ADVANCED MATERIALS

Supporting Information

for *Adv. Mater.*, DOI: 10.1002/adma.201908140

Shine Bright Like a Diamond: New Light on an Old Polymeric Semiconductor

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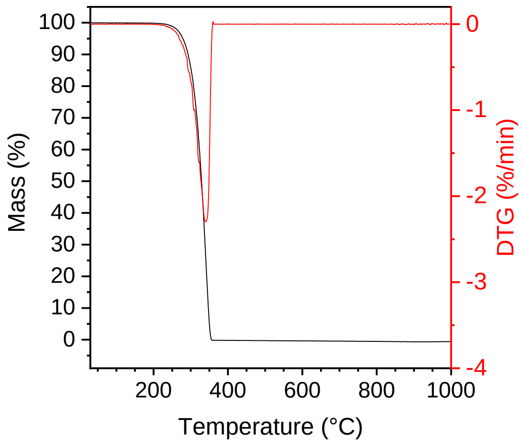

Figure S1. Thermogravimetric analysis of melamine. The steep mass decrease shows the sublimation curve of the melamine.

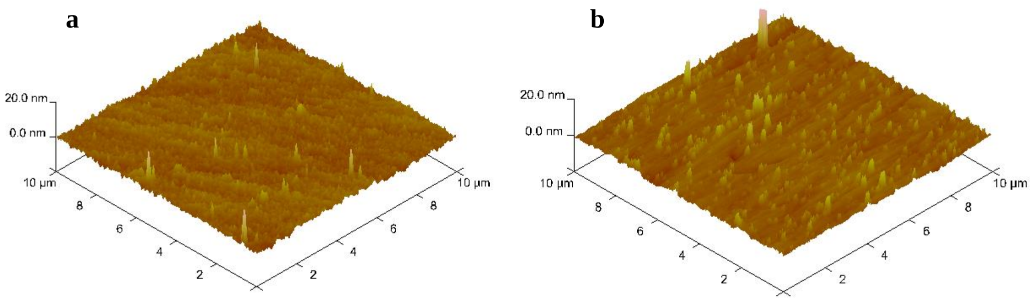

Figure S2. AFM surface map of pCN thin film (a), and the bare fused silica substrate (b).

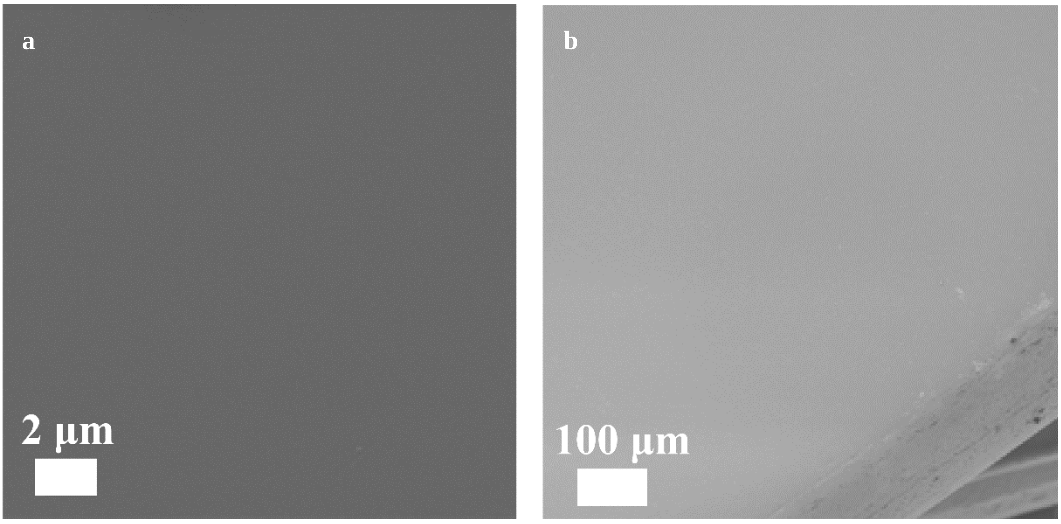

Figure S3. (a) SEM image of the central area of pCN thin film on fused silica; (b) SEM image of pCN thin film on a curved edge of a fused silica substrate.

