Tunable UV Photoexcitation of carbon atomic wires: investigating the roles of chain length, termination groups, and environment

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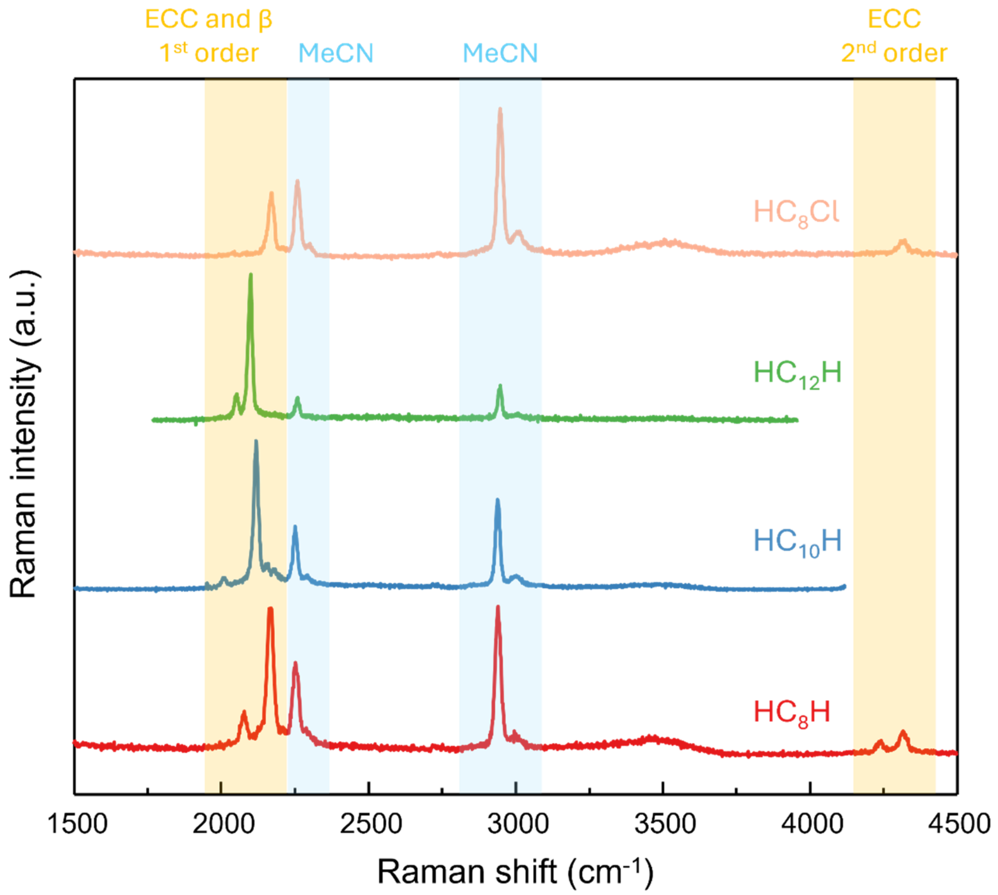

Figure S1 Full spectral range UVRR spectra of polyynes in solution. The first- and second-order regions corresponding to the ECC and β modes for each polyyne are highlighted in light yellow, while the Raman modes of the solvent (acetonitrile, MeCN) are highlighted in light blue. Due to the different excitation wavelengths and the relative variations in the experimental setups used for each polyyne, the reported spectral ranges are not identical for all samples.

