Supporting Information

Luminescent switching behavior achieved by adjusting cocrystal charge transfer excitons under acid stimulation.

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Cocrystal growth and Preperation:

The 3-Aminopyridine as donor and tetracyanobenzene as acceptor were used to make organic cocrystal by solvent evaporation method. Additionally, we mixed donor (3-AP, 2.82 mg/0.03 mmol) and acceptor (TCNB, 5.34 mg/0.03 mmol) with a stoichiometric ratio of donor, accepter was 1:1 and gradually dissolved them in 5 ml dichloromethane (DCM). Specifically, the solvent evaporation method usually dissolves a certain proportion of the reaction mixture solution in a bottle, then stores it in a dark environment and at room temperature, the solute gradually reaches a saturated state in the solution, and forms cocrystal nuclei driven by intermolecular interactions, and gradually precipitates out after a few days. This method usually requires donor and acceptor molecules to have similar solubility in the same solvent and is highly dependent on factors such as solvent, concentration, temperature, and other external conditions.

However, for the crystal structure analyses and more characterization, we used powder X-ray diffraction (PXRD) and optical microscope (OM). For the studies and determination of photophysical chemical properties, we used solid-state samples of the 3-ATC cocrystal with different instrument measurements such as UV-vis, photoluminescence (PL), thermal gravimetric analysis (TGA), differential scanning calorimetry (DSC) and Fourier-transform infrared (FTIR).

Table S1 The single-crystal data of 3-ATC cocrystal.

Chemical formula	$C_{15}H_8N_6$
CCDC	2347457
Formation weight	272.27
Temperature /K	160K
Wavelength	1.54184
Space group	C2/c
Crystal system	Monoclinic
a/Å	7.2422(1)
b/Å	15.4771(1)
c/Å	11.6557(1)
α/°	90
β/°	92.677(1)
γ/°	90
Volume/ Å3	1305.04(2)
Z	4
DX, g/cm^3	1.386
μ /mm−1	0.733
F(000)	560.0
R_{int}	0.03
Goof	1.115
Final R indexes [I>=2σ (I)]	wR_1 = 0.0291, wR_2 = 0.0824

According to the area ratio of crystal planes, (101), (110), (120),(012),(212), and (21-2),(1-21) may be dominant in the formation of bulk crystal. 3-ATC displays different peaks from the constitute components by analyzing the powder X-ray diffractometer (PXRD) pattern. the

measured PXRD result of 3-ATC is consistent with the data calculated through the CIF file. The distances of –N···HC– between adjacent column D–A molecules are 3.12 Å and 3.21Å, and that of A–A molecules is 3.33 Å.

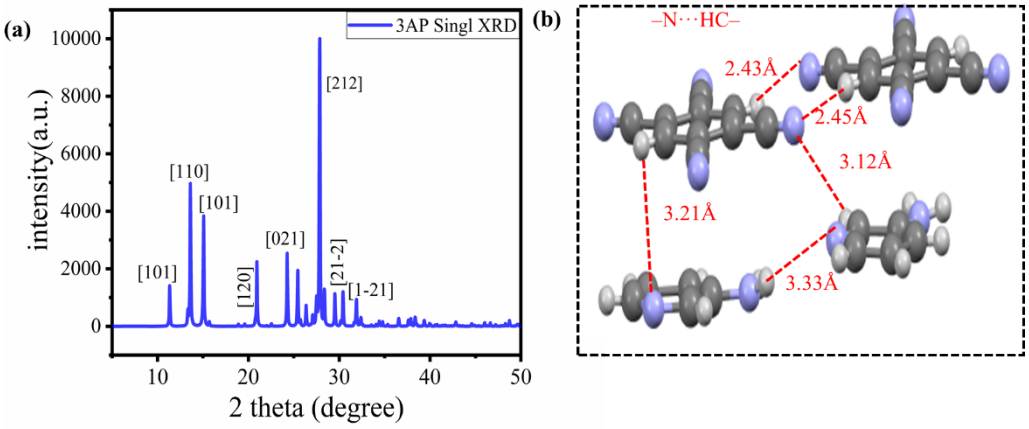

Fig. S1. a) Crystalline nature and lattice parameters, and b) packing structures of 3-ATC.