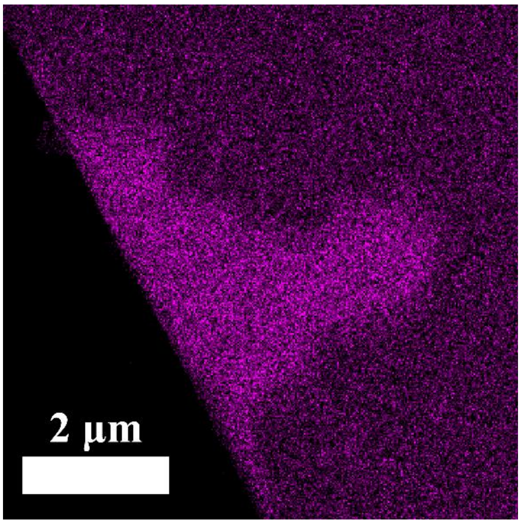

Figure S4. Oxygen EDX elemental map referred to Figure 2.

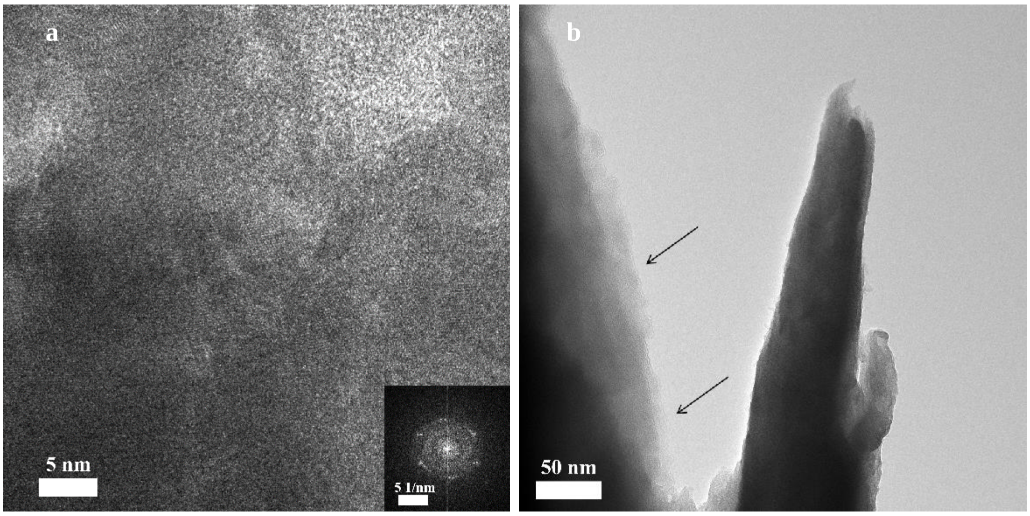

Figure S5. TEM image of pCN thin film. (a) In-plane TEM image of the of pCN thin films showing the hexagonal pattern (inset); (b) black arrows highlight the presence of a layered structure.

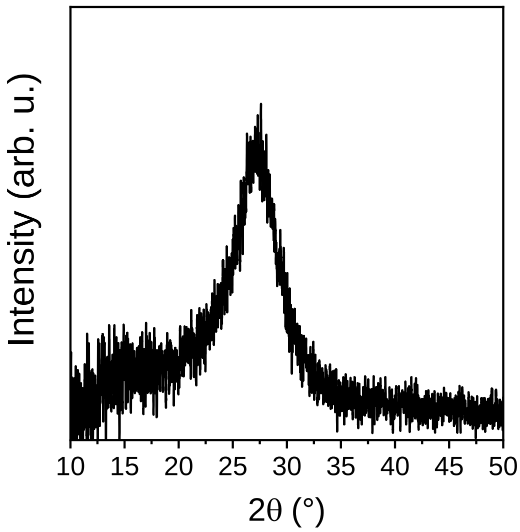

Figure S6. WAXD diffraction pattern of pCN thin film with the diffraction peak occurring at 27.4° (2θ).

