Electronic Supplementary Information (ESI) for:

Organic polarized photonic heterostructure based on tetra(4-pyridylphenyl)ethylene

Li Meng,[a,b] Zhong-Qiu Li,[b] Jiang-Yang Shao,[b] Zili Chen,*[a] Yu-Wu Zhong *[b,c]

[a]*School of Chemistry and Life Resources, Renmin University of China, 59# Zhongguancun Street, Haidian District, Beijing 100872, China. Email: zilichen@ruc.edu.cn (Z.C.)*

[b]*Beijing National Laboratory for Molecular Sciences, CAS Key Laboratory of Photochemistry, CAS Research/Education Center for Excellence in Molecular Sciences, Institute of Chemistry, Chinese Academy of Sciences, 2 Bei Yi Jie, Zhong Guan Cun, Haidian District, Beijing 100190, China. Email: zhongyuwu@iccas.ac.cn (Y.-W.Z.)*

[c]*School of Chemical Sciences, University of Chinese Academy of Sciences, No.19(A) Yuquan Road, Shijingshan District, Beijing 100049, China.*

Instrumental information for physical measurements

The UV-vis absorption spectra were recorded at rt on the TU-1810DSPC spectrometer from Beijing Purkinje General Instrument Co., Ltd. The photoluminescence spectra were obtained at rt with the F-380 spectrofluorimeter from Tianjin Gangdong Sci. & Tech. Development Co., Ltd. The absolute fluorescence quantum yields were determined using the Hamamatsu Absolute PL Quantum Yield Spectrometer C11347 with the aid of an integrating sphere. Hamamatsu C11367-11 instrument with single photon counting were employed to obtain the excited-state lifetimes. The morphologies of microstructures were investigated by SEM on the Hitachi SU8010 instrument at 10 kV. Rigaku Saturn 724 diffractometer was used to perform the single-crystal X-ray analysis at 173 K on a rotating anode (Cu Kα; λ = 1.54184 Å). The structures were solved with SHELXS-97 and refined on Olex2. The powder X-ray diffractions (PXRD) were carried out on the Rigaku D/max-2500 instrument (Cu Kα; λ = 1.54 Å). Fluorescence microscopy characterization was performed on the Olympus IX83 Inverted fluorescence microscope by the UV irradiation at 330-385 nm.

Calculation method on transition dipole moment

The electronic structures of TPPE were first optimized with the Gaussian 09 program package by density functional theory (DFT) calculations with B3LYP/6-31G*. Time-dependent density functional theory (TDDFT) calculations were further performed to get the excited-state information. The obtained fchk files were analysed by the Multiwfn multifunctional wavefunction analyer to obtain the dipole moment information.[1]

General information. Compounds TPPE is prepared according to literature studies.[2]

Preparation of yellow-blue-yellow triblock heterojunction. The middle part of the rod-like crystals of TPPE (50-100 μm in length) was firstly covered with the

commercial glue. After about 5 min at rt, the glue became solidified. The crystal was then exposed to the HCl vapor for 1 min. During this process, the uncovered segments of the crystal turn yellow-emissive, while the covered segments remain blue-emissive, leading to the yellow-blue-yellow triblock heterostructure.

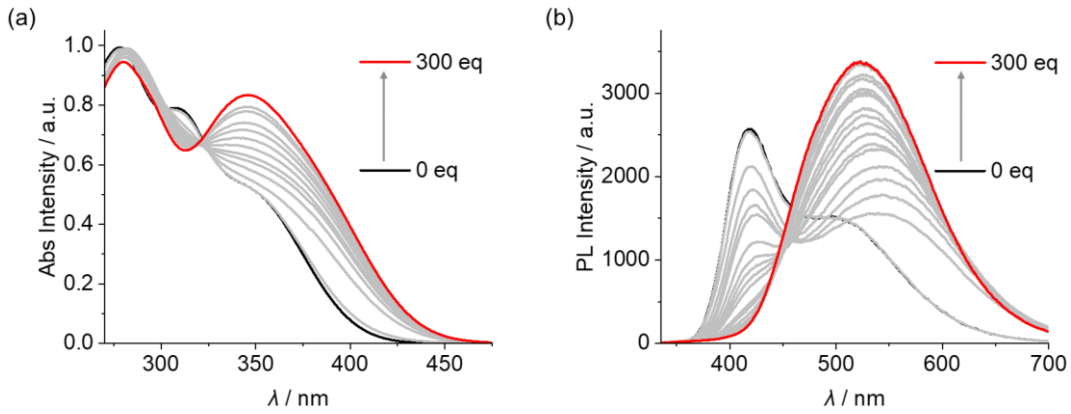

Fig. S1 (a) Absorption and (b) photoluminescence (PL) spectral changes of TPPE upon the treatment of HCl in DMF (1×10^{-5} M).

