

## Utilizing $\pi$ -peptide supramolecular polymers to template growth of hybrid organic-inorganic electronic materials

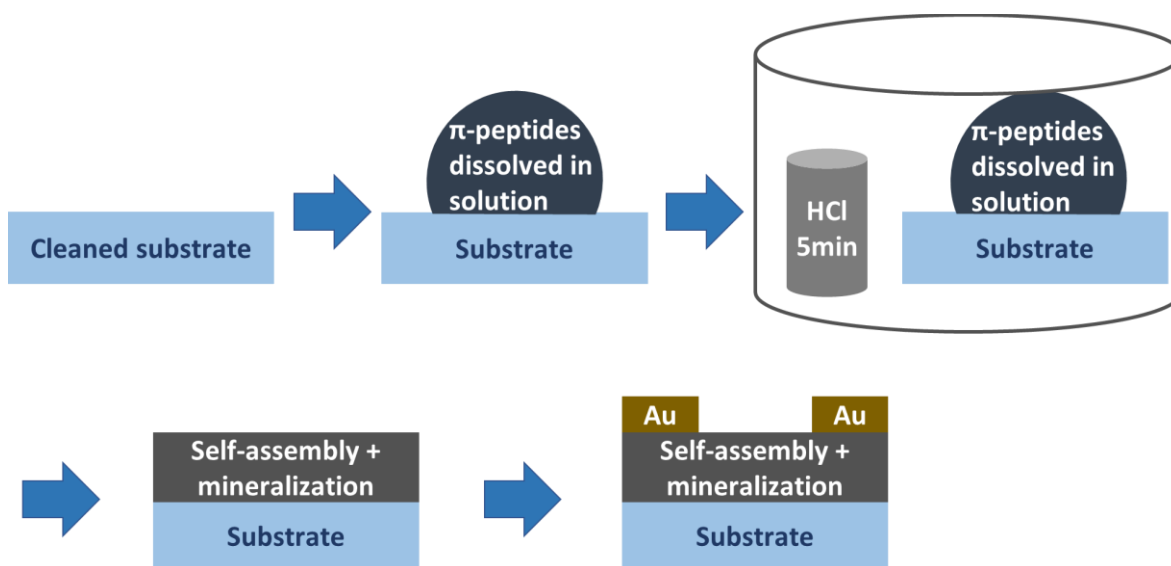
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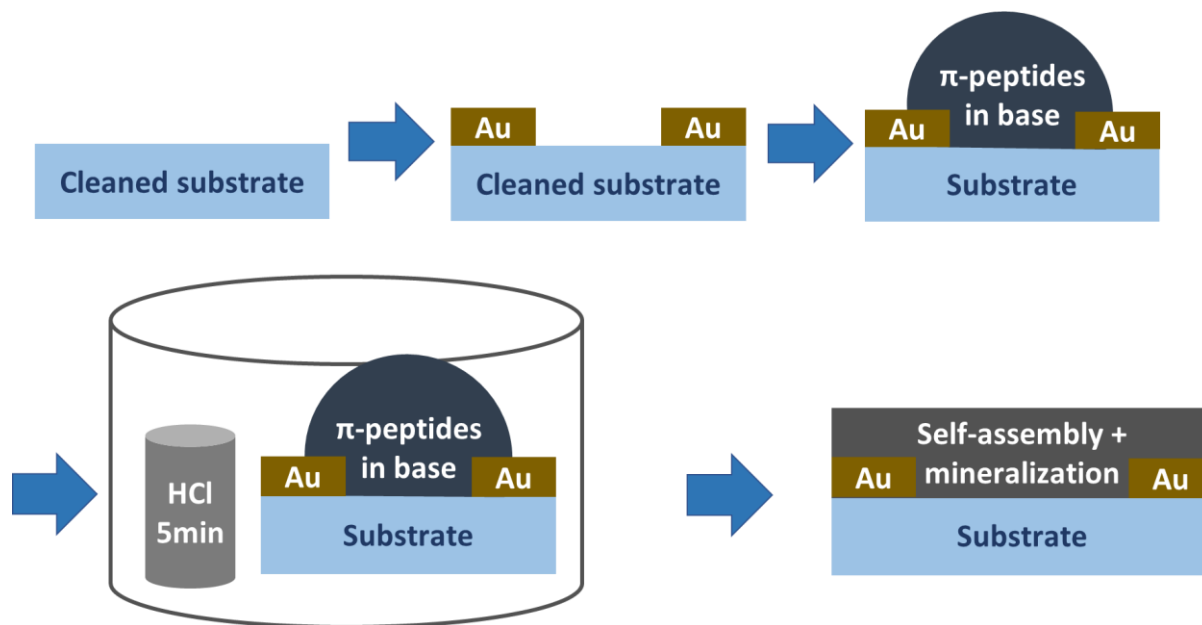
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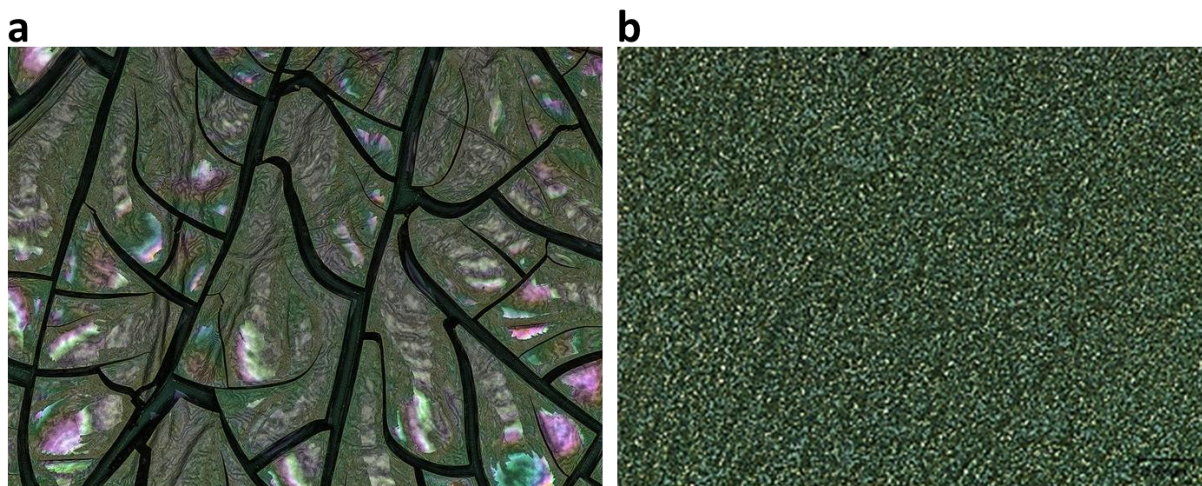
### Supporting Information