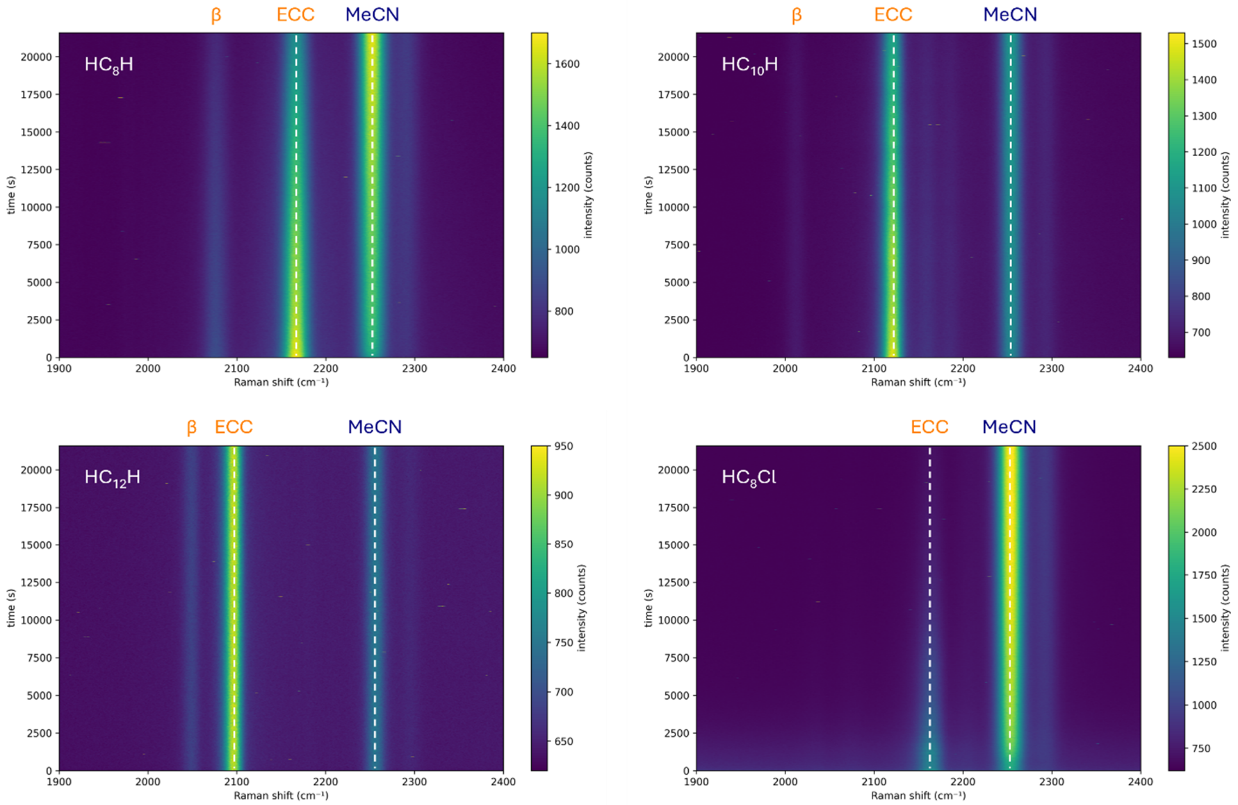

Figure S2. Time evolution of the UVRR spectra of HC_8H, $HC_{10}H$, $HC_{12}H$, and HC_8Cl. The ECC, the β mode, and solvent (MeCN) Raman peaks are indicated with dashed lines.

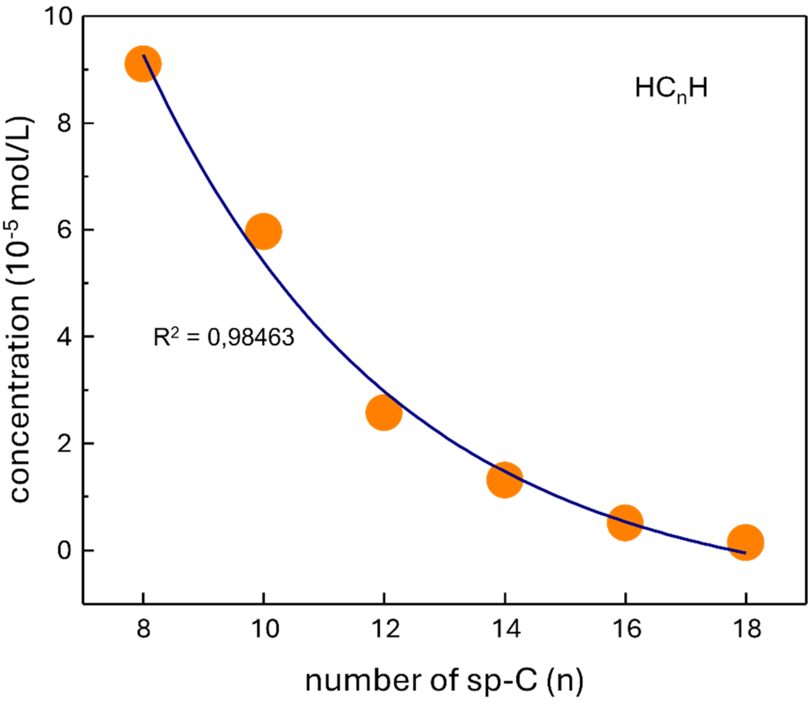

Figure S3. Concentration of PLAL produced HC_nH polyynes as a function of their sp-carbon chain length.

