Supporting Information

Promising lipophilic PyTri extractant for selective trivalent actinide separation from High Active Raffinate

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1. Selectivity towards Ln

Table S1 Separation factors of ^{241}Am over trivalent ^{152}Eu, Y and lighter Ln (La-Gd) as a function of the nitric acid concentration of the aqueous phase. Organic phase: 0.2 M PTEH in kerosene + 10 vol.% 1-octanol mixture. Aqueous phase: HNO_3 solutions loaded with Y and lighter Ln (La-Gd), besides trivalent ^{241}Am and ^{152}Eu as radiotracers

	SF(Am^{3+}/M^{3+})		
	1 M	**2 M**	**3 M**
Y	524 ± 74	321 ± 45	213 ± 30
La	> 1000	300 ± 42	128 ± 18
Ce	724 ± 102	330 ± 46	165 ± 23
Pr	378 ± 53	375 ± 53	237 ± 33
Nd	239 ± 33	378 ± 53	340 ± 48
Sm	132 ± 18	196 ± 27	210 ± 29
Eu	99 ± 14	110 ± 15	102 ± 14
Gd	91 ± 12	76 ± 10	66 ± 9
^{152}Eu	82 ± 11	86 ± 12	79 ± 11

2. Resistance towards hydrolysis and radiolysis

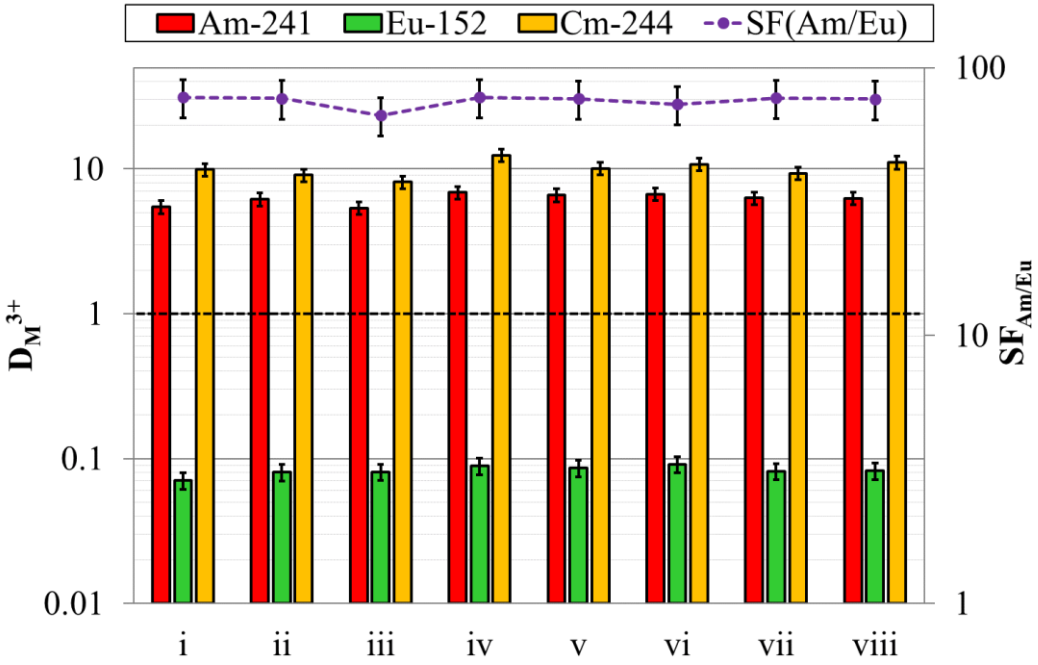


Figure S1 Distribution ratios and separation factors of trivalent ^{241}Am, ^{244}Cm and ^{152}Eu obtained by contacting 3 M HNO_3 solutions spiked with trivalent ^{241}Am, ^{244}Cm and ^{152}Eu (ca. 10 kBq/mL each) with the following PTEH solutions: (i) fresh, (ii) aged for 71 days, (iii) aged for 169 days in contact with 3 M nitric acid, (iv) irradiated at

