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Bioinspired Stable and Photoluminescent Assemblies for Power Generation

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Conflict of Interest

The authors declare no conflict of interest.

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Abstract

Peptide assemblies are ideal components for eco-friendly optoelectronic energy harvesting devices due to their intrinsic biocompatibility, ease of fabrication, and flexible functionalization. However, to date, their practical applications have been limited due to the difficulty in obtaining stable, high-performance devices. Here, it is shown that the tryptophan-based simplest peptide cyclo-glycine-tryptophan (cyclo-GW) forms mechanically robust (elastic modulus up to 24.0 GPa) and thermally stable up to 370 °C monoclinic crystals, due to a supramolecular packing combining dense parallel β -sheet hydrogen bonding and herringbone edge-to-face aromatic interactions. The directional and extensive driving forces further confer unique optical properties, including aggregation-induced blue emission and unusual stable photo-luminescence. Moreover, the crystals produce a high and sustained open-circuit voltage (1.2 V) due to a high piezoelectric coefficient of 14.1 pC N⁻¹. These findings demonstrate the feasibility of utilizing self-assembling peptides for fabrication of biointegrated microdevices that combine high structural stability, tailored optoelectronics, and significant energy harvesting properties.

Keywords

crystallization; cyclo-dipeptides; mechanics; photoluminescence; piezoelectricity

Increasing demand for miniaturized energy harvesting devices requires safe, inexpensive materials with suitable optical, electrical, and mechanical properties.[1–3] However, state-of-the-art inorganic-containing components show limited eco-friendliness, and their smallest manufactured dimensions are limited by “top-down” fabrication that severely restricts their potential use in nano/bio applications.[4,5] Organic candidates have attracted increasing interest owing to their diverse and tuneable properties, cost effectiveness, and ease of modulation.[6,7] However, their device fabrication and commercialization are still limited due to several issues, including their limited eco-friendliness, poor optical, electrical, or mechanical properties, and in many cases, complicated synthesis procedures.[6] By contrast, self-assembling aromatic short peptides, with the representative model of diphenylalanine (FF), can form biocompatible nanoarchitectures with highly engineerable properties.[8–13] In addition, these supramolecular structures can be tailored to give desired functionality.[14–16] For example, self-assembled phenylalanine-tryptophan (FW) nanostructures present a much smaller bandgap than FF nanotubes.[17] The resulting improvements in conductivity and photoluminescence,[18,19] indicate that supramolecular architectures self-assembled by W-based peptides may provide better device properties than the F-based counterparts.

In this work, we designed the simplest W-containing peptide, cyclo-glycine-tryptophan (cyclo-GW, Figure 1a), determined its crystal packing, and demonstrated its excellent thermal stability, mechanical strength, stable visible photoluminescence, and high piezoelectric properties. Our findings indicate that W-based peptide self-assemblies are promising supramolecular materials for miniaturized bioorganic devices for power

generation (such as biomechanical forces harvesting) or sensing (such as heartbeat detection) with technologically useful optical, electrical, and mechanical properties.

Briefly, after dissolving cyclo-GW powder in 10% (v/v) methanol in water and heating to 80 °C, needlelike crystals slowly appeared and grew during gradual cooling to room temperature (Figure 1b). Their monoclinic crystal structure (Table S1, Supporting Information) shows dense packing along the **b** direction (Figure 1b,c), with hydrogen bonds (N—H···O=C) of 2.83 Å (donor···acceptor) in a parallel β -sheet hydrogen bonding network that is further stabilized by interstitial herringbone-type aromatic packing as the indole units (Figure 1c, circled by the green ellipses) make close C···N contacts of ≈ 3.4 Å. Notably, the herringbone stacking is directed by the five-membered pyrrole ring as opposed to the six-membered benzene ring (Figure 1c and Figure S1, Supporting Information). By contrast, the diketopiperazine rings are oriented antiparallel and well-separated from each other by ≈ 4.0 Å along the **a** direction (Figure 1d) and relatively sparse packing is seen along the **c** direction. Molecular dynamics computer simulations corroborated these measured distances and further confirmed the stability of the crystal packing modes (Figure S2, Supporting Information).

