Supporting Information

Tunable Mechanical and Optoelectronic Properties of Organic Co-Crystals by Unexpected Stacking Transformation from H- to J- and X-Aggregation

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Experimental Procedures

Materials. All the solvents and chemicals are commercially available. Chemicals were used without further purification. Water was processed using a Millipore purification system (Darmstadt, Germany) with a minimum resistivity of 18.2 MΩ cm. 4,4’-Bpy and AcA were purchased from Sigma at a purity level of >99%, and ultrapure water was obtained from Biological Industries.

SEM images. A small amount of solid crystals (4,4’-Bpy, AcA, or 4,4’-Bpy/AcA) was placed onto a conductive tape in a clean glass slip at ambient conditions overnight for drying and coated with Au. SEM images were recorded using a JSM-6700F FE-SEM (JEOL, Tokyo, Japan) operating at 10 kV.

Fluorescence microscope. The formed crystals (4,4’-Bpy, AcA, or 4,4’-Bpy/AcA) in a glass vial were directly observed by using a Nikon Eclipse Ti-E fluorescence microscope at different fluorescence channels, as follows: Blue: Ex 325-375 nm, Em 435-485 nm; Green: Ex 450-490 nm, Em 500-550 nm; Red: Ex 532-557 nm, Em 570-640 nm.

Fluorescence spectrophotometer. The fluorescence properties of the crystals (4,4’-Bpy, AcA, or 4,4’-Bpy/AcA) were analyzed using a FluoroMax–4 Spectrofluorometer (Horiba Jobin Yvon, Kyoto, Japan) at ambient temperature. For the excitation-dependent maximal emission evolution experiment, the excitation wavelengths were set to 320–380 nm for 4,4’-Bpy and 370-430 nm for 4,4’-Bpy/AcA with a slit of 5 nm, and the emission wavelengths were set to 400-600 nm for 4,4’-Bpy and 450-650 nm for 4,4’-Bpy/AcA with a slit of 5 nm. The air was used as background and subtracted.

DSC and TGA. Thermal stability of the crystals (4,4’-Bpy, AcA, or 4,4’-Bpy/AcA) was examined by melting and decomposition temperatures using a Differential Scanning Calorimetry (NETZSCH STA 449F5, Germany) at a heating rate of 5 K min⁻¹ under nitrogen atmosphere with a flow rate of 50 mL min⁻¹ and at a temperature range between 50 °C and 500 °C.

CD spectroscopy: CD spectra of the three crystal powder samples were collected on an Applied Photophysics Chirascan Spectrometer with a bandwidth of 1.0 nm in the ultraviolet (UV) region (190-400 nm) using a 0.1 mm quartz cuvette. All scans were performed at a scan speed of 40 nm min⁻¹ with a data pitch of 0.5 nm at ambient temperature. The air was used as background and
subtracted. All spectra were obtained following blank background subtraction. The reported spectra represent the average of 3 scans.

**Single crystal X-ray diffraction (XRD).** All crystals were coated in Paratone Oil (Hampton Research) and mounted on MiTeGen cryo-loops before being flash frozen in the Liquid Nitrogen gasous stream from Oxford Cryostream. Diffraction data were collected on a Bruker KappaApexII diffractometer with Mo radiation (λ = 0.71073Å). Data were integrated and reduced with Bruker Apex2 Suite of programs. Structures were solved with Shelxt 2016/4 and refined to convergence with Shelxl 2016/4. See Supplementary Table 1. Data has been deposited in the CCDC.

**Powder X-ray diffraction (PXRD).** PXRD spectra of all the crystals (4,4’-Bpy, AcA, or 4,4’-Bpy/AcA) were recorded using a BRUKER d8 ADVANCE DIFFRACTOMETER equipped with Goebels mirrors to parallelize the beam and LYNXEYE-XE linear detector.