100 kGy, (v) irradiated at 200 kGy, (vi) irradiated at 300 kGy, (vii) irradiated at 100 kGy in contact with 3 M nitric acid and (viii) irradiated at 200 kGy in contact with 3 M nitric acid

2. By-products identification

The ESI-MS^2 spectrum of the protonated adduct of the by-product with molar mass 563.6 $g \cdot mol^{-1}$ and identification attempts of some fragments are reported in Figure S2 and in Table S2, respectively. It was hypothesized to be the outcome of 1-octanal radical addition on the lateral chain. 1-octanal is supposed to be produced by secondary reaction of 1-octanol by-product. The ESI-tandem mass spectrometry attested that the proposed structure for by-product with molar mass 563.6 $g \cdot mol^{-1}$ is reasonable.

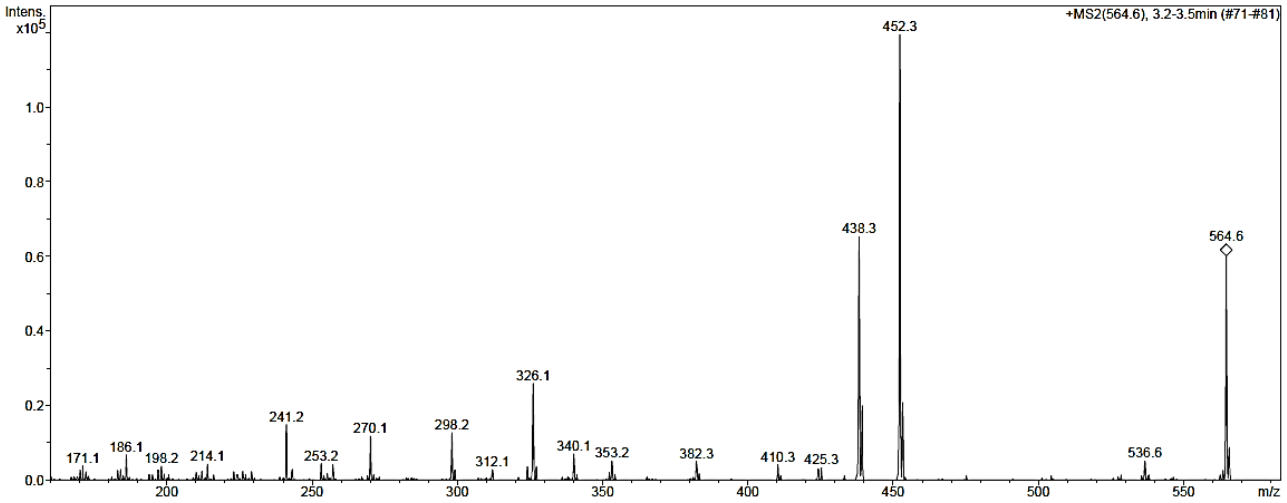
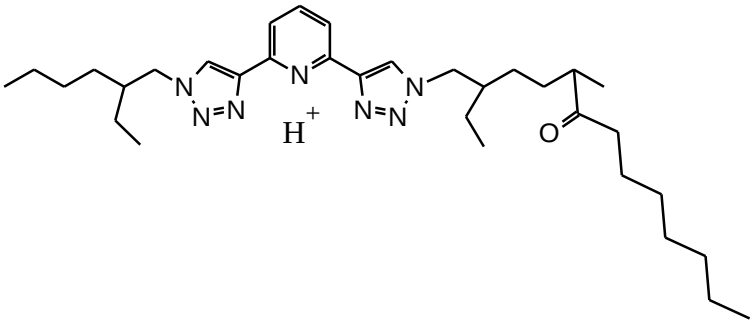


Figure S2 HPLC coupled with ESI-MS^2 spectrum of protonated adduct of PTEH by-product with molar mass 563.6 $g \cdot mol^{-1}$