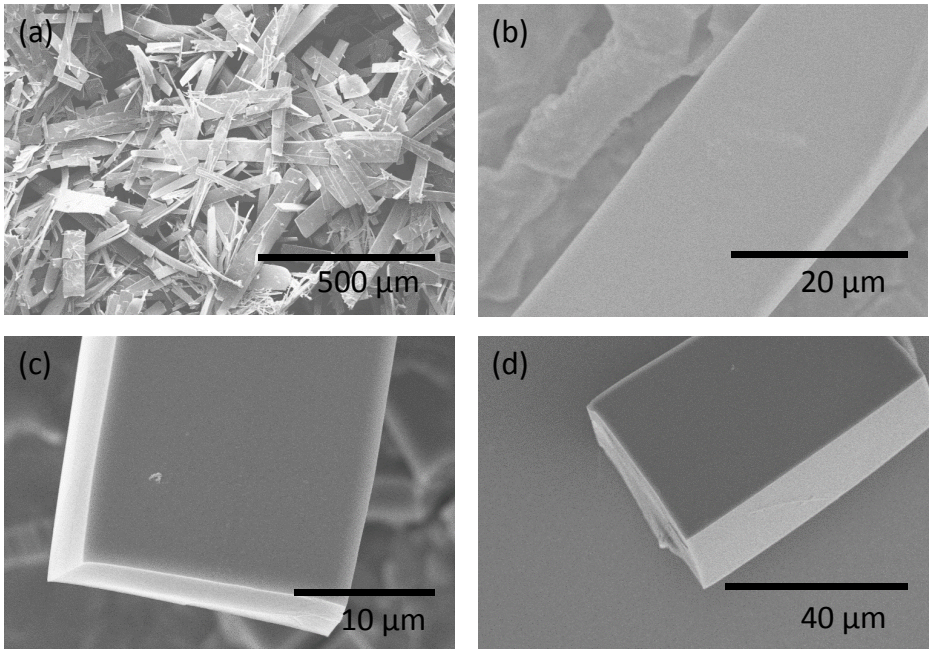

Fig. S2 Scanning electron microscopy (SEM) images of the blue-emissive crystals of TPPE.

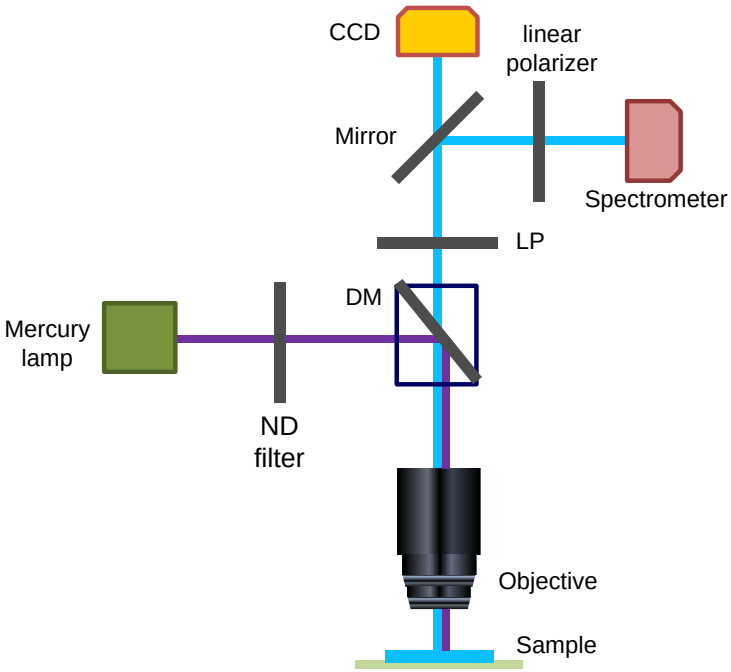

Fig. S3 The home-made setup for the LPL measurement.[3] The crystals were excited by the mercury lamp altered by a neutral density (ND) filter. The photoluminescence signal was collected by the microscope objective (Olympus M Plan, × 20, N.A. =0.4), passed through the dichroic mirror (DM). By rotating the linear polarizer in front of the detector, the polarization of the light signal can be obtained and recorded with a thermoelectric-cooled PIXIS 256BR CCD and analyzed by the Prinston Instrument HRS-300S spectrometer on the photoexcited plane exposed on the substrate.