The optoelectronic properties of the peptide assemblies are encoded in the supramolecular packing motifs which are in turn directed by the kinetic and thermodynamics of the crystallization process.[20–22] Therefore, the compact packing patterns inspired us to investigate the structural stability and the mechanical strength of the cyclo-GW crystals. From density function theory (DFT) computations the relative stability of cyclo-GW monomers and dimers was -0.758 and -0.765 eV per atom, respectively (Table S2, Supporting Information), indicating the aggregation-induced stabilization by packing. At the macroscopic level, thermal gravimetric analysis (TGA) characterizations demonstrated the thermal stability up to 370 °C (Figure 2a, red curve). In control experiments, the well-characterized FF tubular crystals transformed to cyclo-FF fibrils at 170 °C (Figure S3, Supporting Information) and started to degrade at 303 °C (Figure 2a, black curve).[23,24] DFT calculations showed that linear-FF and cyclo-FF dimers are less stable than the cyclo-GW dimers, with smaller-magnitude calculated relative stabilities of -0.625 and -0.619 eV per atom (Table S2, Supporting Information), respectively, substantiating the TGA finding that cyclo-GW crystals are more thermally stable.

The remarkable thermal stability suggests that the cyclo-GW crystals may possess high mechanical strength at the microscopic level as well.[23] To test this hypothesis, we applied nanoindentation through atomic force microscopy (AFM) to measure the micromechanical properties of the crystals (Figure 2b; Note S1 and Figures S4–S6, Supporting Information). [25,26] The measured elasticity of the crystals showed a high Young's modulus of 24.0 ± 7.3 GPa along the thickness direction (Figure 2c and Figure S7, Supporting Information), a particularly high value for bioorganic materials, which led to a point stiffness of 16.3 ± 5.8 N m $^{-1}$ of the crystals (Figure 2d) and confirmed the strong supramolecular packing. Correspondingly, the shear modulus perpendicular to the crystal axis direction was measured to be 2.9 ± 1.1 GPa (Figure 2e), nearly 14-fold higher than that of FF nanotubes (0.21 ± 0.03 GPa)[27] and tenfold higher than that of insulin self-assembling nanofibers (0.28 ± 0.2 GPa),[8] indicating a high shear rigidity. The crystals finally broke after the loading force

reached around 5 μN , showing a breaking modulus of up to 238.9 ± 97.6 GPa (Figure 2f). These experimental findings reveal that the cyclo-GW crystals are sufficiently mechanostable for micromechanical applications.[2,8]

Hydrogen bonding and aromatic supramolecular packing networks can confer unique optoelectronic properties on peptide self-assemblies.[6] Recent studies reported that the interacting aromatic rings can exhibit through-space conjugation,[28,29] while the hydrogen atoms can shuttle between donor and acceptor groups in hydrogen bonds.[9] The resulting changes in the electronic structures can decrease the energy bandgap and facilitate the redshift of photoluminescence to the visible light region.[30] Our calculations confirm that the bandgap decreases from 5.14 to 4.60 eV after dimerization of the cyclo-GW monomer (Figure 3a and Table S3, Supporting Information). The computed highest occupied molecular orbital (HOMO) of the dimer is mostly localized on the indole ring of one of the tryptophan moieties, while the lowest unoccupied molecular orbital (LUMO) sits on the indole ring of the opposite tryptophan (Figure 3a, right panel), thus forming a configuration amenable to charge transfer through the aromatic networks in the crystal. Fluorescence experiments show that the cyclo-GW crystals emit at 420 nm, in the blue light region, when excited with wavelengths in the range of 300–400 nm (Figure 3b). In a control experiment, the cyclo-GW solution only showed emission in the UV region, with maximum at 345 nm (Figure S8, Supporting Information), indicating that the visible photoluminescence indeed results from crystallization. Fluorescence microscopy confirmed the photoluminescent properties of the crystals (Figure 3c) and demonstrated the optical waveguiding potential of the crystals as a remarkable increase in brightness could be detected at the termini (red circles in Figure 3c).[13,31] Photons can be transmitted along the crystal axis by continuous excitation-emission, thus implying the potential use of the supramolecular structures in fiber optics.[6] Fluorescent lifetime microscopy (FLIM) experiments revealed that the statistical fluorescence lifetime of the crystals was 2.1 ± 0.6 ns (Figure 3d and Figure S9, Supporting Information). Aggregation of organic dyes generally leads to photoquenching,[32] yet the photoluminescence of the cyclo-GW crystals did not decline during 10 min of continuous excitation (Figure 3e). We propose that restriction of molecular rotations and vibrations in the crystal structure impedes intermolecular energy transfer, which allows photons to be constantly emitted and so enables use of the device in optoelectronic applications.