Table S2 Attempt of identification of some fragments in the MS^2 spectrum of PTEH by-product with molar mass 563.6 g·mol1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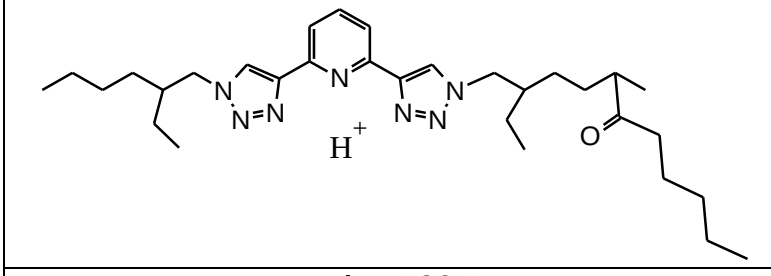
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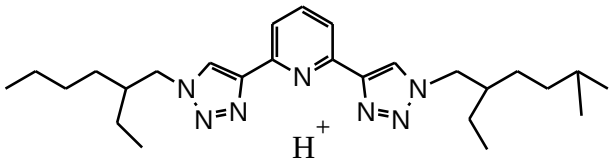
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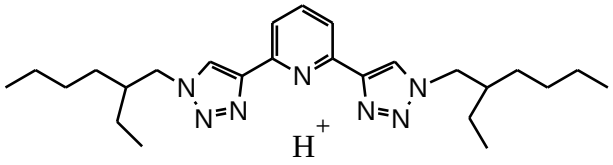
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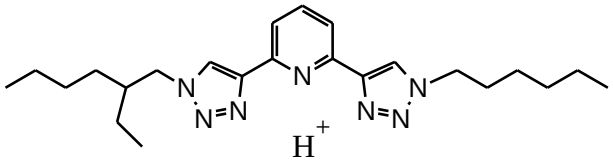
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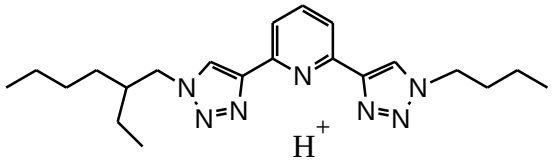
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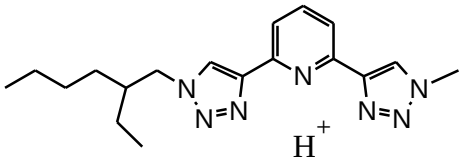
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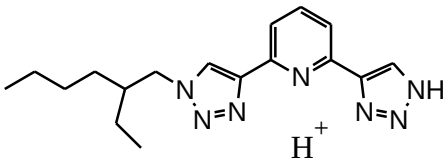
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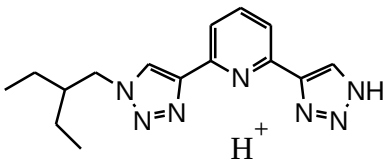
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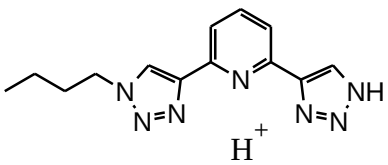

***m/z* = 270.3**

The MS^2 spectrum of the protonated adduct of the by-product with molar mass 599.5 $g \cdot mol^{-1}$ and identification attempts of some fragments are reported in Figure S3 and in Table S3, respectively. It was hypothesized that a kerosene carbon-centered radical is added on the lateral chain. As in the previous case, the ESI-tandem mass spectrometry attested that the proposed structure for by-product with molar mass 599.5 $g \cdot mol^{-1}$ is reasonable.