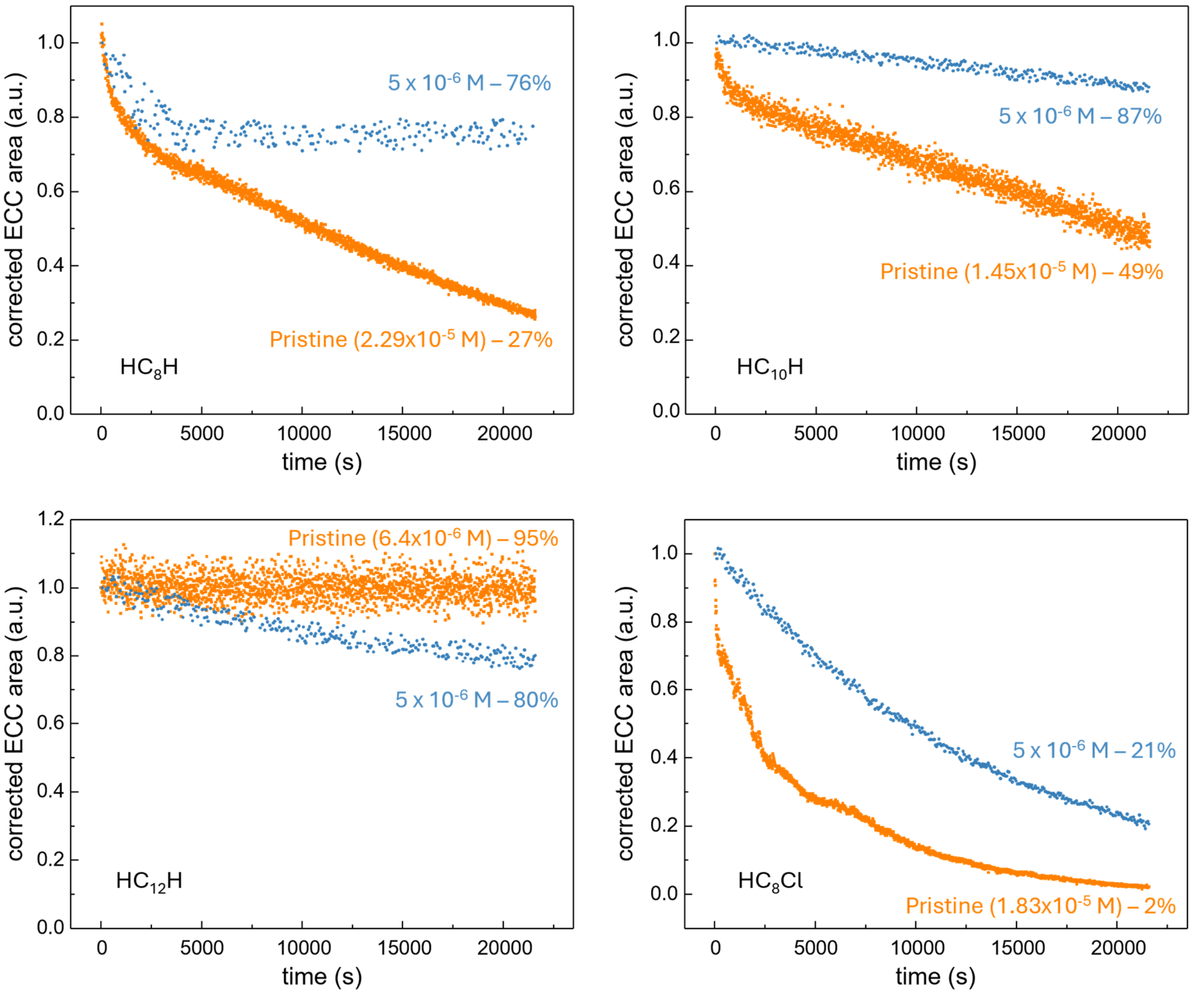

Figure S4. Time-dependent evolution of the self-absorption (SA) corrected Raman ECC area for HC_nH (n = 8, 10, and 12) and HC_8Cl under monochromatic synchrotron irradiation. For each polyyne, photostability trends are compared between pristine and 5 x 10^{-6} M samples. The numbers indicate the percentage of non-photodegraded polyynes after 6 hours of irradiation for each species.