The noncentrosymmetric structure with directional hydrogen bonding and aromatic packing networks signifies internal polarization, which implies piezoelectric properties.[6] DFT calculations reveal that cyclo-GW crystals have small relative permittivity (ϵ_r), with a value of only 2.9 (Table S4, Supporting Information), similar to glycine crystals ($\epsilon_r = 2.5$) which show high piezoelectricity.[33] Computed piezoelectric charge constants of cyclo-GW crystals are shown in Figure 4a. The predicted highest piezoelectric coefficients, d_{16} and d_{36} , are ≈ 14 pC N $^{-1}$ (Table 1), higher than traditional inorganic piezoelectric materials such as ZnO ($d_{33} = 12$ pC N $^{-1}$) and CdS ($d_{15} = 12$ pC N $^{-1}$),[34] and biological materials such as γ -glycine ($d_{33} = 10$ pC N $^{-1}$),[33] bone (6 pC N $^{-1}$),[35] viruses (8 pC N $^{-1}$),[36] and fibrillar rat tail collagen (12 pC N $^{-1}$).[37]

To test the predicted high piezoelectricity and so gauge the potential of the peptide crystals for use as bioorganic energy harvesting devices, a coin-size power generator was designed

and fabricated by tightly sandwiching the cyclo-GW crystals film between two Ag-coated silicon substrates connected to an external measuring instrument (Figure 4b). Every part of the system was firmly contacted and the whole device was tightly sealed with Kapton tape (Figure 4b and Figure S10, Supporting Information), to avoid creation of air gaps or contact separation during the impacting process, thus eliminating potential interference from, e.g., triboelectricity.[38] When a periodic compressive force of 65 N was applied, the output open-circuit voltage (V_{oc}) after offset calibration reached up to 1.2 V (Figure 4c), significantly higher than that of γ -glycine crystals (0.45 V)[33] and M13 bacteriophage (0.4 V).[36] Correspondingly, the short-circuit current (I_{sc}) reached 1.75 nA (Figure 4d), which is an order of magnitude higher than the current generated by zinc oxide nanogenerators.[39] We expect that the device performance can be further increased in future development through creation of highly ordered aligned arrays[40] and large scale integration. Switching connection tests showed that the output flipped to -1.2 V when the connection to the measurement instrument was reversed (Figure S11, Supporting Information), thus confirming that the detected electrical signal was indeed from the piezoelectric cyclo-GW crystals, which excludes the possibility of artefacts from the variation of contact resistance or parasitic capacitance. Furthermore, the voltage output values scale with the applied force, with a slope of 18.8 mV N^{-1} (Figure 4e), demonstrating linear piezoelectric response of the peptide crystals. Finally, the high mechanical strength suggests that power generation can be sustained under a cyclic force (65 N) (Figure 4f) and the output voltage showed no degradation over 2500 press/release cycles for more than half an hour (Figure 4g), indicating the high durability of the peptide-based devices. Especially, the high thermal stability of the cyclo-GW crystals indicates their potential use in a broad temperature window. Given also their stable photoluminescence in the visible light region, these supramolecular materials can be used as bioorganic components in highly integrated optoelectronic microdevices for energy harvesting or piezoelectric sensing, such as touch screens in consumer electronic devices.

In conclusion, the W-based simplest peptide, cyclo-GW, was demonstrated to crystallize into needlelike crystals in which the compact and orderly arrangement of the molecules led to significant structural stability and mechanical rigidity. The extensive and directional hydrogen bonding and aromatic interaction network lowered the bandgap and conferred aggregation-induced emission in the visible light range, optical waveguiding properties, and especially, stable photoluminescence. The crystals show relatively large piezoelectric response, which generated high, stable power outputs under high press forces in proof-of-concept devices. While the piezoelectric coefficients are below those of state-of-the-art inorganic (such as lead-free barium titanate or sodium bismuth titanate)[41] and organic (such as polyvinylidene fluoride polymer)[42] piezoelectric materials, we note that similar noncovalent peptide nanotubes can exhibit a higher or comparable voltage constant ($\approx 0.55 \text{ V m N}^{-1}$). Intrinsic bioinspired nature makes the cyclo-GW crystals appealing candidates to be used for eco-friendly powder harvesting devices and in complicated biological systems, thus extensively expanding the application fields of piezoelectric materials.