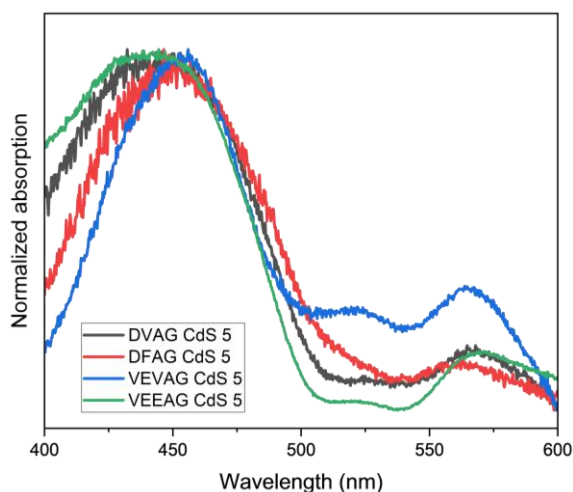
**Figure S1.** Schematic of procedure to fabricate top electrode  $\pi$ -peptide solid-state thin films on substrates. “Three-terminal” refers to the electrode configuration in the lower right, where the substrate is conductive and is used to verify lack of gate switching activity. Leakage current into the substrate is designated as IG. “Two-terminal” refers to using the pair of gold electrodes where the substrate is not part of the measured system.



**Figure S2.** Schematic of procedure to fabricate bottom electrode  $\pi$ -peptide solid-state thin films on substrates.