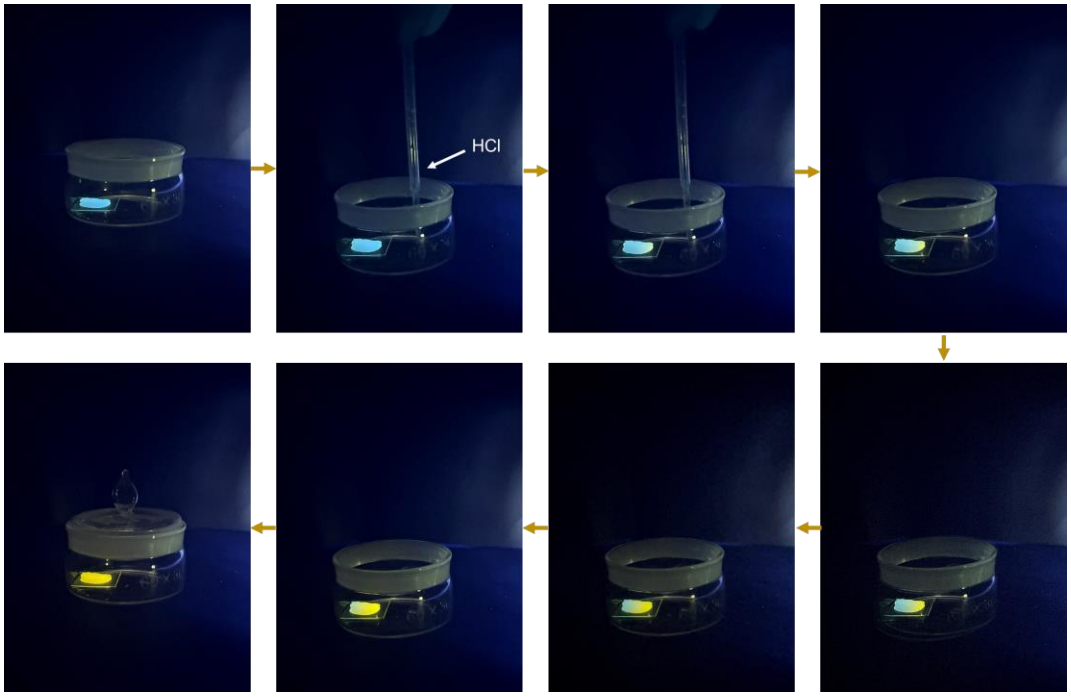

Fig. S4 The protonation procedure of TPPE to give TPPE-H.