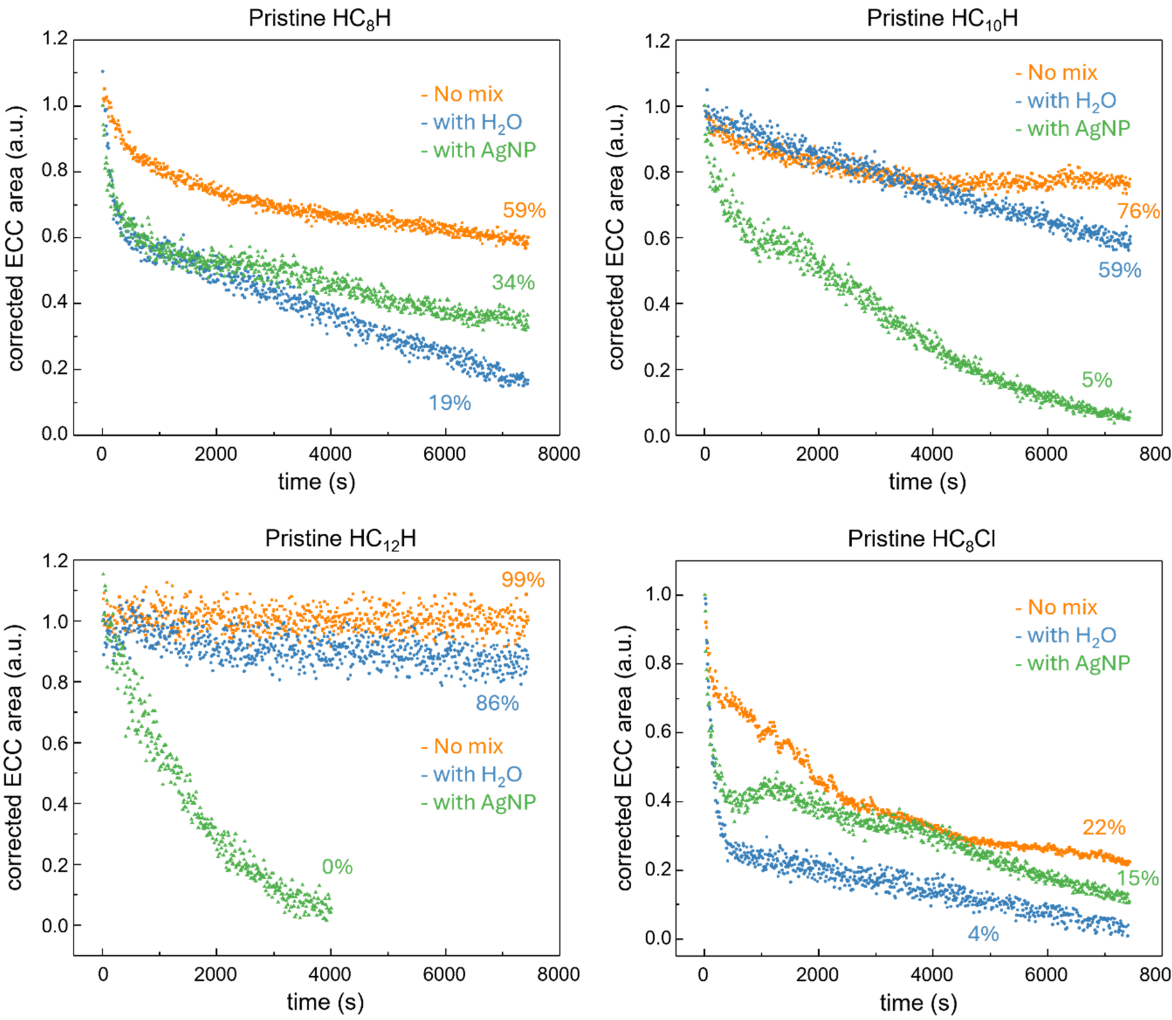

Figure S5. Time-dependent evolution of the SA-corrected Raman ECC area for HC_nH (n = 8, 10, and 12) and HC_8Cl under monochromatic synchrotron irradiation. For each polyyne, photostability is compared among pristine samples (as obtained from PLAL+HPLC and not mixed), pristine samples mixed 1:1 V/V with distilled water (with H_2O), and pristine samples mixed 1:1 (V:V) with an aqueous colloidal solution of AgNPs (with AgNP). The numbers indicate the percentage of non-photodegraded polyynes after 7440 seconds of irradiation for each species.