**Figure S3.** (a) 50x micrograph of CdS-only grown from 1M CdA and excess thioacetamide (1M CdS) (b) 50x micrograph of CdS-only grown from 0.01M CdA and excess thioacetamide (0.01M CdS)



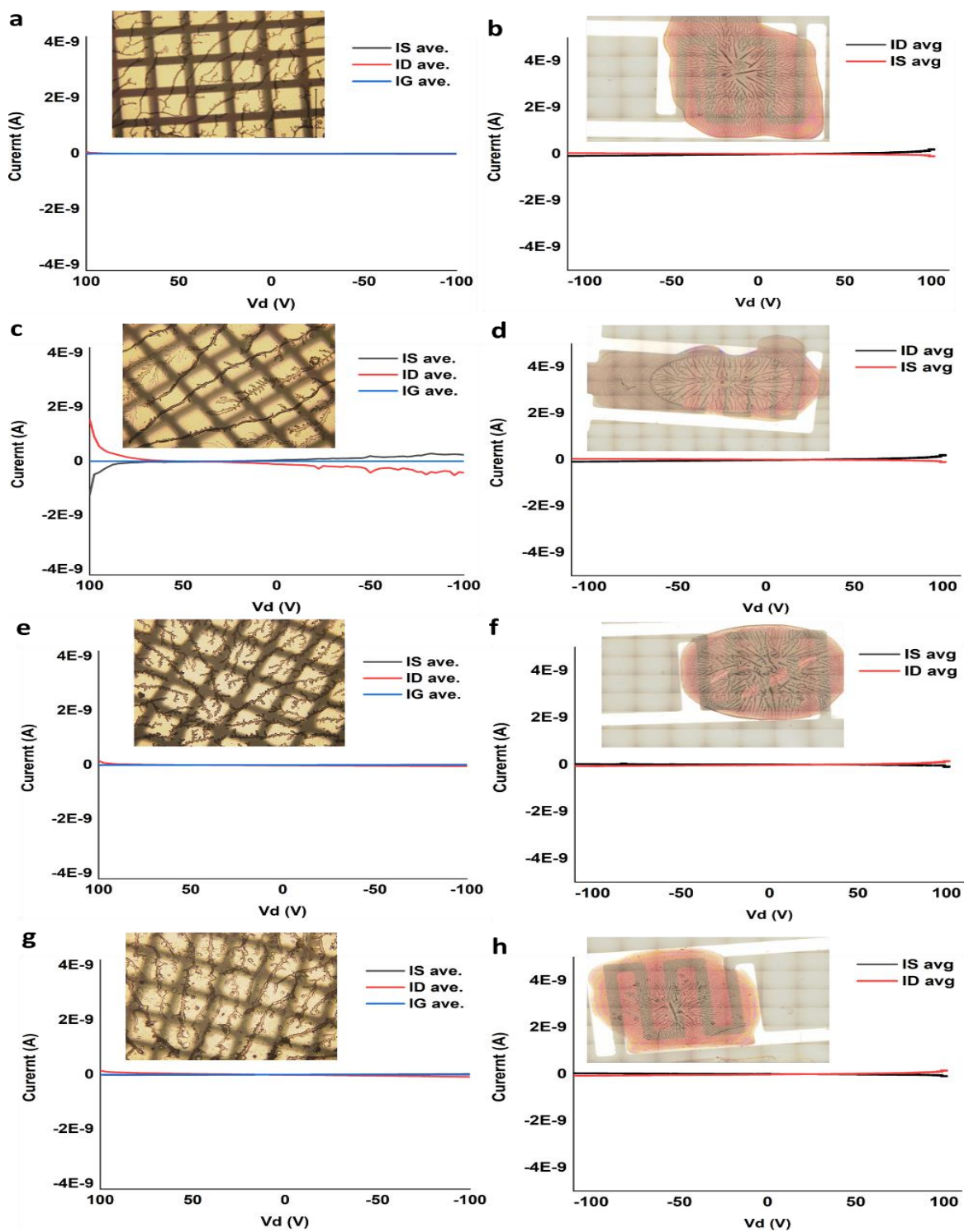
**Figure S4.** Absorbance spectra of DVAG-, DFAG-, VEVAG-, and VEEAG-PDI mineralized with CdS using the sample preparation method used for electrical measurements.

**Further explanation of CdS spectra.** Measuring absorbance spectra of the heavily mineralized CdS samples that were prepared for electrical measurements proved difficult (see supplemental spectra), so a modified CdS mineralization approach with thioacetamide was used to obtain the spectra. When mineralized in this way, the general shapes of the absorbance spectra were similar to those obtained when mineralized with KCl and CsCl, but there were no characteristic trends observed that correspond to previous observations. DFAG- and VEEAG-PDI no longer showed noticeably blue shifted peaks in the mid-energy region, and their shapes more closely resembled the shapes of the more strongly coupled DVAG- and VEVAG-PDI. The differences between amino acid sequences seems to have been dampened by the co-mineralization of CdS.