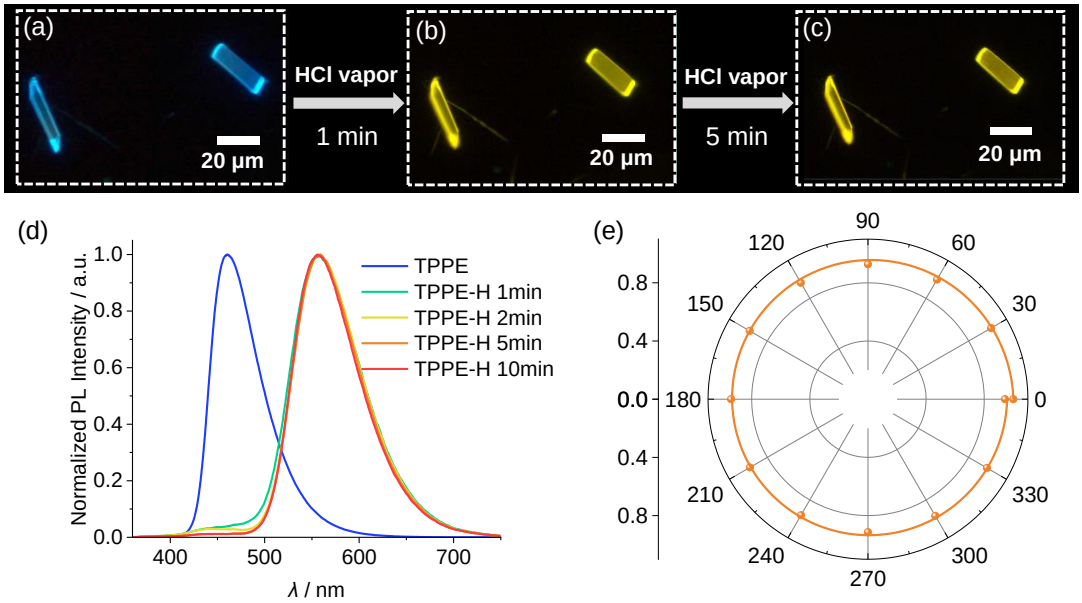

Fig. S5 (a-c) Fluorescence microscopy changes of TPPE microcrystals upon the treatment with HCl vapor. (d) PL spectra of microcrystals of TPPE and TPPE-H (obtained after treatment with HCl vapor for 1, 2, 5, 10 min). (e) Relevant photoluminescence polarization profile of TPPE-H (5 min).

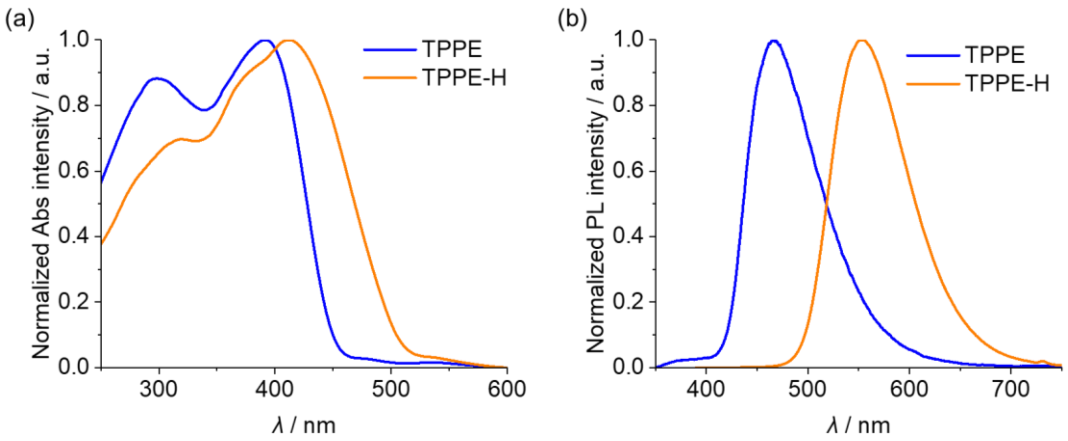

Fig. S6 (a) Absorption and (b) photoluminescence (PL) spectra of the microcrystals of TPPE and TPPE-H.