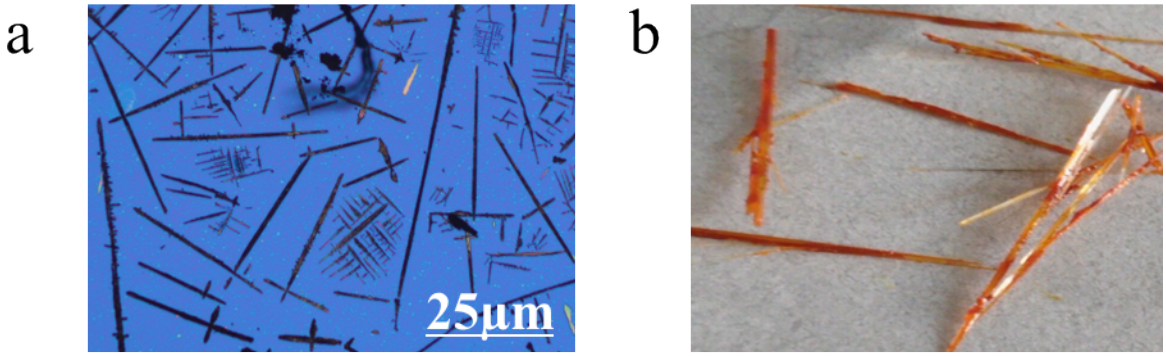

Fig. S2. a) The OM image, b) The picture of 3-ATC.

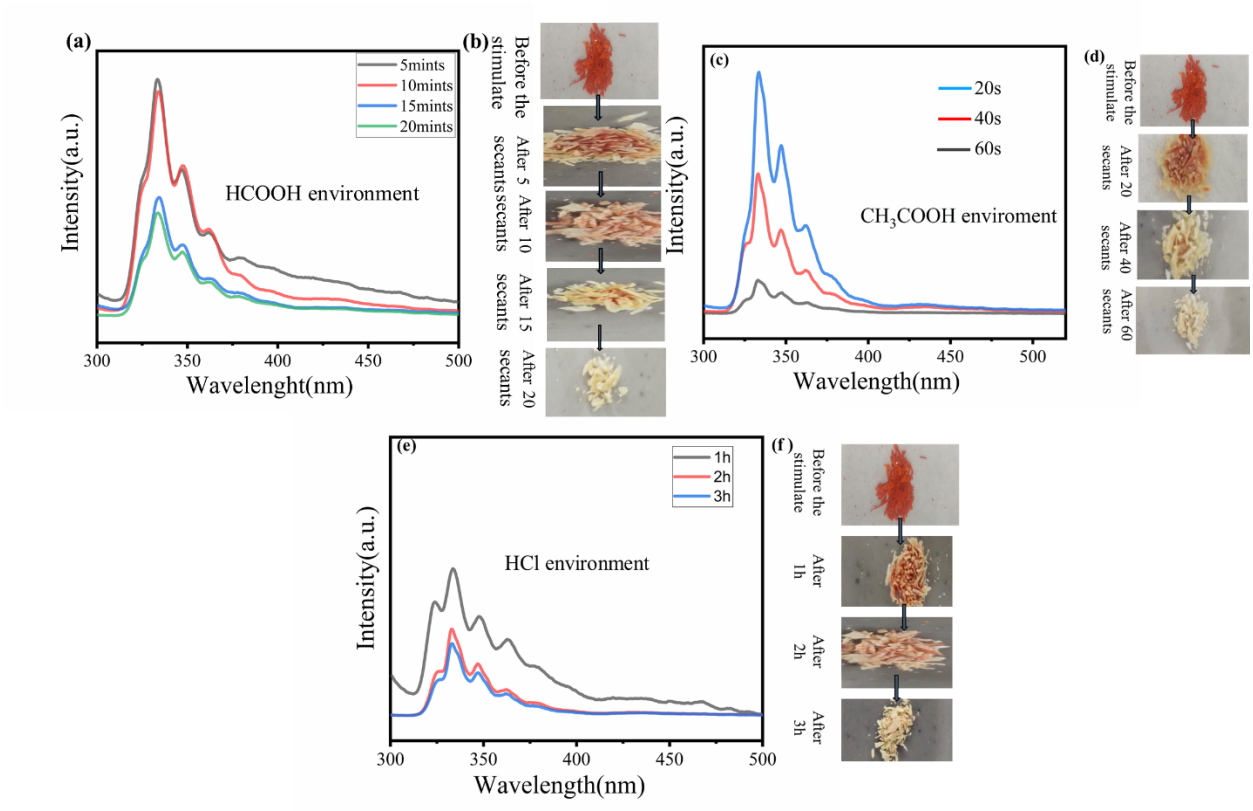

Fig. S3. a-b) Intensities of fluorescence and color change in formic acid environment,c-d) in acetic acid environment, e-f) and in hydrochloric acid environment.