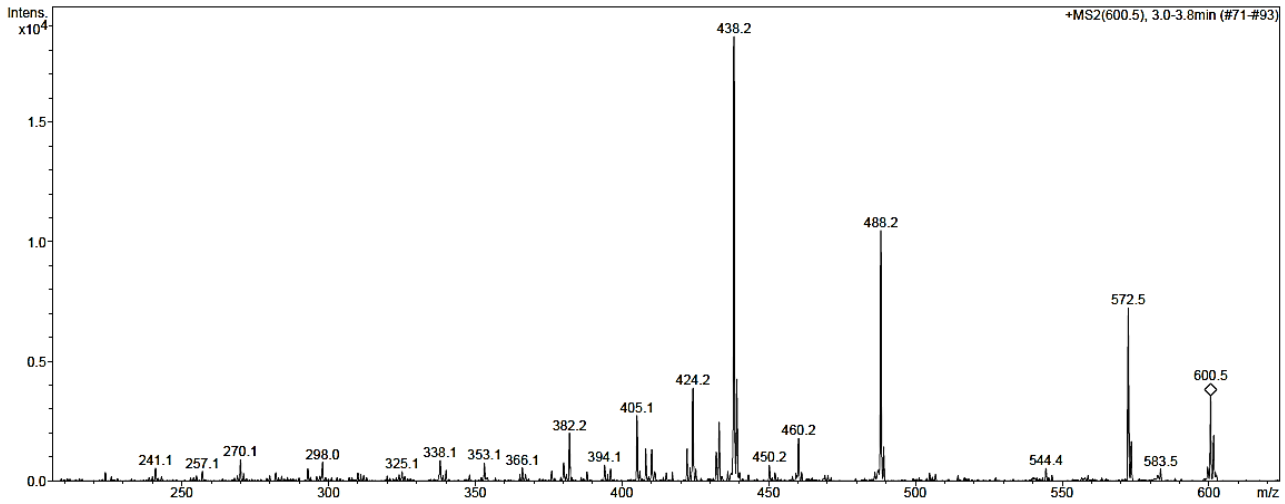
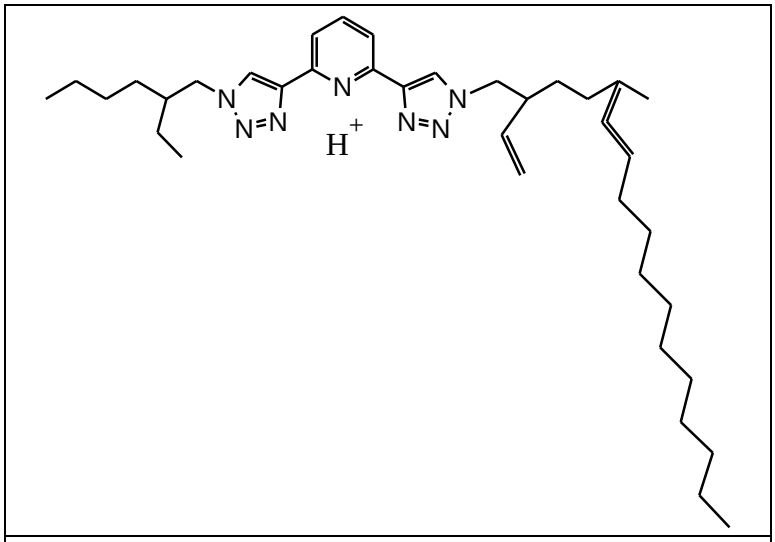
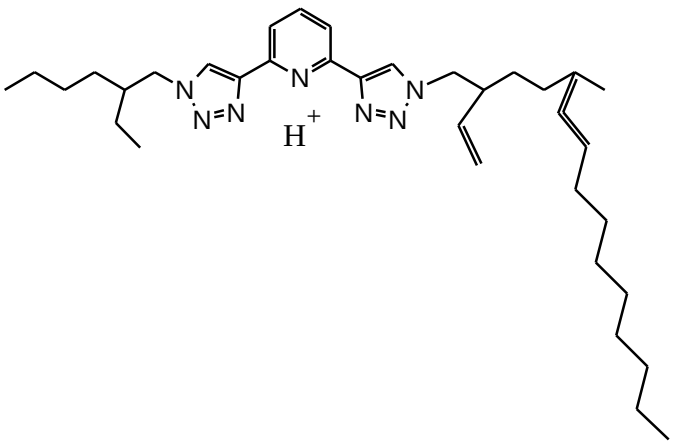


Figure S3 HPLC coupled with ESI-MS^2 spectrum of protonated adduct of PTEH by-product with molar mass 599.5 $g \cdot mol^{-1}$