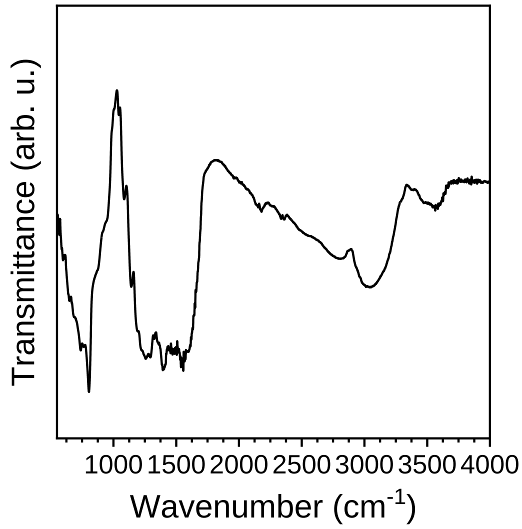

Figure S7. FTIR transmittance spectrum of pCN thin film in the range 4000-550 cm^{-1}.

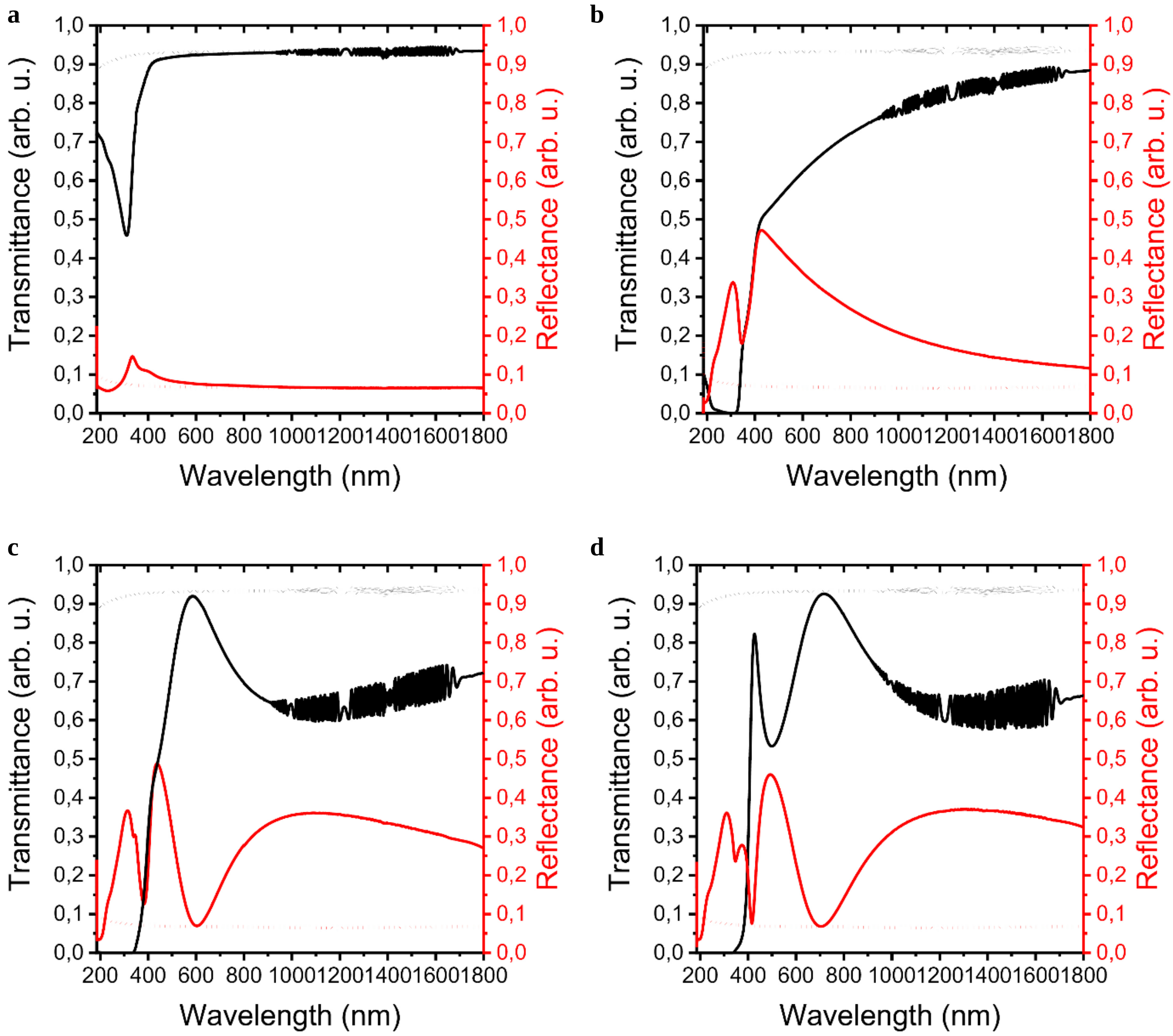

Figure S8. Transmittance and reflectance spectra of pCN thin films with different thicknesses on fused silica substrates. (a), transmittance and reflectance spectra of a 5 nm pCN thin film; (b), transmittance and reflectance spectra of a 38 nm pCN thin film; (c), transmittance and reflectance spectra of a128 nm pCN thin film; (d), transmittance and reflectance spectra of a 130 nm pCN thin film. The dotted curves reported shows the transmittance and reflectance spectra of the bare fused silica substrate.