**Raman spectroscopy.** Raman spectra of the crystals (4,4’-Bpy, AcA, or 4,4’-Bpy/AcA) were collected using a spectrophotometer from Horiba Jobin Yvon LabRAM HR. The maximal power of the laser on the spot was 10 mW. The laser was a frequency doubled Nd:Yag with 532nm wavelength. Edge filter was used to cut the laser line. The detector was a Synapse CCD with thermoelectric cooling operating at -70 °C. The grating was 600 holes/mm (denoting the number of holes in the grating per millimeter).

**FTIR spectroscopy.** All the crystals (4,4’-Bpy, AcA, or 4,4’-Bpy/AcA) were deposited onto a real crystal KBr IR card (International Crystal Labs, Garfield, New Jersey, USA). The FTIR spectra of all samples were recorded on a Nicolet 6700 FTIR spectrometer (Thermo Scientific, Waltham, Massachusetts, USA), from 4000 to 400 cm⁻¹ at room temperature. The background signal was recorded using blank and subtracted to obtain each FTIR spectrum.

**Nuclear magnetic resonance (NMR).** The powder of single crystals and co-crystal (4,4’-Bpy, AcA, or 4,4’-Bpy/AcA) was dissolved in D₂O at the concentration of 5 mg/mL. ¹H NMR studies were carried out on a Bruker Advance 400 MHz spectrometer at 278 K. ¹H NMR chemical shifts are reported relative to Me₄Si and were referenced via residual proton resonances of the corresponding deuterated solvent (D₂O). Chemical shifts are given in ppm and the spectra are calibrated using the residual D₂O signals.
Computational analysis of HOMO-LUMO. Density functional theory (DFT) calculations were performed using the Gaussian 09 package. The typical dimers and trimers were extracted from the crystal structures of 4,4'-Bpy and 4,4'-Bpy/AcA. The frontier molecular orbitals of such dimers and trimers were calculated at the B3LYP/6-311++g(d,p) level based on the extracted geometries in gas phase.

Young’s modulus calculation. The elastic constants were calculated in the form of the stiffness tensor (C), presented as a 6 x 6 matrix:

\[
C = \begin{pmatrix}
  c_{11} & c_{12} & c_{13} & c_{14} & c_{15} & c_{16} \\
  c_{21} & c_{22} & c_{23} & c_{24} & c_{25} & c_{26} \\
  c_{31} & c_{32} & c_{33} & c_{34} & c_{35} & c_{36} \\
  c_{41} & c_{42} & c_{43} & c_{44} & c_{45} & c_{46} \\
  c_{51} & c_{52} & c_{53} & c_{54} & c_{55} & c_{56} \\
  c_{61} & c_{62} & c_{63} & c_{64} & c_{65} & c_{66}
\end{pmatrix}
\]

Young’s moduli were derived from the stiffness and compliance matrix components, the compliance matrix being the inverse of the stiffness matrix calculated by vienna ab initio simulation package (VASP). Values are presented as an average of three calculation methods: the orthorhombic and triclinic approximations of Nye, and the Voigt-Reuss-Hill method. All three methods gave a reasonable match with known experimental values for organic and inorganic crystals, so an arithmetic mean of the three analysis methods was used to estimate any previously unknown Young’s moduli.

Optical waveguiding. To evaluate the potential of the 4,4'-Bpy crystals as active waveguide materials, rhodamine 6G (Rh6G) was used as a probe. Rh6G (1 mg/mL) in double distilled water was incubated with 4,4'-Bpy needles for overnight, leading to the spontaneous accommodation of the dye within the needles. The crystals were then cleaned with double distilled water three times to remove residual Rh6G. The optical waveguide image was obtained using an Olympus FV1000 microscope with a CCD camera or a Leica DM IRBE microscope equipped with a digital camera. A laser with an excitation source of 488 nm was employed for the measurement. A schematic diagram of the experimental setup for the 4,4'-Bpy crystal waveguide characterization is shown in Figure S19.

