Supporting information

Solvent-dependent termination, size and stability in polyynes synthesis by laser ablation in liquids

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Table S.1 State of art of different polyynes obtained by physical methods in terms of length and terminations. The references are listed below.

n. of carbon atoms (end-cap)	*H_2O*	*ACN*	*MeOH*	*EtOH*	*1-propanolo*	*1-butanolo*	*t-butyl alcohol*	*hexane*	*n-hexane*	*c-hexane*	*n-heptane*	*n-hoctane*	*decane*	*toluene*	*benzene*	*decalin*	*TEOS*
6 (H)	1	2															
6 (CH_3)																	
6 (CN)		3															
8 (H)	1, 2, 4-8	2, 3, 7, 9	7, 10-12	10, 13-15	10	10	10	16-18	5, 9, 11, 12, 19	7, 9	19	19	18	12, 20, 21	21, 22	23, 24	25
8(CH_3)																	
8(CN)		3															
10(H)	1, 4, 5, 7, 8	2, 3, 7, 9	7, 10-12 ,7, 10-12 ,	10, 13-15	10	10	10	16-18	5, 9, 11, 12, 19	7, 9	19	19	18	12, 20, 21	21, 22	23, 24	25
10(CH_3)																	
10(CN)		3															
12 (H)	7	2, 7, 9	10, 11	10, 13-15	10	10	10	16, 17	5, 9, 11, 12, 19	9	19	19		12, 20, 21	21, 22	23, 24	25
12(CH_3)																	
12(CN)		3															
14 (H)		2, 7, 9	10, 11	10, 13-15	10	10	10	16, 17	5, 9, 11, 19	9	19	19		12, 20, 21	21, 22	23, 24	25
14(CH_3)		20															
16(H)		2, 9	10, 11	10, 13-15	10	10	10	16, 17	5, 9, 11	9		19		12, 20, 21	21	23, 24	25
16(CH_3)																	
18(H)			11					16, 17	5, 11					20, 21		23, 24	
18(CH_3)																	
20(H)			11					16, 17	5, 11							23, 24	
22(H)								17	11							23, 24	

Table S.2 Molar concentration (mol/L) of H-polyynes of different size in different solvents. Polarity values indicated with "p" are taken from the Handbook of organic solvents properties [26] and "l" for Oswald coefficient, defined as the ratio of concentrations of the gas in the liquid and gas phases.

	ACN p=46 l=0.00083[27]	IPA p=54.6 l=0.2463[28]	EtOH p=65.4 l=0.2417[28]	MeOH p=76.2 l=0.2476[28]	H_2O p=100 l=0.031[29]
C_8	$(1.42\pm0.07)\times10^{-4}$	$(1.09\pm0.02)\times10^{-4}$	$(1.07\pm0.01)\times10^{-4}$	$(7.50\pm0.05)\times10^{-5}$	$(3.13\pm0.02)\times10^{-6}$
C_{10}	$(7.3\pm0.4)\times10^{-5}$	$(4.57\pm0.08)\times10^{-5}$	$(4.07\pm0.06)\times10^{-5}$	$(2.72\pm0.03)\times10^{-5}$	0
C_{12}	$(2.6\pm0.1)\times10^{-5}$	$(1.8\pm0.1)\times10^{-5}$	$(9.3\pm0.6)\times10^{-6}$	$(1.17\pm0.02)\times10^{-5}$	0
C_{14}	$(7.8\pm0.4)\times10^{-6}$	$(1.1\pm0.4)\times10^{-5}$	$(8.0\pm0.3)\times10^{-6}$	$(4.6\pm0.2)\times10^{-6}$	0
C_{16}	$(6.5\pm0.3)\times10^{-6}$	$(3.4\pm0.1)\times10^{-6}$	$(3.0\pm0.1)\times10^{-6}$	$(1.6\pm0.1)\times10^{-6}$	0

Table S.3 Polyynes ended by −H/ $-CH_3$/ −CN obtained after ablation of graphite target in acetonitrile with the corresponding times on the chromatogram and the positions of the experimental, simulated and literature UV-Vis absorption peaks. References are listed below.

n. of C atoms (end-cap)	t_R(min)	Wavelength(nm)		
		Experimental	*Simulated*	*Literature*
6(H)	9.919	198	200	199 [1]
6(CN)	11.484	216 208 200	218 209 201	215.6 207.2 198.9 [3]
6(CH_3)	11.98	205 197	205	/
8(H)	14.149	226 216 207	226 216 208	226 216 206 [23]
8(CN)	15.323	239/244.5 231 222	244 232 222	239/244 231 222 [3]
8(CH_3)	16.058	230 220 211	231 221 212	/
10(H)	17.89	251 238 228	249 237 227	251 239 227 [23]
10(CN)	18.627	265 253 242	266 253 241	264.5 253.3 242.0 [3]
10(CH_3)	19.623	256 242 231	254 242 231	257 243 232 [30]
12(H)	21.092	273 260 247	271 257 245	275 260 247 [23]
12(CN)	21.468	287 273 261	287 271 258	287.4 273.7 261.1[3]
12(CH_3)	22.64	278 263 251	276 261 249	279 264 251 [20]
14(H)	23.777	295 280 265	291 275 261	296 280 267 [23]
14(CH_3)	25.120	299 283 268	295 279 264	302 285 269 [20]
16(H)	26.004	315 296 281	308 290 275	316 298 281 [23]
16(CH_3)	27.251	319 301 285	312 294 278	/
18(H)	28.045	333 313 295	324 304 287	334 314 295 [23]
18(CH_3)	29.691	335 316 299	327 307 290	/
20(H)	30.795	348 326 309	337 316 298	350 328 310 [23]
22(H)	34.288	362 339 321	350 327 308	364 341 321 [23]