Table S3 Attempt of identification of some fragments in the MS^2 spectrum of PTEH by-product with molar mass 599.5 $g \cdot mol^{-1}$



***m/z* = 600.9**



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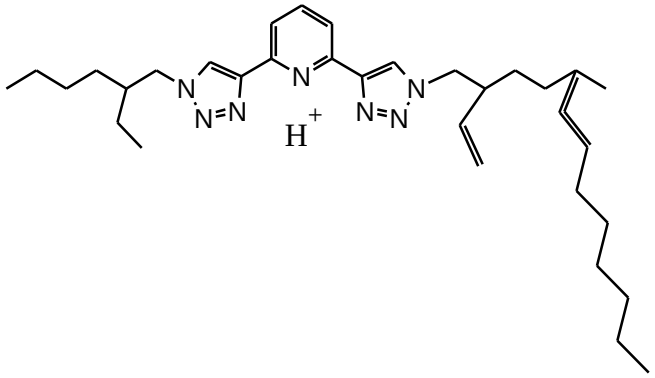

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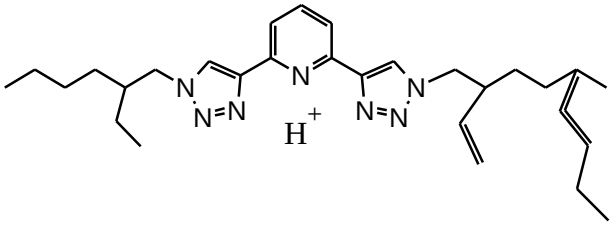
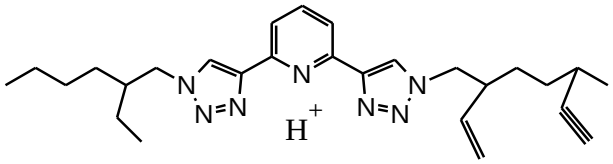


***m/z* = 488.7**



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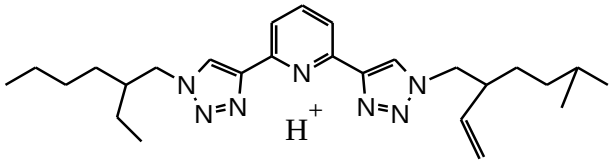

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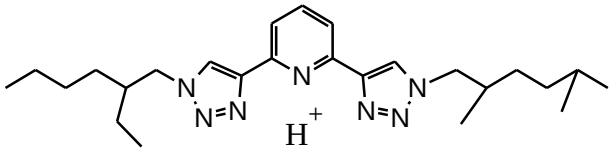

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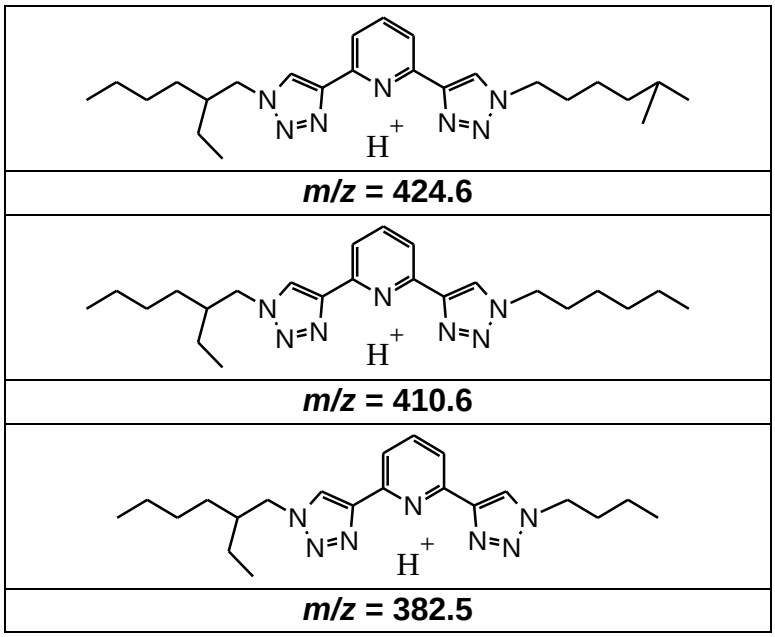


Finally, the MS^2 spectrum of the protonated adduct of the by-product with molar mass 580.5 $g \cdot mol^{-1}$ and identification attempts of some fragments are reported in Figure S4 and in Table S4, respectively. In this case, the addition of C_6 and nitric acid radicals produced an adduct on the lateral chain. Once again, the ESI-tandem mass spectrometry proved that the proposed structure for by-product with molar mass 580.5 $g \cdot mol^{-1}$ is realistic.