Piezoelectricity prediction. Calculations are performed using periodic DFT with the VASP code. Electronic structures were calculated using the PBE functional, projector augmented
wave (PAW) pseudopotentials\textsuperscript{11} with a plane wave cut-off of 600 eV, and k-point sampling of 4x4x4. A finite differences method was used to calculate the stiffness tensor, with each atom being displaced in each direction by ± 0.01 Å (plane wave cut-off of 600 eV, and k-point sampling of 2x2x2). Piezoelectric strain constants and dielectric tensors were calculated using Density Functional Perturbation Theory\textsuperscript{12} (DFPT) (plane wave cut-off of 600 eV, and k-point sampling of 2x2x2). It is important to note that negative piezoelectric constants can appear counterintuitive but are becoming more accepted\textsuperscript{13-16}. They can be seen in classical piezoelectric materials like AlN\textsuperscript{17} and quartz\textsuperscript{18}. Negative $e_{ij}$ values have been investigated in detail by Liu and Cohen\textsuperscript{19} using DFT methods similar to those presented here. Assuming positive elastic stiffness constants, these materials will also demonstrate negative $d_{ij}$ (and $g_{ij}$) constants, as can be observed in the widely used piezoelectric polymer PVDF and its counterparts. We emphasize the absolute magnitudes of the predicted $d_{ij}$ and $g_{ij}$ values since negative signs indicate the polarity of the piezoelectric surface charge generated under either stretching or compression and are arbitrary for energy harvesting applications\textsuperscript{20-23}.

**Computational calculations of band structures and density of states.** Similar to the piezoelectricity calculations above, electronic structures were solved based on the Kohn-Sham theory and the projector augmented wave (PAW) pseudopotentials as implemented in the VASP package. The \textit{ab initio} DFT package (VASP) with the generalized gradient approximation (GGA) of Perdew-Burke-Emnzerhof (PBE) was used to perform the first-principles calculations. The kinetic cutoff energy was set to 200 eV. Gamma-centered k-point meshes of 5×5×5 was used to sample the Brillouin zone of the 4,4’-Bpy, AcA and 4,4’-Bpy/AcA crystals.

**Conductivity measurement.** Crystals were fixed on a SiO$_2$ substrate. Tungsten needle electrodes were gently moved to contact the ends of the crystals using a three-dimensional displacement table under an optical microscope. Lights at different wavelengths (bandwidth: 5 nm) was then applied directly to the samples as shown in Figure S25. Voltage (10 V) was then applied to the samples with a digital power (N6705B, Agilent, US) and the resistances were recorded (sample rate: 1 Hz).
Figure S1. Dipole stacking modes in the solid state, including face-to-face stacking (H-aggregate), staggered stacking (J-aggregate), and crossed stacking (X-aggregate).

Figure S2. SEM image of AcA crystals.
Figure S3. Images of the 4,4’-Bpy, AcA, and 4,4’-Bpy/AcA crystals in bright field (left) and in different fluorescence channels, as indicated.

Figure S4. UV-Vis absorption of 4,4’-Bpy, AcA, and 4,4’-Bpy/AcA in water (1 mM).
Figure S5. DSC and TGA spectra of the AcA crystal.

Table S1. Peak assignments of powder XRD patterns.

| 4,4'-Bpy | AcA  | 4,4'-Bpy/AcA |
|----------|------|---------------|
| 2θ (°)   | d (Å) | 2θ (°)        | d (Å) | 2θ (°) | d (Å) |
| 10.47    | 8.4  | 11.54         | 7.7   | 12.07  | 7.3   |
| 12.41    | 7.1  | 15.56         | 5.7   | 14.15  | 6.3   |
| 19.00    | 4.7  | 17.55         | 5.1   | 17.55  | 5.1   |
| 19.54    | 4.5  | 23.08         | 3.9   | 20.75  | 4.3   |
| 21.04    | 4.2  | 24.48         | 3.6   | 22.35  | 4.0   |
| 22.30    | 4.0  | 26.96         | 3.3   | 24.24  | 3.7   |
| 24.97    | 3.6  | 27.88         | 3.2   | 24.63  | 3.6   |
|     |     |     |     |     |     |
|-----|-----|-----|-----|-----|-----|
| 25.45 | 3.5 | 29.14 | 3.1 | 25.45 | 3.5 |
| 28.99 | 3.1 | 30.69 | 2.9 | 26.91 | 3.3 |
| 30.50 | 2.9 | 31.27 | 2.9 | 28.26 | 3.2 |
| 31.27 | 2.9 | 34.71 | 2.6 | 29.29 | 3.0 |
| 31.86 | 2.8 |       |     | 29.82 | 3.0 |
| 34.08 | 2.6 |       |     | 31.37 | 2.9 |
| 34.33 | 2.6 |       |     | 32.19 | 2.8 |
Figure S6. Raman spectroscopy measurements using a laser to detect the signal of crystal surface.
(a) 4,4’-Bpy. (b) AcA. (c) 4,4’-Bpy/AcA.