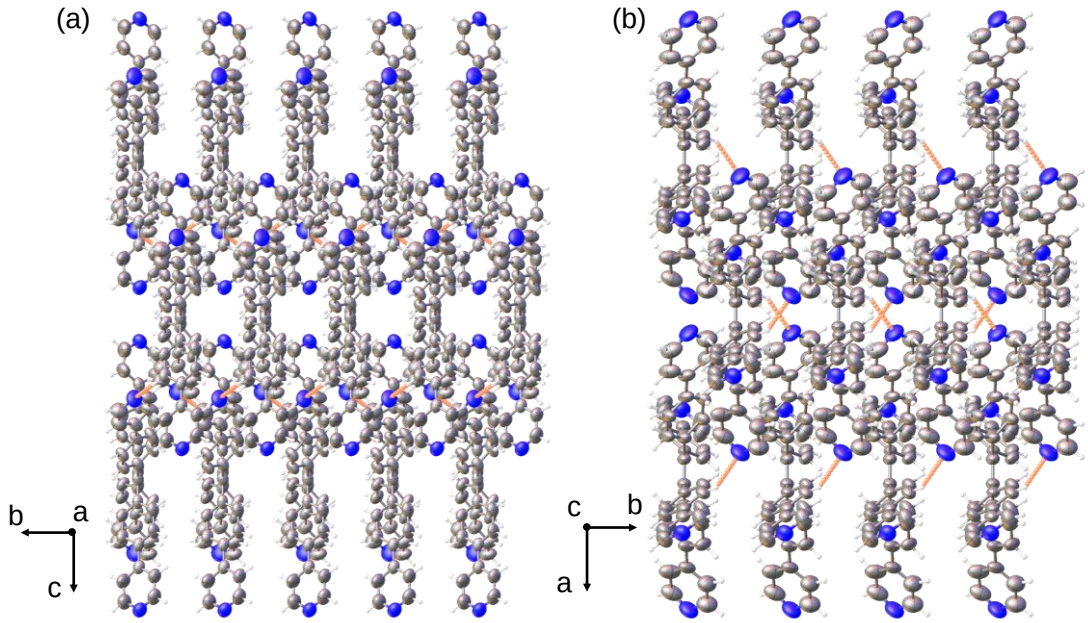

Fig. S7 Single-crystal molecular packing structure of TPPE crystal viewed from (a) crystallographic *a* axis and (b) from *c* axis, respectively. The orange lines indicate the hydrogen bondings with a N···H distance of 2.455 Å.

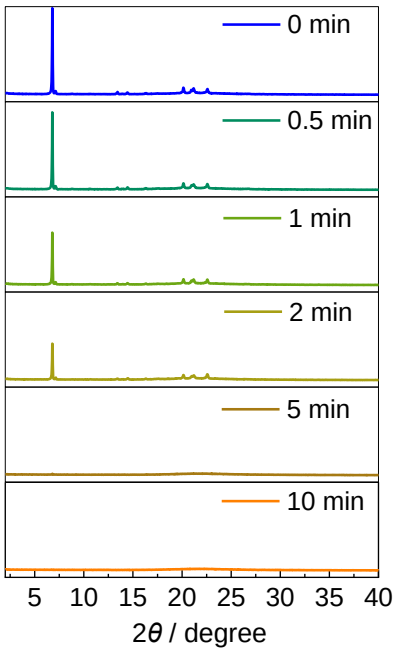

Fig. S8 In-situ PXRD spectral changes of the TPPE microcrystals (0 min) upon treating with HCl gas for 0.5 min, 1 min, 2 min, 5 min, and 10 min, respectively.

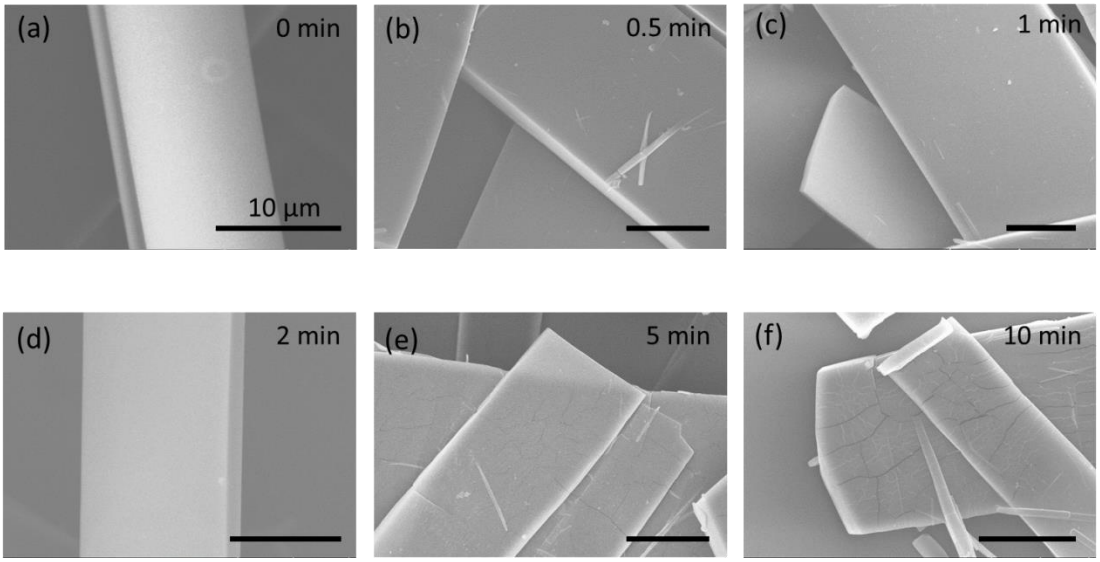

Fig. S9 SEM images of (a) TPPE microcrystals and (b-f) TPPE-H crystals obtained from TPPE crystals after treating with HCl gas for 0.5 min, 1 min, 2 min, 5 min, and 10 min, respectively.