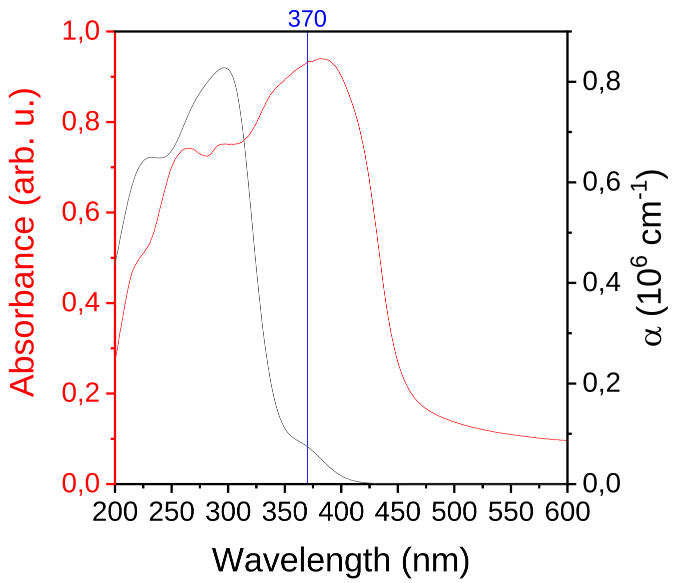

Figure S9. Absorbance spectrum of bulk pCN (red line) and absorbance coefficient (α) of pCN thin film (black line). The blue line is set at 370 nm.

Table S1. Sellmeier equation and parameters of the optical functions pCN thin films**.**

Sellmeier equation	
$n(\lambda) = \left(A + \frac{B\lambda^2}{\lambda^2 - C^2} + \frac{D\lambda^2}{\lambda^2 - E^2}\right)^{0.5}$	
Parameters	
A	1.545254
B	2.891273
C	$2.226221*10^3$ μm^2
D	$6.917342*10^{-1}$
E	$3.296790*10^3$ μm^2

Table S2. pCN thin film thickness on fused silica substrates as derived by optical characterization**.**

Melamine Amount (g)	Synthesis Time (min)	Film Thickness (nm)
5	300	6
5	90	38
10	300	128
10	90	130