Figure S7. FTIR spectra of the 4,4’-Bpy, AcA and 4,4’-Bpy/AcA crystals.
Figure S8. Positions of the hydrogen atoms in the chemical structures of 4,4'-Bpy and AcA for NMR spectra analysis.

Figure S9. ORTEP diagram of 4,4'-Bpy with the thermal ellipsoids set at 50% probability.
Figure S10. (a) Water-mediated single molecular chain formation in the crystal packing of 4,4′-Bpy. (b) Parallel stacking of chains led to fabrication of a single sheet.

Figure S11. Comparison of experimental PXRD of AcA crystals solved in this work with previously published simulated crystal structures\textsuperscript{24}.
Figure S12. (a) ORTEP diagram of AcA with the thermal ellipsoids set at 50% probability. (b) H-bonding connections producing a supramolecular helical packing in the crystallographic $a$-direction.

Figure S13. ORTEP diagram of the 4,4$'$-Bpy/AcA co-crystal with the thermal ellipsoids set at 50% probability.
Figure S14. (a) Single molecular chain formation in the co-crystal of 4,4’-Bpy/AcA. (b-c) Two different types of interactions between the chains - stacking *via* 2₁-screw operation and crisscross arrangement.

Figure S15. Layer-by-layer arrangement in the higher order packing of the 4,4’-Bpy/AcA crystal viewed from two different crystallographic axes.
Table S2: Data collection and refinement statistics

Experimental details:

| Crystal data | 4,4'-Bpy | 4,4'-Bpy/AcA |
|--------------|----------|--------------|
| Chemical formula | C10 H8 N2, 2(H2 O) | C10 H8 N2, 2(C5 H9 N O3) |
| *Mr*         | 96.11    | 418.45       |
| Crystal system | Monoclinic | Orthorhombic |
| Space group  | *P*2₁    | *C* 2 2 2    |
| *a* (Å)      | 9.128(6)  | 12.216(2)    |
| *b* (Å)      | 7.415(7)  | 14.294(2)    |
| *c* (Å)      | 14.724(10)| 11.882(2)    |
| *α* (°)      | 90        | 90           |
| *β* (°)      | 100.94(1) | 90           |
| *γ* (°)      | 90        | 90           |
| *V* (Å³)     | 978.5(13) | 2074.8(6)    |
| *Z*, *Z'*    | 8         | 4            |
| *μ* (mm⁻¹)   | 0.093     | 0.100        |
| Temperature (K) | 100 (2)  | 100 (2)      |

Data collection

| Diffractometer | Bruker KappaApexII CCD | Bruker KappaApexII CCD |
|----------------|------------------------|------------------------|
| Wavelength λ= (Å) | 0.71073                | 0.71073                |
| Crystal size (mm)  | 0.24/0.1/0.1           | 0.20/0.02/0.02         |
| Absorption correction | multi-scan | multi-scan |
|-----------------------|------------|------------|
| $T_{\text{min}}, T_{\text{max}}$ | 0.989, 0.991 | 0.998, 0.998 |
| $N_{\text{measured}}$ | 17382 | 14477 |
| $R_{\text{int}}$ | 0.0310 | 0.1100 |
| $\theta_{\text{max}}$ (°) | 30.529 | 27.155 |

