (several regioisomers)
  - 714.5
- **m/z 728.6**
  - (one of the R1 groups replaced by a CH₃)
- **m/z 687.3**
  - 544.4 (one R1 or R2 group replaced by H and one R1 group replaced by CH₃)
- **m/z 502.5**
  - 332.4
  - 318.5

**Chemical Structures**

1. **[M-H]⁻ ion for bi-alkylated AMP (several regioisomers)**
   - ![Schematic](structure1)
   - R₁ (or R₂)
   - R₁ (H)
   - R₁ (or R₂)
   - R₁ (H)

2. **m/z 899.3**
   - (one of the R₁ groups replaced by a CH₃)

3. **m/z 728.6**
   - (one of the R₁ groups replaced by a CH₃)

4. **m/z 687.3**
   - 544.4 (one R₁ or R₂ group replaced by H and one R₁ group replaced by CH₃)

**Chemical Formulas**

- **R₁**
  - ![Chemical formula](formula1)
- **R₂**
  - ![Chemical formula](formula2)
- **R₁’**
  - ![Chemical formula](formula3)
- **R₂’**
  - ![Chemical formula](formula4)

**Molecular Model**

![Molecular model](model_image)