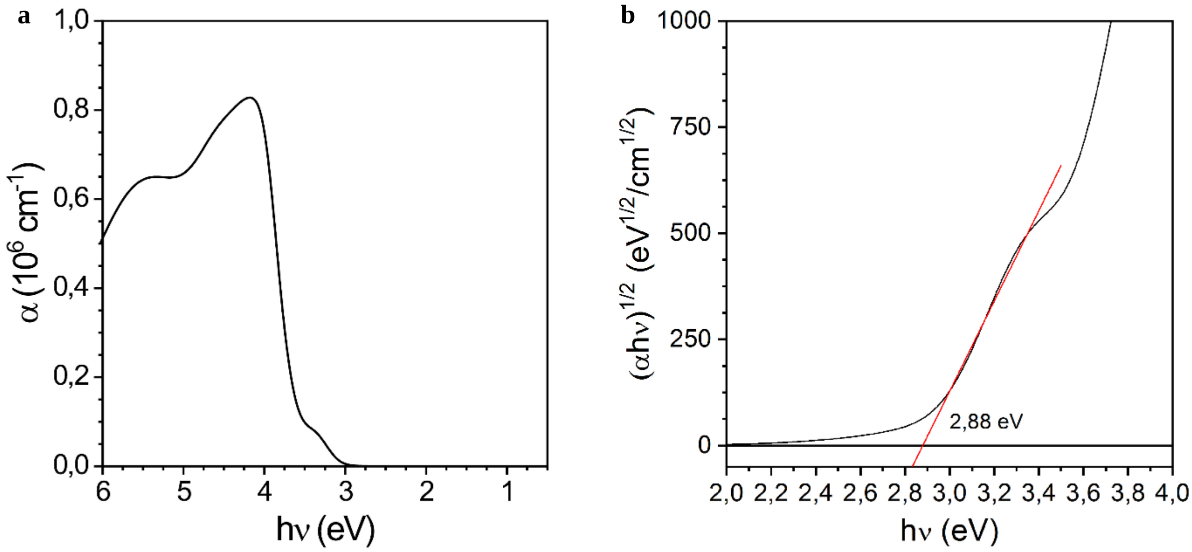

Figure S10. (a) Absorption coefficient of pCN thin films; (b) Tauc plot elaboration to define the optical bandgap of pCN thin films.

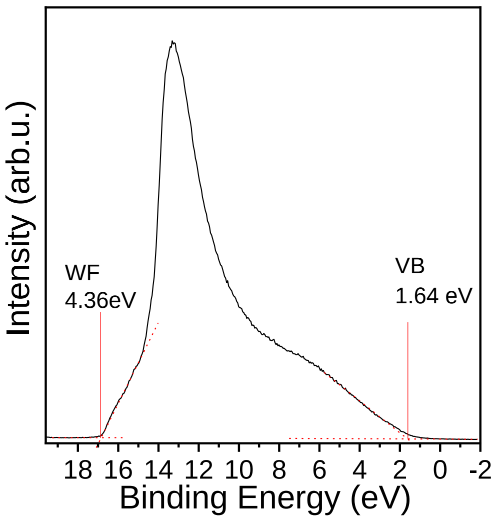

Figure S11. UPS spectrum of pCN thin film, where the workfunction is indicated by WF and the HOMO level by VB.

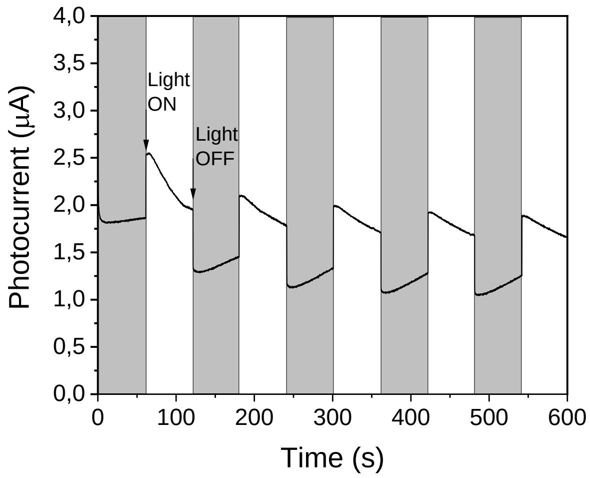

Figure S12. pCN thin film periodic on/off photocurrent tests. Periodic on/off photocurrent test under illumination centered at 465 nm and fixed applied voltage at 1.4 V.

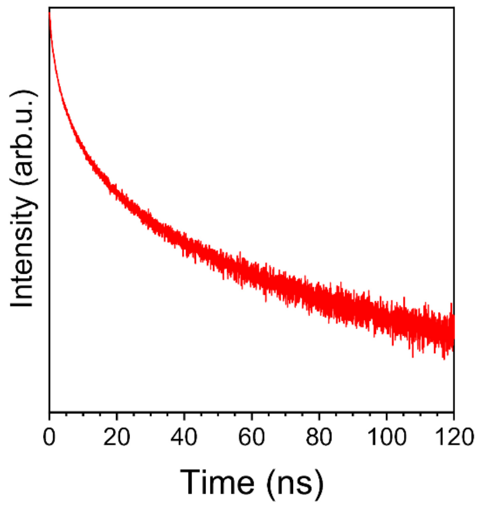

Figure S13. Time resolved photoluminescence of pCN thin films. Time resolved spectrum, in logarithmic scale, which shows the highly non-exponential behavior at 405 nm excitation. The photoluminescence lifetimes obtained are 2.1, 11.4 and 61.4 ns. The average lifetime of 6.5 ns has been calculated weighted on the amplitudes.

a

b

In order to evaluate the oxygen sensitivity to phosphorescence emission, the pCN thin film was dried at 50°C for one hour and flushed with pure nitrogen for 30 minutes (red line). Subsequently, the sample was flushed with air for 30 minutes (black line). The delayed emission intensity slightly decreases. Eventually, to further prove the effect of oxygen on the delayed emission intensity, the photoresponse in acetonitrile was measured (Figure S14 (b)). The pure acetonitrile was first flushed for 30 minutes with nitrogen and then injected in a quartz cuvette containing the pCN thin film (red line). Afterwards, the acetonitrile was flushed for 30 minutes with pure oxygen and then injected in the cuvette containing the pCN thin film for the measurement (black line).