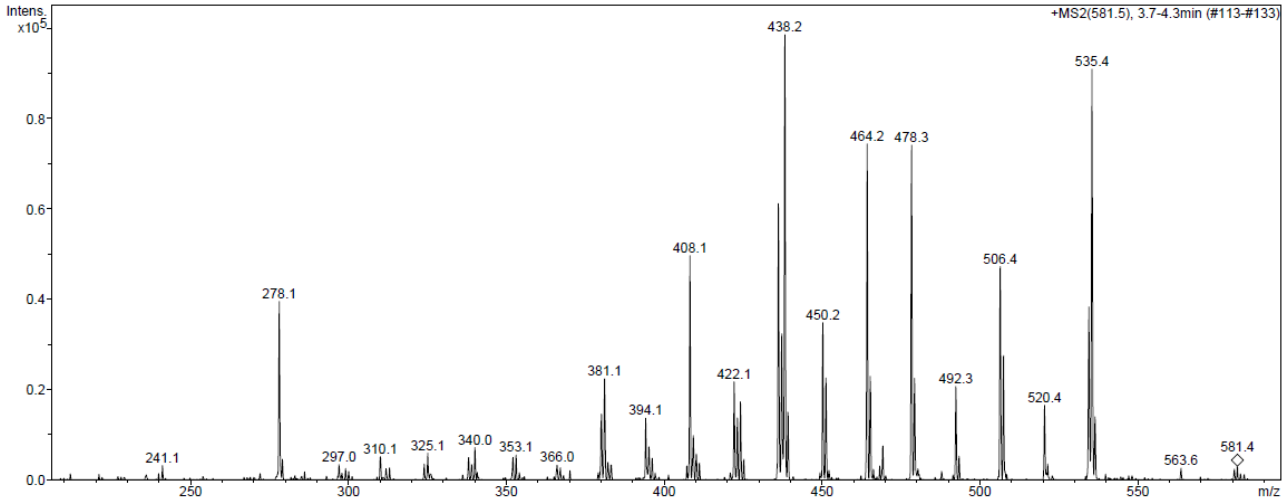
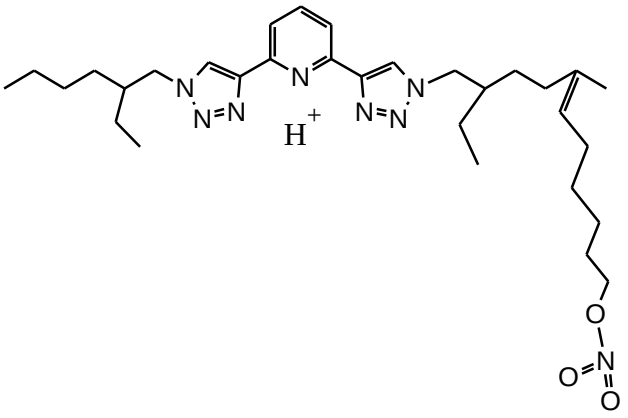
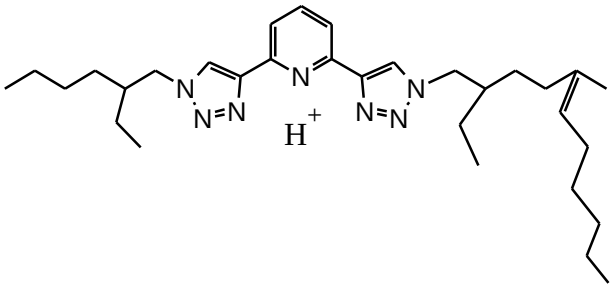


