Supplementary information for "Direct measurement of single-molecule dynamics and reaction kinetics in confinement using time-resolved transmission electron microscopy"

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Section 1: Computational details for calculation of PCC-PCC interaction energy confined inside SWNT.

Density functional theory (DFT) calculations were performed using the Q-Chem 5 quantum chemistry software package[1] to calculate the binding energy of a pair of perchlorocoronene (PCC) molecules confined within a single-walled nanotube (SWNT). Atoms of PCC molecules were modelled at the B3LYP/6-31G level of theory and the SWNT was represented using the AIRBED (Atomic Interactions Represented By Empirical Dispersion) method with α = 0.[2] PCC@SWNT structures were optimised for SWNTs of chirality (10,10), (11,11), (12,12), (13,13), and (14,14) to find the lowest energy configuration, which was found to be the (13,13) nanotube with diameter 1.76 nm.

Using the (13,13) SWNT, the binding energy was calculated as the difference in energy between the optimised PCC_2@SWNT structure and the two individual optimised PCC@SWNT structures (molecules 'A' and 'B'), using the counterpoise method (CP) to correct for basis set superposition error:

Binding Energy (CP corrected) = $E_{AB@SWNT}$ - ($E_{A@SWNT}$* + $E_{B@SWNT}$*)

Where * indicates a calculation performed in the presence of the basis functions of the other PCC molecule. This resulted in a binding energy of 83.1 kJ mol^{-1} for the PCC pair in the one-dimensional molecular 'stack'; this value can be taken as the barrier to molecular PCC dissociation in order to estimate the characteristic timescale for thermally activated separation of two molecules in the stack at various temperatures using the Arrhenius equation:

k = A exp(-E_a/RT)

Where k is the rate constant, A is the pre-exponential factor (taken as 10^{12} s^{-1}), E_a is the activation energy (83.1 kJ mol^{-1}), R is the ideal gas constant, and T is the temperature. Assuming a first order reaction PCC_2 (stack) -> 2PCC (separated), the characteristic times at the temperatures used experimentally, and the temperature corresponding to a characteristic time of one second, are:

Temperature (°C)	Time
-175	10^{24} years
23	7.6 minutes
89	1 s
200	1.5 ms
400	2.8 µs

Section 2: PCC crystal after irradiation (for comparison to irradiation of PCC@SWNT)
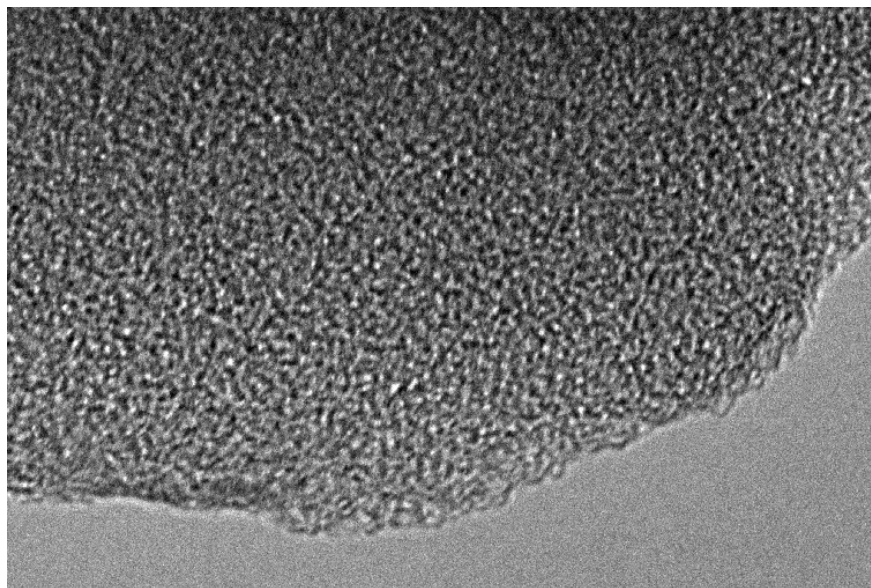
SI Fig. 1 A nanoscale crystal of PCC was imaged at an electron flux of 2.25×10^5 e$^-$ nm^{-2} s^{-1}. The scale bar is 5 nm. The electron beam may have been positioned over this crystal for a number of seconds before acquiring this first image. Even before the camera could capture a micrograph, the PCC crystal had turned amorphous under the electron beam and d-spacing could not be imaged. This is in stark contrast to the PCC molecules encapsulated within SWNTs, which were stable for many minutes (see main text).