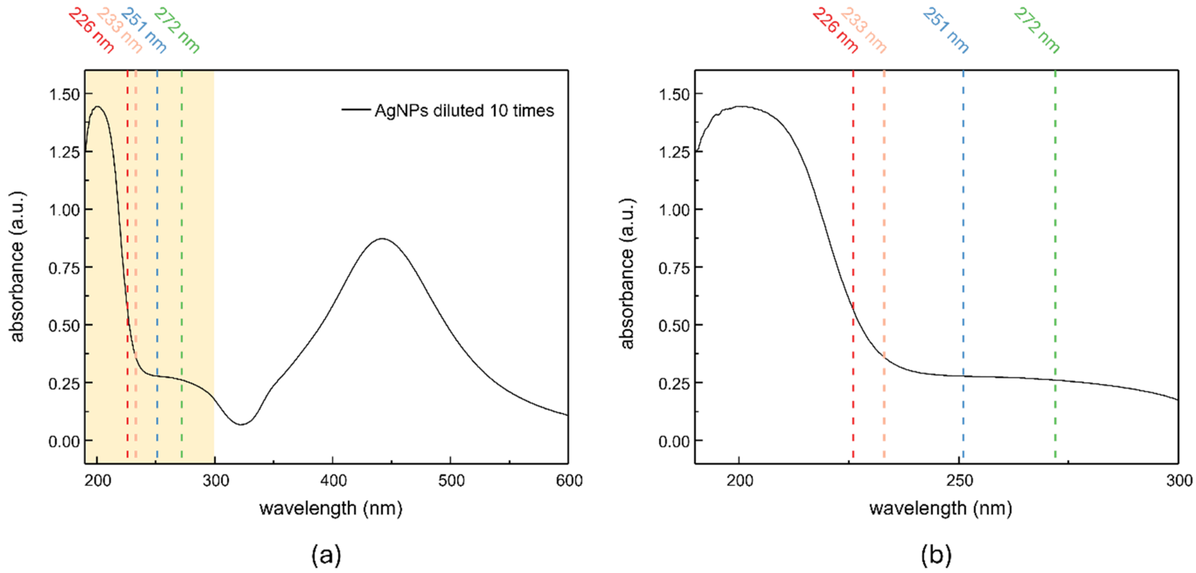

Figure S6. (a) UV-Vis spectrum of the AgNP dispersion in water (diluted ten times with distilled water to avoid detector saturation). (b) Magnified view of the region highlighted in (a). In both panels, dotted lines indicate the synchrotron excitation wavelengths used for each of the investigated polyynes.

Model for correcting UV resonance Raman signals affected by self-absorption phenomena

UV resonance Raman (UVRR) spectroscopy of polyynes (see Fig. S1) requires the excitation wavelength to be tuned to one of their characteristic vibronic absorption peaks (see Fig. 1 in the main text). This ensures enhancement of the Raman signal and enables the detection of even low-concentration samples. As reported in previous works[1–4], resonance Raman measurements are affected by self-absorption (SA) phenomena. Since the excitation wavelength lies in resonance with a strong absorption band, a fraction of both the excitation and Raman-scattered photons is absorbed by the sample itself, reducing the detected Raman intensity, which is proportional to the number of photons reaching the sample and the detector.

During photodegradation experiments, as polyynes are consumed, their optical absorption decreases, leading to a progressive reduction of SA over time. Consequently, the SA effect is not constant but time-dependent.

As detailed in the main text, photodegradation has been evaluated from the time evolution of the Raman area of the ECC mode. However, this parameter is affected by the non-constant SA. To account for this effect, the ECC Raman area was corrected using a procedure similar to that described in our previous work[4]. This model also relies on the assumption that the degradation products formed from the polyynes do not absorb (or absorb strongly) in the UV region that belongs to polyyne vibronic series, thus ensuring that the only significant change in self-absorption is due to the consumption of the original polyyne species. This hypothesis is further corroborated by the observation that the increase in MeCN's CN Raman peak mirrors the decrease in polyynes'ECC signal, as shown in Fig. S5a.