It should be noted that the current material is remarkably flexible and highly engineerable. [43] Diverse modulation strategies, such as amino acid substitution (changing to other aromatic residues such as histidine, *D*-type enantiomers, peptide derivatives such as peptide

nucleic acids, and even artificially synthetic chromophores), complexation with metal ions, self-assembly under different conditions (different solvents or vapor deposition), design of larger cyclo-oligopeptides (cyclotripeptides, cyclo-tetrapeptides, etc.), and flexible assembly approaches (coassembly, covalent conjugation), can be further employed to tune the structures and so the optoelectronic properties of cyclo-peptide assemblies. Given their innate advantages of low-cost, eco-friendliness, and ease of preparation, the peptide supramolecular structures may serve as bioorganic components for “bottom-up” fabrication of microelectronic systems for optical, electric, and energy uses.

CCDC 1823369 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Supplementary Material

Refer to Web version on PubMed Central for supplementary material.

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Figure 1. Molecular packing of cyclo-GW crystals.

a) Molecular structure of cyclo-GW. b) SEM image of the cyclo-GW needles. The red arrows mark the growth direction along the crystallographic **b** axis. c,d) Supramolecular packing in the (c) **b-c** and (d) **a-c** planes. Dashed black lines show hydrogen bonds, and green ellipses highlight the indole rings forming the herringbone-type aromatic interactions. Purple double-headed arrows mark the antiparallel stacking of the backbone diketopiperazine rings. The primitive unit cell is marked by a black rectangle. White, gray, blue, and red spheres represent hydrogen, carbon, nitrogen, and oxygen atoms, respectively.

Figure 2. Mechanostability of the cyclo-GW crystals.

a) TGA curves of the cyclo-GW and reference FF crystals. Note that at 170 °C (marked by an arrow), linear-FF condenses to cyclo-FF through intramolecular dehydration condensation. b) Schematic model showing how AFM nanoindentation is used to measure the mechanical properties of microstructures. c) Young's modulus, d) Point stiffness, e) Shear modulus, and f) Breaking modulus statistical distributions of cyclo-GW crystals. The normal distribution curves are also shown (black). At least 3500, 4500, and 400 counts were used for Young's modulus, Shear modulus, and Breaking modulus statistics, respectively.

Figure 3. Optoelectronic properties of the cyclo-GW crystals.

a) Calculated molecular orbital surfaces of the HOMO and LUMO of cyclo-GW monomers and dimers, showing conductance gaps of 5.14 and 4.60 eV, respectively. b) Fluorescent emission spectra at different excitations. c) Fluorescent microscopy image of the crystals, magnification: 100X. The red circles mark the brighter ends, showing the optical waveguiding feature of the crystals. d) Statistical fluorescence lifetime distribution of the crystals. e) Emission photostability of the crystals.

Figure 4. Piezoelectric properties of cyclo-GW crystals.

a) 3D surface plot of computed piezoelectric coefficients of cyclo-GW single crystal. The extracted predicted d_{ij} coefficients are listed in Table 1. b) Schematic configuration of the generator as a direct power source using cyclo-GW crystals as active components. The inset on the left shows a photograph of the generator. c) Open-circuit voltage and d) short-circuit current obtained from the generator. e) Linear dependence of the open-circuit voltage on the applied force, with the standard deviation estimated from three replicates as the error bars. f) Time-resolved open-circuit voltage evolution as the generator was pressed under 65 N force for over 30 min at 1 Hz. The time was set based on the working and storage limits of our measuring instrument. g) Periodic magnified view of the voltage output from red frames of (f), showing the large and unchanging voltage output.

Table 1
Calculated piezoelectric coefficients extracted from Figure 4a.

d_{ij} [pC N ⁻¹]	1	2	3	4	5	6
1				4.6		13.8
2	3.4	-0.4	-2.0		2.8	
3				6.3		14.1