Section 3: ^{13}C NMR of PCC
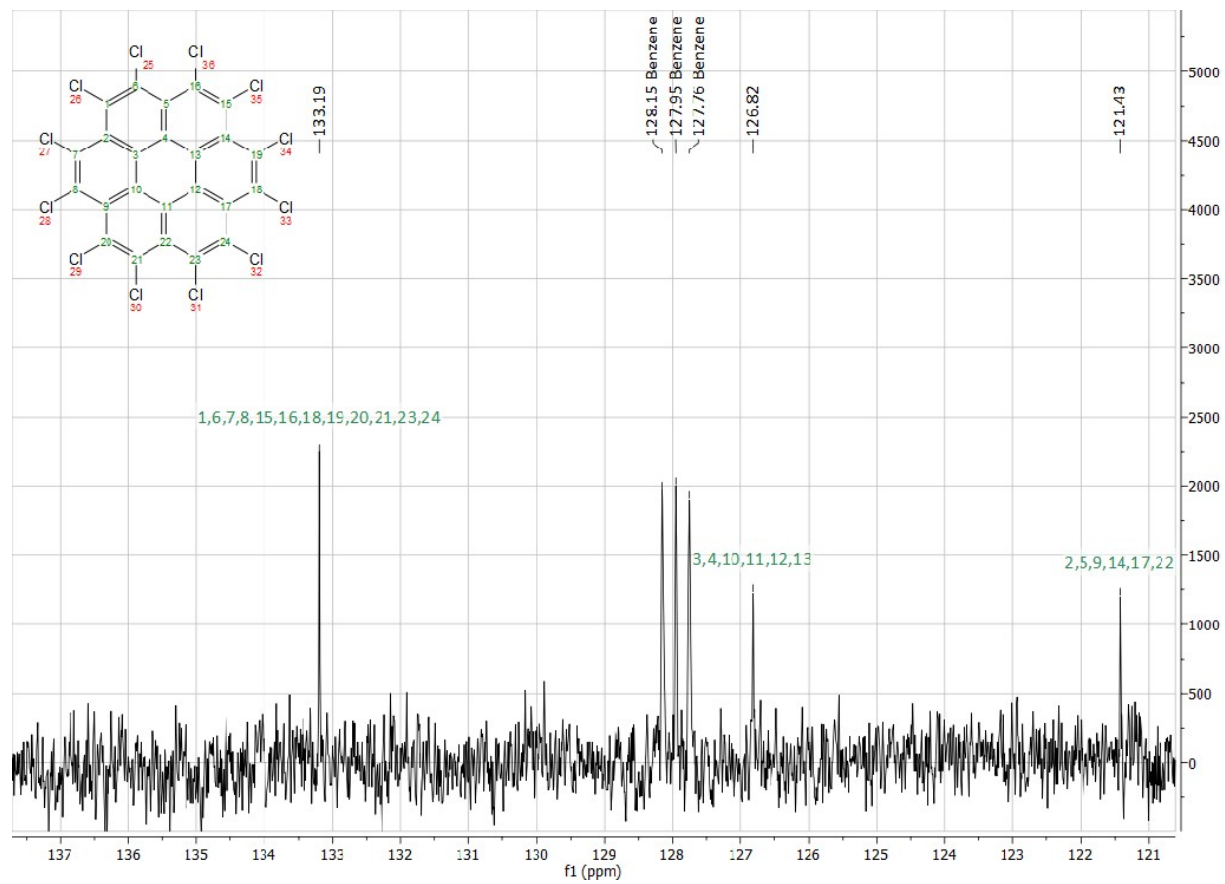
SI Fig. 2 The ^{13}C NMR spectrum of PCC. The PCC peaks are labelled with the structure adjacent.

1. Epifanovsky, E. *et al.* Software for the frontiers of quantum chemistry: An overview of developments in the Q-Chem 5 package. *J. Chem. Phys.* **155**, 084801 (2021).

2. Mason, S. E., Beton, P. H. & Besley, N. A. AIRBED: A Simplified Density Functional Theory Model for Physisorption on Surfaces. *J. Chem. Theory Comput.* **15**, 5628–5634 (2019).