Assuming that the solvent is not affected by irradiation and the laser spot remains fully “immersed” in the solvent throughout the experiment, its Raman peak area should ideally remain unchanged. However, for the CN stretching mode of acetonitrile (MeCN) at ≈2258 cm^{-1}, an apparent increase in intensity is observed over time due to the decreasing SA (Fig. S5a).

To correct this artifact, a time-dependent SA correction factor, $f(t)$, was derived from the MeCN Raman peak:

$$f(t) = \frac{A_{MeCN}(t)}{A_{MeCN}(6h)}$$

where $A_{MeCN}(t)$ is the Raman area of MeCN's CN stretching peak at time t, and $A_{MeCN}(6h)$ is the corresponding value after 6 hours, when the polyyne consumption is maximum and SA is minimal (i.e., Raman areas are least affected by SA phenomena). Measuring the final solution is preferable to using the pristine solvent without polyynes. Residual impurities carried over from the chromatographic separation can slightly alter the Raman response of the solvent. Therefore, the solvent's Raman signal at the end of the experiment provides a more robust normalization standard for our data.

This correction factor was then applied to each Raman band. For the ECC peak, the corrected values are given by:

$$A_{ECC,\ corrected}(t) = \frac{A_{ECC}(t)}{f(t)}$$

where $A_{ECC}(t)$ is the measured ECC Raman area at time t, and $A_{ECC,correct}(t)$ is the corresponding SA-corrected value. A representative example, together with a comparison of corrected and non-corrected ECC Raman areas, is shown in Fig. S5.

Finally, the corrected ECC areas were normalized to allow comparison across different polyynes according to:

$$A_{ECC,normalized}(t) = \frac{A_{ECC,correct}(t)}{A_{ECC,correct}(0)}$$

where $A_{ECC,correct}(0)$ is the initial SA-corrected ECC Raman area at $t = 0$.