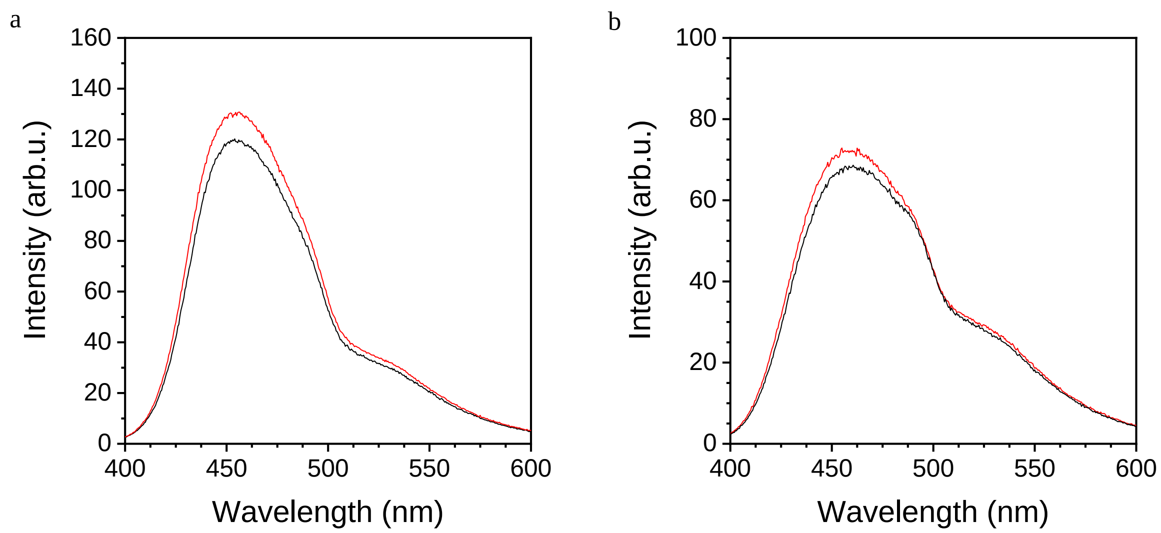

Figure S14. (a) Long-living emission of pCN thin film after exposure to air (black line) and nitrogen (red line). (b) Long-living emission of pCN thin film immersed in acetronitrile flushed with oxygen (black line) and nitrogen (red line).