**Refinement**

| $R(F^2 > 2\sigma(F^2))$ | 0.0341 | 0.0573 |
| $wR(F^2)$ | 0.1077 | 0.1145 |
| Goodness-of-fit | 0.992 | 1.087 |
| No. of reflections | 5951 | 2314 |
| No. of parameters | 283 | 139 |
| No. of restraints | 1 | 0 |
| H-atom treatment | H-atom parameters mixed | H-atom parameters constr |
Table S3. Calculated energy of HOMO, LUMO and HOMO-LUMO gap of H-, J-, X-dimers and H-, JX-trimers in the 4,4’-Bpy and 4,4’-Bpy/AcA crystals.

|                | HOMO (eV) | LUMO (eV) | HOMO-LUMO gap (eV) |
|----------------|-----------|-----------|-------------------|
| H-dimer        | -7.30     | -2.10     | 5.19              |
| X-dimer        | -7.35     | -2.37     | 4.98              |
| J-dimer        | -7.30     | -2.13     | 5.17              |
| H-trimer       | -7.20     | -2.15     | 5.05              |
| JX-trimer      | -7.29     | -2.32     | 4.96              |

Figure S16. Energy diagram of HUMO-LUMO of H-, J-, X-dimers and H-, JX-trimers in the 4,4’-Bpy and 4,4’-Bpy/AcA crystals.
Figure S17 Schematic diagram of AFM indentation on crystal samples. Crystals were placed on a quartzite coverslip and the cantilever tip was reversely pushed into the crystal sample surface and retracted to obtain the force-distance trace on each spot, allowing to calculate the modulus using the Hertz model.

Figure S18. Typical force-distance traces of (a) 4,4’-Bpy, (b) AcA and (c) 4,4’-Bpy/AcA crystals. The blue line represents extension and the grey line represents retraction.
Figure S19. AFM indentation experiments of (a) 4,4′-Bpy, (b) AcA and (c) 4,4′-Bpy/AcA. Crystals were fixed to the surface of the quartz substrates and the cantilever was moved onto crystal surface with a positioning system and the help of an optical microscope. Scale bar is 50 μm.

Table S4. Calculated and experimental Young’s modulus of 4,4′-Bpy, AcA, and 4,4′-Bpy/AcA crystals.

| Crystal name | 4,4′-Bpy | AcA  | 4,4′-Bpy/AcA |
|--------------|----------|------|--------------|
| Calculated Young’s modulus (GPa) | 4.2      | 8.5  | 26.4         |
| Experimental Young’s modulus (GPa) | 4.31 ± 1.84 | 10.70 ± 1.07 | 23.76 ± 3.26 |

Figure S20. AFM images of point stiffness distributions of (a) 4,4′-Bpy, (b) AcA, and (c) 4,4′-Bpy/AcA. Scale bar is 2μm.
Figure S21. SEM image and fluorescence image of 4,4’-Bpy and 4,4’-Bpy/AcA crystals.

Figure S22. Schematic diagram of the experimental setup for the optical waveguiding measurement of 4,4’-Bpy crystal.
Figure S23. (a) 4,4’-Bpy unit cell with water molecules, showing full molecules including periodic image atoms for clarity. (b) AcA unit cell, showing the hydrogen bonds between molecules (blue lines). (c) View down the y-z plane of the 4,4’-Bpy/Ac-A co-crystal, showing the layered structure. AcA molecules link at the edges of the unit cell, with the 4,4’-Bpy molecules lying perpendicular to the plane (into the page). The molecular orientation in the pores increases the longitudinal and shear stiffness constants perpendicular to this plane ($c_{11}$ and $c_{44}$). The elongated pores also provide resistance to shear forces parallel to the plane, as shown by a predicted increase in $c_{55}$. (d) View down the y-x plane of the 4,4’-Bpy/AcA co-crystal, showing the highly ordered layers formed by the constituent molecules. The maximum piezoelectric polarization is perpendicular to the plane (into the page), orientated parallel to the elongated pore formed by the interconnection of the 4,4’-Bpy and AcA molecules.
Table S5. Computed relative permittivity and dielectric constants of 4,4'-Bpy, Ac-A, and 4,4'-Bpy/Ac-A single crystals. All values are unitless.