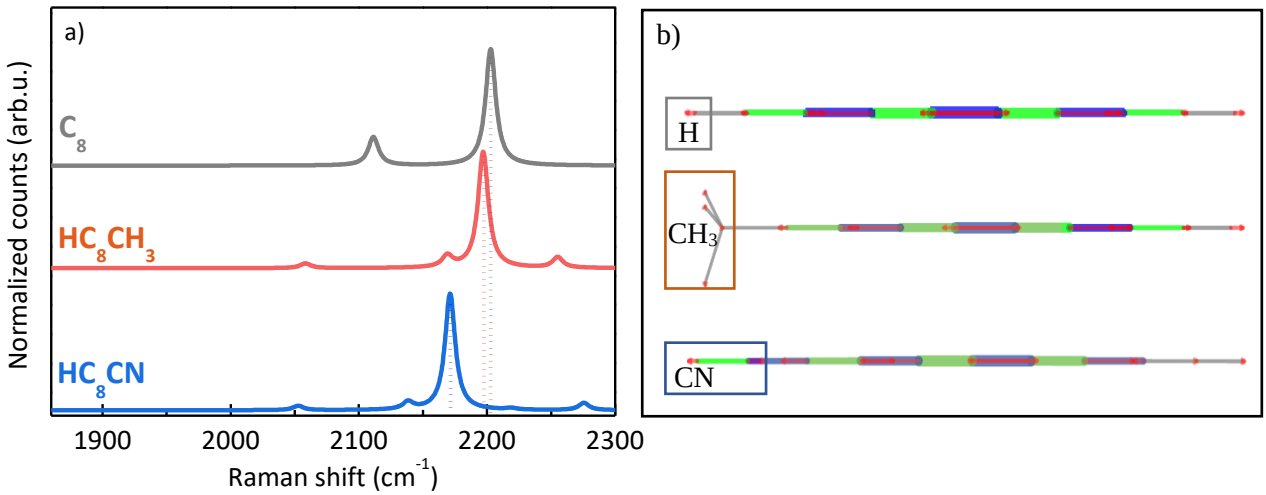

Figure S.1 a) Normalized simulated Raman spectra of hydrogen-, methyl-, cyano-capped polyynes with four triple bonds –(C≡C)$_4$–. b) The collective vibrational mode of CC bond related to the same molecules. Simulated Raman spectra and relative vibrational mode have been computed by PBE0/cc-pVTZ calculations (see Section 2).

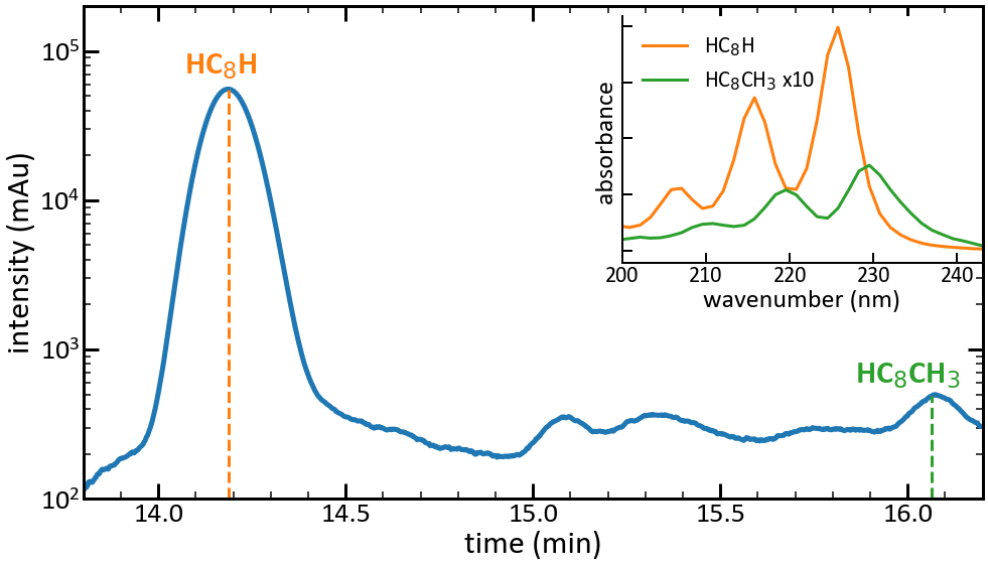

Figure S.2 HPLC chromatogram of the ablation in pure water taken at 225 nm. The dashed orange line highlights the chromatographic peak of HC_8H, while the dashed green line indicates HC_8CH_3. The assignation of this last peak is confirmed by the UV-Vis spectra reported in the inset. The spectrum of HC_8CH_3 is multiplied by a factor of 10 because of its low absorbance.

Table S.4 Decay time constant and corresponding R^2 of the fit of polyynes changing length, termination and solvent.

Length	τ(days)	R^2
C_8	-382.381 ± 31.578	0.93575
C_{10}	-198.860 ± 24.259	0.86876
C_{12}	-70.187 ± 5.949	0.93252
C_{14}	-29.223 ± 2.206	0.94579
C_{16}	-15.708 ± 0.837	0.97235
C_{18}	-11.002 ± 0.600	0.97104
C_{20}	-7.553± 0.464	0.96353
Termination	τ(days)	R^2
-H	-382.381 ± 31.578	0.93575
-CN	-6.105 ± 0.413	0.95606
Solvent	τ(days)	R^2
H_2O	-1.8191 ± 0.018	0.99929
ACN	-382.381 ± 31.578	0.93575
IPA	-155.438 ± 10.500	0.95617
EtOH	-223.464 ± 17.020	0.94487

References of Table S.1 and S.3

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