In UV-vis spectra of peptides mineralized with the CdS method used for electrical measurements, the influence of the mineralized CdS overwhelms the signals from the chromophores. Since CdS mineral itself has a strong absorbance in this region, it shrouds many of the peaks and makes the spectra difficult to interpret. Still, the major peaks in the absorbance spectra are visible, and there seems to be much less variation between the amino acid sequences compared to when mineralized with KCl or CsCl. Overall, this method produced a large amount of mineralized CdS on the surface of the substrate, but that also made interpretation of the spectra inconclusive.

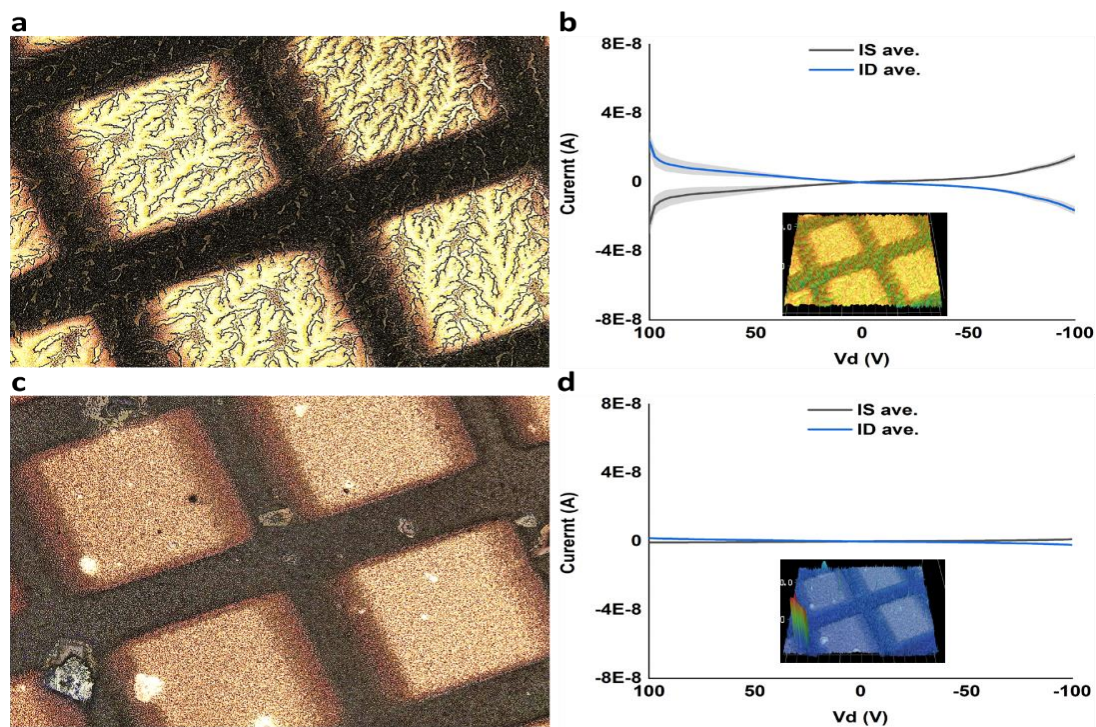
For CdS samples for spectroscopy, 5 mg/mL solutions of pi-peptide were prepared, made soluble using minimal amounts of  $\text{NH}_4\text{OH}$ . 100  $\mu\text{L}$  of this solution were deposited onto an Ossila ultra-flat 20 nm synthetic quartz coated polished soda lime, float glass substrate. The samples were then immediately put into a chamber of  $\sim 2$  L capacity, which contained a full uncapped 20 mL vial of glacial acetic acid, for 10 minutes. After the acid chamber exposure, the samples were removed and left to dry slowly in a partially covered petri dish. Once the film was fully dry, cadmium acetate solution (50  $\mu\text{L}$ , 0.01 M aqueous), and thioacetamide solution (50  $\mu\text{L}$ , 0.1 M aqueous) were mixed together on a sheet of parafilm on the benchtop and then immediately deposited onto the substrate. The substrate was then left to dry slowly in a humid chamber (2 L capacity, damp Kimwipe added to make it humid).