| Dielectric Constant | 4,4’-Bpy | Ac-A  | 4,4’-Bpy /Ac-A |
|---------------------|----------|-------|-----------------|
| $\varepsilon_1$     | 3.39     | 3.57  | 4.84            |
| $\varepsilon_2$     | 2.01     | 2.11  | 2.05            |
| $\varepsilon_3$     | 2.99     | 2.25  | 2.52            |
| $\varepsilon_r$     | 2.80     | 2.64  | 3.13            |
Table S6. Computed elastic constants of 4,4'-Bpy, AcA, and 4,4'-Bpy/AcA single crystals. All values are in GPa. $c_{11}$, $c_{22}$, and $c_{33}$ are the longitudinal stiffness constants, and the shear stiffness constants are $c_{44}$, $c_{55}$ and $c_{66}$.

| Elastic Stiffness Constant | 4,4'-Bpy | Ac-A  | 4,4'-Bpy/Ac-A |
|----------------------------|----------|-------|---------------|
| $c_{11}$                   | 13.9     | 8.6   | 19.3          |
| $c_{22}$                   | 4.7      | 10.0  | 3.9           |
| $c_{33}$                   | 36.1     | 18.6  | 20.4          |
| $c_{44}$                   | 0.9      | 2.3   | -2.1          |
| $c_{55}$                   | 5.1      | 5.1   | 8.6           |
| $c_{66}$                   | 0.9      | 5.1   | -1.7          |
Table S7. Calculated piezoelectric charge tensor components $e_{ij}$ (in units of C/m$^2$), strain tensor components $d_{ik}$ (pm/V), and voltage tensor components $g_{ij}$ (mV m/N) of the 4,4$^{\prime}$-Bpy single crystal.

| Charge Tensor (C/m$^2$) |
|-------------------------|
| (0 0 0 0.013 0 -0.014) |
| (-0.032 -0.006 0.018 0 0.019 0) |
| (0 0 0 0.006 0 -0.003) |

| Strain Tensor (pm/V) |
|----------------------|
| (0 0 0 2.5 0 -16.2) |
| (-2.3 -1.3 0.5 20.9 0) |
| (0 0 0 6.8 0 -3.4) |

| Voltage Tensor (mV m/N) |
|-------------------------|
| (0 0 0 59 0 -379) |
| (-127 -71 27 0 1151 0) |
| (0 0 0 306 0 -154) |
Table S8. Calculated piezoelectric charge tensor components $e_{ij}$ (in units of C/m$^2$), strain tensor components $d_{ik}$ (pm/V), and voltage tensor components $g_{ij}$ (mV m/N) of the AcA single crystal.

| Charge Tensor (C/m$^2$) |
|-----------------|
| 0 0 0 -0.014 0 0 |
| 0 0 0 0 -0.012 0 |
| 0 0 0 0 0 0.022 |

| Strain Tensor (pm/V) |
|----------------|
| 0 0 0 -2.8 0 0 |
| 0 0 0 0 -2.5 0 |
| 0 0 0 0 0 9.5 |

| Voltage Tensor (mV m/N) |
|-----------------|
| 0 0 0 -88 0 0 |
| 0 0 0 0 -132 0 |
| 0 0 0 0 0 477 |
Table S9. Calculated charge tensor components $e_{ij}$ (C/m$^2$), strain tensor components $d_{ik}$ (pm/V), and voltage tensor components $g_{ij}$ (mV m/N), of the 4,4’-Bpy/AcA co-crystal.