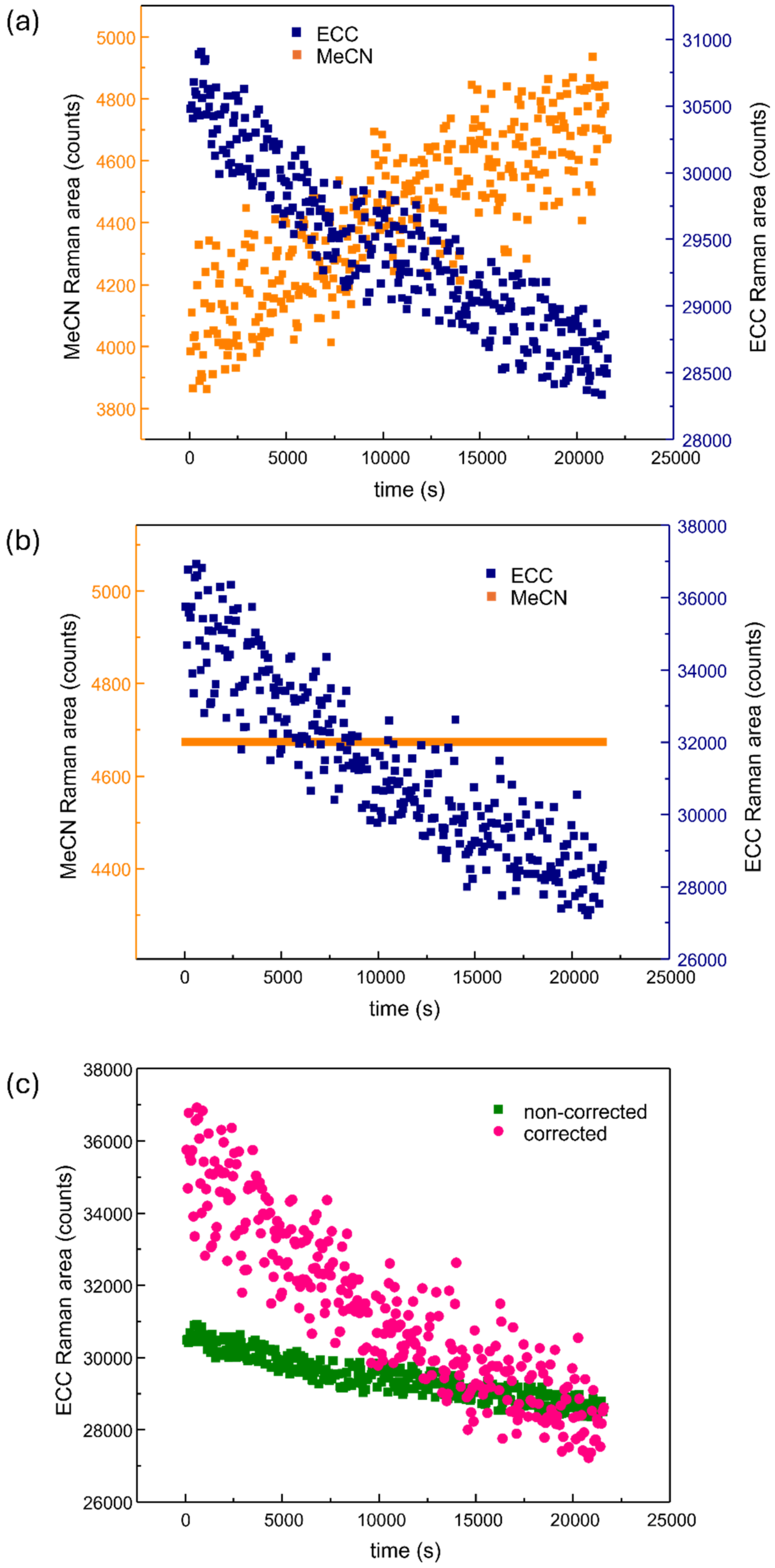

Figure S7 Raman areas of MeCN and ECC as a function of time. Panels (a) and (b) show the values before and after SA correction, respectively, while panel (c) compares the corrected and non-corrected ECC Raman values.

Calculation of the percentage variation in the ECC final intensity passing from pristine to diluted samples

The effect of concentration on the photodegradation stability of polyynes with different sp-carbon chain lengths was evaluated by comparing the variation in the final ECC Raman intensity of polyynes of different lengths in the pristine and diluted (i.e., 5×10^{-6} M) samples.

The final ECC Raman intensities, measured after 6 hours of light irradiation, are expressed as the percentage of their initial ECC Raman intensity retained.

$$ECC_{6\ hours}(\%) = \frac{A_{ECC}(t=0)}{A_{ECC}(t=6\ hours)} \cdot 100$$

Where $A_{ECC}(t=0)$ and $A_{ECC}(t=6\ hours)$ are the ECC Raman areas before (t=0) and after (t=6 hours) photon irradiation, respectively.

These values were calculated for each polyyne in both pristine and diluted ($5\text{x}10^{-6}$ M) samples. The variation between the two concentrations was evaluated using the following equation:

$$variation\ (\%) = \frac{ECC_{6h,5\times10^{-6}\ M} - ECC_{6h,pristine}}{ECC_{6h,pristine}} \cdot 100$$

Since shorter polyynes are more concentrated in the pristine solutions, they undergo a greater dilution to reach the final concentration of $5\text{x}10^{-6}$ M. This must be taken into account when evaluating the percentage variation between the two concentrations for each polyyne. To do so, a dilution factor (f) is introduced and calculated as follows:

$$f = \frac{[HC_nH]_{pristine}}{5 \times 10^{-6}\ M}$$

Where $[HC_nH]_{pristine}$ is the concentration of each HC_nH polyyne in the pristine solution before dilution. These values were determined by UV-Vis spectroscopy of the pristine solutions after HPLC separation and are reported, together with the dilution factor, in the following table:

	$[\boldsymbol{HC_nH}]_{\boldsymbol{pristine}}$	**f**
HC_8H	2.29×10^{-5} M	4.58
$HC_{10}H$	1.45×10^{-5} M	2.90
$HC_{12}H$	6.41×10^{-6} M	1.28

Lastly, the normalized percentage variation, which accounts for the different initial concentrations of each polyyne, was calculated as follows:

$$normalized\ variation\ (\%) = \frac{variation\ (\%)}{f}$$

References

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