For CdS samples for electrical measurements, 5 mg/mL solutions of pi-peptide were prepared, made soluble using minimal amounts of  $\text{NH}_4\text{OH}$ . 100  $\mu\text{L}$  of this solution were deposited onto an Ossila ultra-flat 20 nm synthetic quartz coated polished soda lime, float glass substrate. The samples were then immediately put into a chamber of  $\sim 2$  L capacity, which contained a full uncapped 20 mL vial of glacial acetic acid, for 10 minutes. After the acid chamber exposure, the samples were removed and left to dry slowly in a partially covered petri dish. Once the film was fully dry, cadmium acetate solution (100  $\mu\text{L}$ , 0.01 M aqueous) was deposited onto the substrate. While the substrate was still wet, a balloon was filled with  $\text{H}_2\text{S}$  gas ( $\sim 1$  L), and the neck was pinched under the lip of an inverted crystallizing dish (2 L capacity) that housed the substrate. The  $\text{H}_2\text{S}$  gas was left to slowly release into the chamber. The balloon was refilled and replaced once, so the volume of  $\text{H}_2\text{S}$  gas was approximately 2 L. The sample was left to dry slowly.



**Figure S5.** Three-terminal top electrode measurement and image of device morphology in inset for (a) DVAG-PDI / KCl, (b) DFAG-PDI / KCl, (c) VEVAG-PDI / KCl, (d) VEEAG-PDI / KCl. Two-terminal bottom electrode measurement and image of device morphology in inset for (e) DVAG-PDI / KCl, (f) DFAG-PDI / KCl, (g) VEVAG-PDI / KCl, (h) VEEAG-PDI / KCl.





**Figure S6.** (a) Highly dendritic regions of DFAG-PDI / CsCl with thermally evaporated Au electrodes. (b) Electrical measurements of dendritic region showed notable conductivity. (c) Blank regions of DFAG-PDI / CsCl with thermally evaporated Au electrodes. (d) Electrical measurements of blank region showed no conductivity. Insets at (b) and (d) shows 3D height scan of electrodes measured.

## Tabulation of Prior Work on Peptide Self-Assembly and KCl Interactions

Title of paper	Paper	Key points
<b>Controlling Supramolecular Chirality in Peptide-<math>\pi</math>-Peptide Networks by Variation of the Alkyl Spacer Length</b>	<i>Langmuir</i> 2019, 35, 43, 14060-14073	<ol style="list-style-type: none"> <li>1. can modulate the chirality by incorporating alkyl spacers of various lengths</li> <li>2. even numbers of alkyl carbons in the spacer units (0, 2) induce M-type helical character whereas odd numbers (1, 3) induce P-type</li> </ol>
<b>Computationally Guided Tuning of Peptide-Conjugated Perylene Diimide Self-Assembly</b>	<i>Langmuir</i> 2021, 37, 28, 8594-8606	<ol style="list-style-type: none"> <li>1. For PDI cores, altering glycine to alanine at the closest residue position, we observed significantly different electronic properties</li> <li>2. Type I: DAVG-PDI, VEVxG-PDI = cofacial stacking   Type II: DAIA-PDI, VEVxA-PDI = rotationally shifted stacking</li> </ol>
<b>Computationally Guided Tuning of Amino Acid Configuration Influences the Chiroptical Properties of Supramolecular Peptide-<math>\pi</math>-Peptide Nanostructures</b>	<i>Langmuir</i> 2020, 36, 24, 6782-6792	<ol style="list-style-type: none"> <li>1. For VEVAG-<math>\pi</math>-GAVEV type peptidic materials varying the stereogenic centers (carbon spacer 0,1,2,3) of these residues has a profound impact on the optoelectronic properties of the supramolecular aggregates</li> <li>2. whereas the variation of stereogenic centers of other residues has only nominal influence on these properties</li> </ol>
<b>Unusually Conductive Organic-Inorganic Hybrid Nanostructures Derived from Bio-Inspired Mineralization of Peptide/Pi-Electron Assemblies</b>	<i>ACS Nano</i> 2020, 14, 2, 1846-1855	<ol style="list-style-type: none"> <li>1. Electronic/ionic mixed conductivity mechanism for VEVAG-3spacer-PTP peptides</li> <li>2. KCl mineralization forming hybrid structures enables formation of highly conductive dendritic macrostructures</li> </ol>
<b>Relation among absorbance shifts, mineralization morphology, and electronic conductivity of <math>\pi</math>-peptide aggregates with different amino acid residues</b>	<i>Mater. Adv.</i> , 2023, 4, 1964-1977	<ol style="list-style-type: none"> <li>1. Confirmed details of paper 1. and 2. by making electrical devices out of these materials to relate the morphological cues to structural (images/xrd) and electrical properties</li> </ol>