| Charge Tensor (C/m$^2$) |
|-------------------------|
| $0$  $0$  $0$  $-0.010$  $0$  $0$  |
| $0$  $0$  $0$  $0$  $-0.012$  $0$  |
| $0$  $0$  $0$  $0$  $0$  $0.025$  |

| Strain Tensor (pm/V) |
|----------------------|
| $0$  $0$  $0$  $5.0$  $0$  $0$  |
| $0$  $0$  $0$  $0$  $-1.4$  $0$  |
| $0$  $0$  $0$  $0$  $0$  $-14.9$  |

| Voltage Tensor (mV m/N) |
|-------------------------|
| $0$  $0$  $0$  $116$  $0$  $0$  |
| $0$  $0$  $0$  $0$  $-79$  $0$  |
| $0$  $0$  $0$  $0$  $0$  $-670$  |
Table S10. The piezoelectric coefficients of different biological and non-biological materials, as well as the 4,4’-Bpy, AcA, and 4,4’-Bpy/AcA crystals.

| Material type           | Material name                  | Piezoelectric coefficient (pC/N) | Reference |
|-------------------------|--------------------------------|---------------------------------|-----------|
| Organic crystals        | 4,4’-Bpy                       | 20.9                            | This work |
|                         | AcA                            | 9.5                             | This work |
|                         | 4,4’-Bpy/AcA                   | 14.9                            | This work |
| Biological materials    | Bone                           | 6                               | 25        |
|                         | Virus                          | 8                               | 26        |
|                         | Fibrillar rat tail collagen    | 12                              | 27        |
|                         | Tyrosine                       | 9.7                             | 28        |
| Non-biological materials| Aluminium nitride             | 5                               | 29        |
|                         | Zinc oxide                     | 12                              | 30        |
|                         | Cadmium sulphide               | 12                              | 31        |
|                         | PVDF                           | 22                              | 32        |
Figure S24. The photograph of the generators for studying the piezoelectric property of 4,4’-Bpy and 4,4’-Bpy/AcA crystals.

Figure S25. Open-circuit voltage of (a) 4,4’-Bpy and (b) 4,4’-Bpy/AcA crystals obtained from the generator in reverse setups by applying a force of 56 N. (i) Linear fitting of the open-circuit voltage of 4,4’-Bpy and 4,4’-Bpy/AcA crystals as a function of the applied force from 4 N to 56 N in reverse setups.
Figure S26. (a-b) First Brillouin zone of primitive unit cell of (a) 4,4’-Bpy and (b) AcA single crystal. The high-symmetry lines and points are given as well. (c-d) Band structures and density of states of (c) 4,4’-Bpy and (d) AcA single crystal. The horizontal dashed line denotes the Fermi level.
Figure S27. Schematic representation of the electronic band structure near the Fermi level for (a) direct and (b) indirect band gap material.

Figure S28. Orbital charge densities of CBM and VBM bands of the 4,4’-Bpy/AcA co-crystal viewed in different directions.
Figure S29. Orbital charge densities of CBM and VBM bands of the 4,4’-Bpy single crystal viewed in different directions.

Figure S30. Orbital charge densities of CBM and VBM bands of the AcA single crystal viewed in different directions.
Figure S31. Schematic diagram of conductive experiments under light irradiation on crystal samples.

Figure S32. Statistical distribution of conductivity characterization of the 4,4’-Bpy single crystal in the dark and under light irradiation at (a) 365 nm, (b) 405 nm, (c) 460 nm, (d) 500 nm, (e) 595 nm, (f) 700 nm. (g) Resistance of the 4,4’-Bpy single crystal in the dark and under light irradiation at different wavelengths, as indicated.
Figure S33. Statistical distribution of conductivity characterization of the AcA single crystal in the dark and under light irradiation at (a) 365 nm, (b) 405 nm, (c) 460 nm, (d) 500 nm, (e) 595 nm, (f) 700 nm. (g) Resistance of the AcA single crystal in the dark and under light irradiation at different wavelengths, as indicated.
Figure S34. Statistical distribution of conductivity characterization of the 4,4’-Bpy/AcA co-crystal under light irradiation at (a) 365 nm, (b) 405 nm, (c) 460 nm, (d) 500 nm, (e) 595 nm, (f) 700 nm. (g) Resistance of the 4,4’-Bpy/AcA co-crystal in the dark and under light irradiation at different wavelengths, as indicated.
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