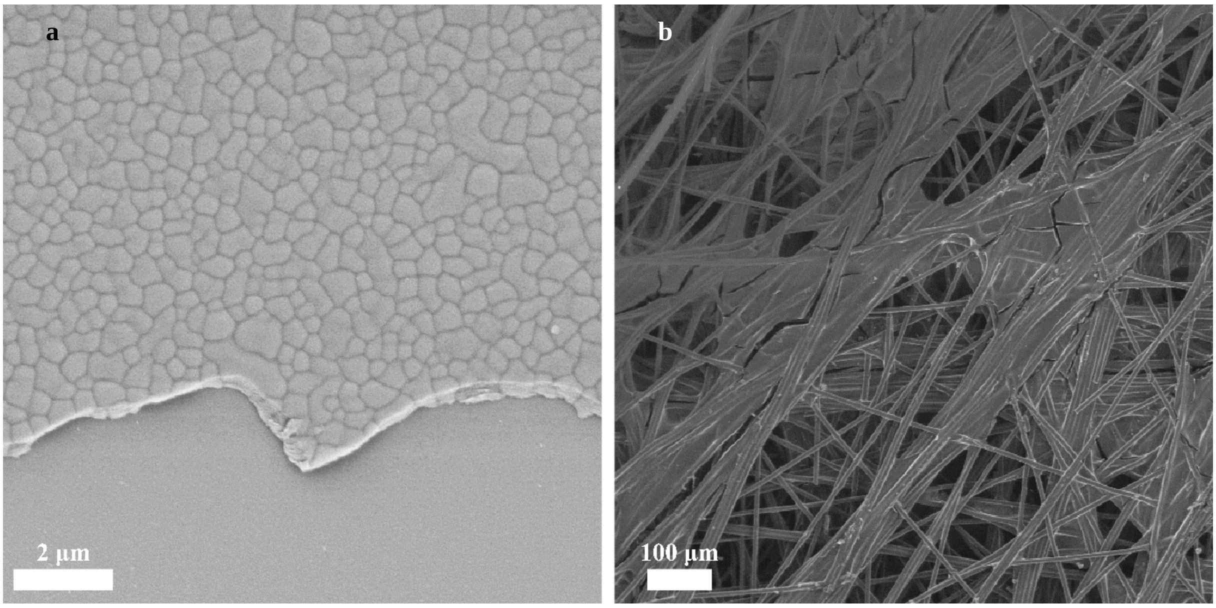

Figure S15. SEM images of pCN thin film on glass slide (a) and carbon paper (b) substrates.

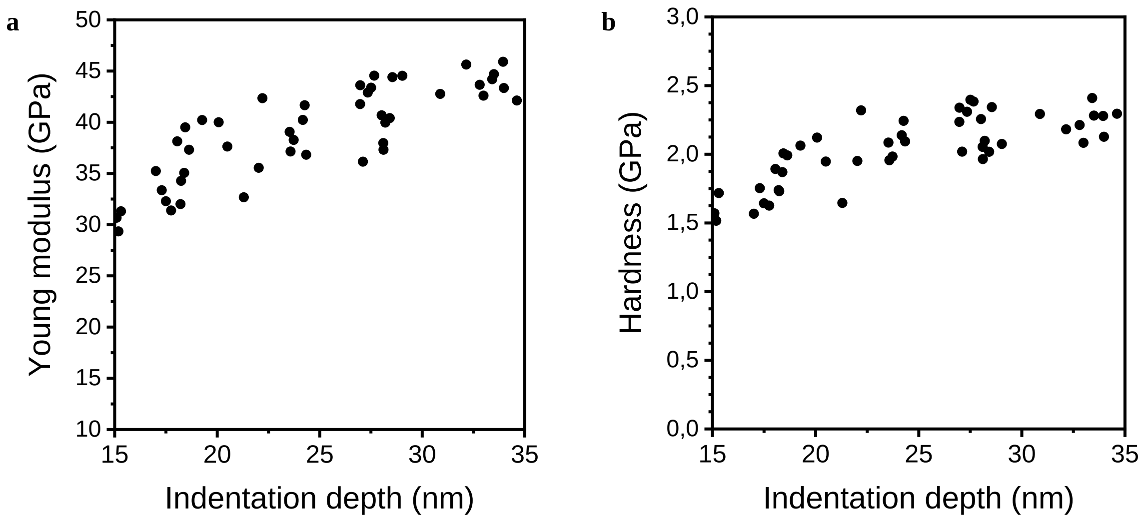

Figure S16. Typical force curve profile of a pCN thin film obtained by nanoindentation. (a) Young modulus as a function of indentation depth. (b) hardness as a function of indentation depth.

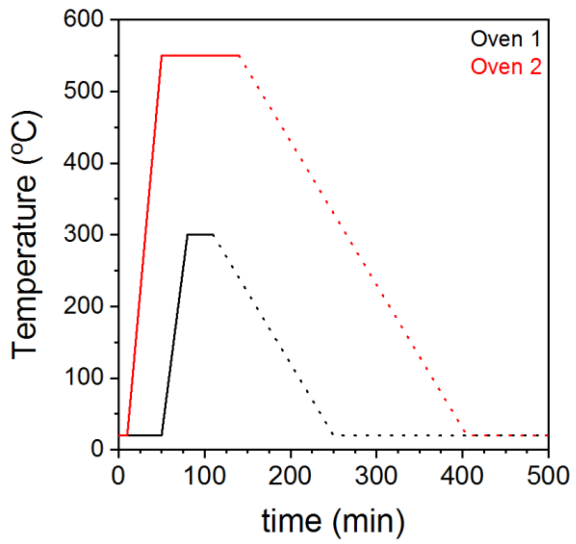

Figure S17. Typical growth profile of pCN thin films. Dotted lines are assumed for natural cooling rate.