Figure S4 HPLC coupled with ESI-MS^2 spectrum of protonated adduct of PTEH by-product with molar mass 580.5 $g \cdot mol^{-1}$

Table S4 Attempt of identification of some fragments in the MS^2 spectrum of PTEH by-product with molar mass 580.5 $g \cdot mol^{-1}$



***m/z* = 581.7**



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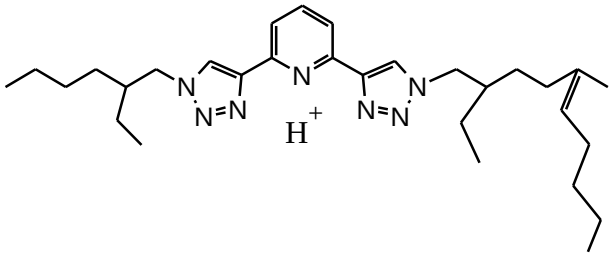

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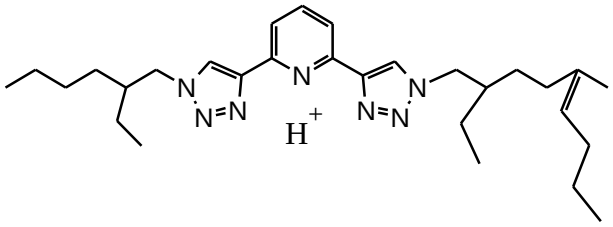

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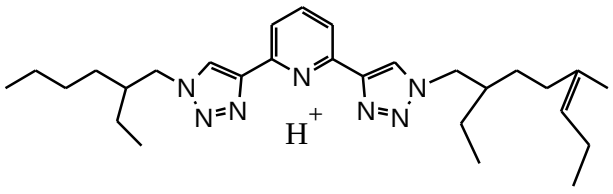

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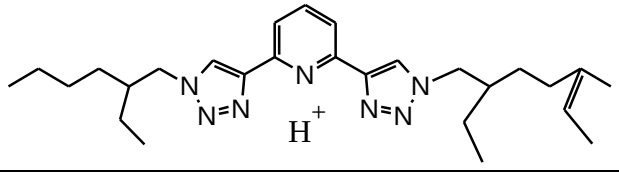

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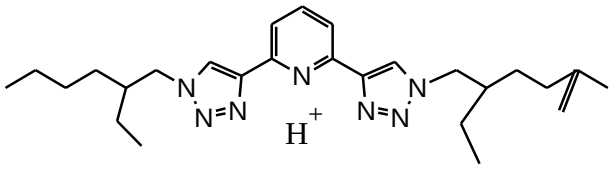
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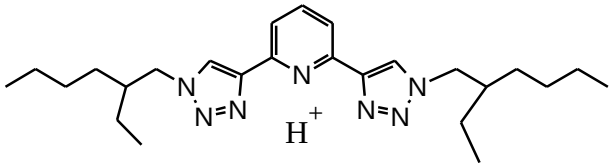
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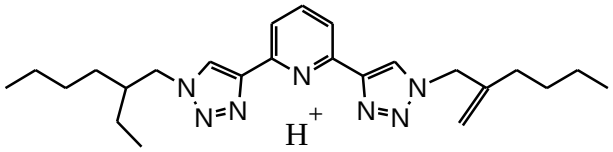
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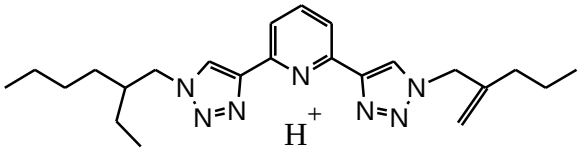
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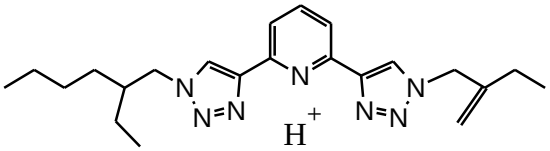
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