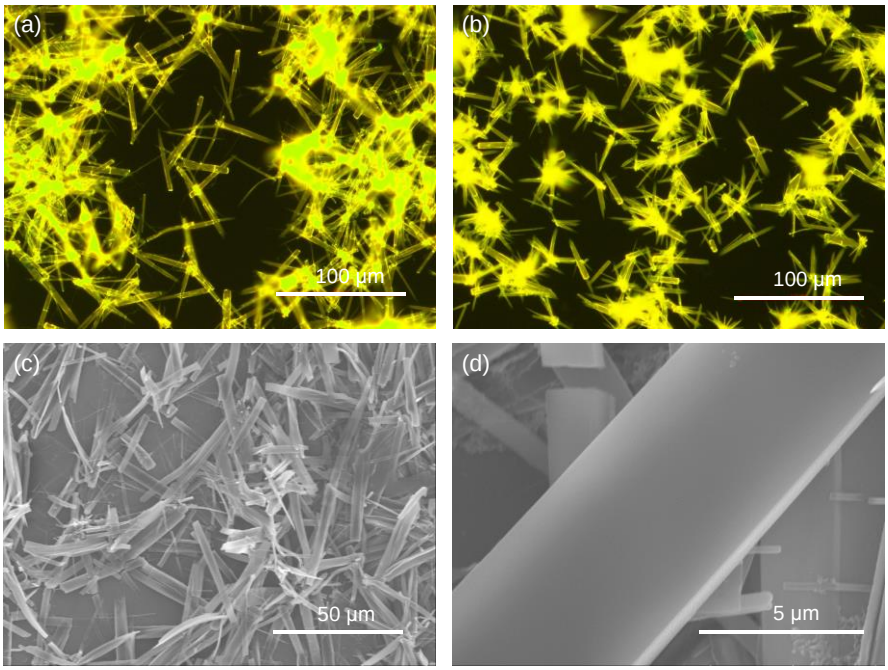

Fig. S10 (a,b) Fluorescence microscopy images of TPPE-H microcrystals after (a) vacuum treatment for 24 h or (b) keeping at room temperature for 7 days. (c,d) SEM images of TPPE-H microcrystals after vacuum treatment for 24 h.

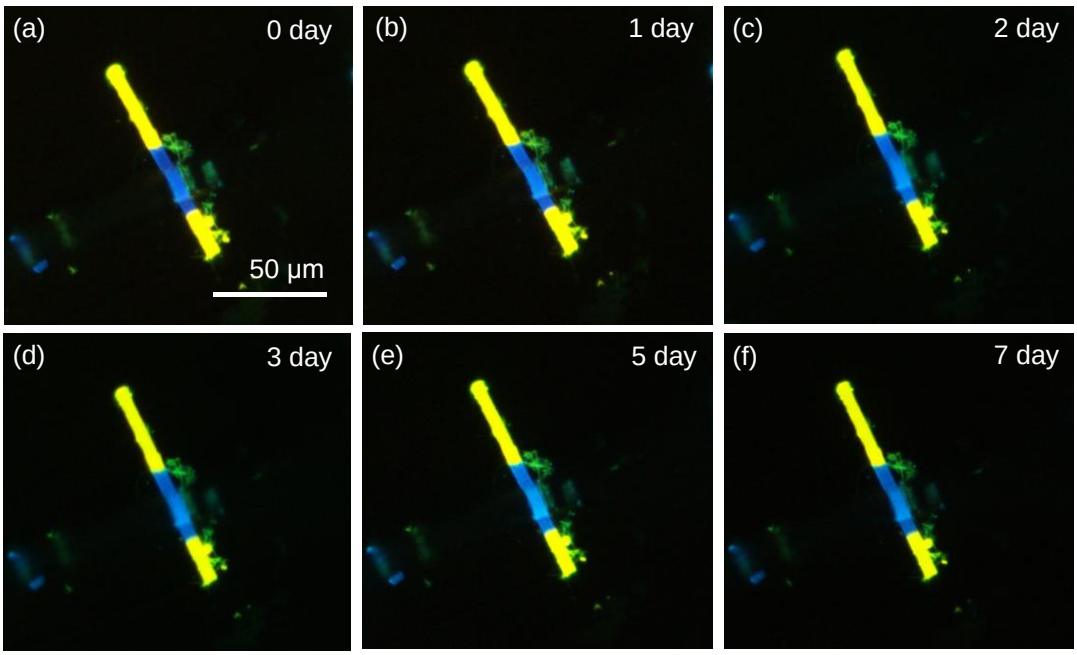

Fig. S11 (a-f) Fluorescence microscopy images of TPPE-H microcrystals after keeping at room temperature for 7 days.

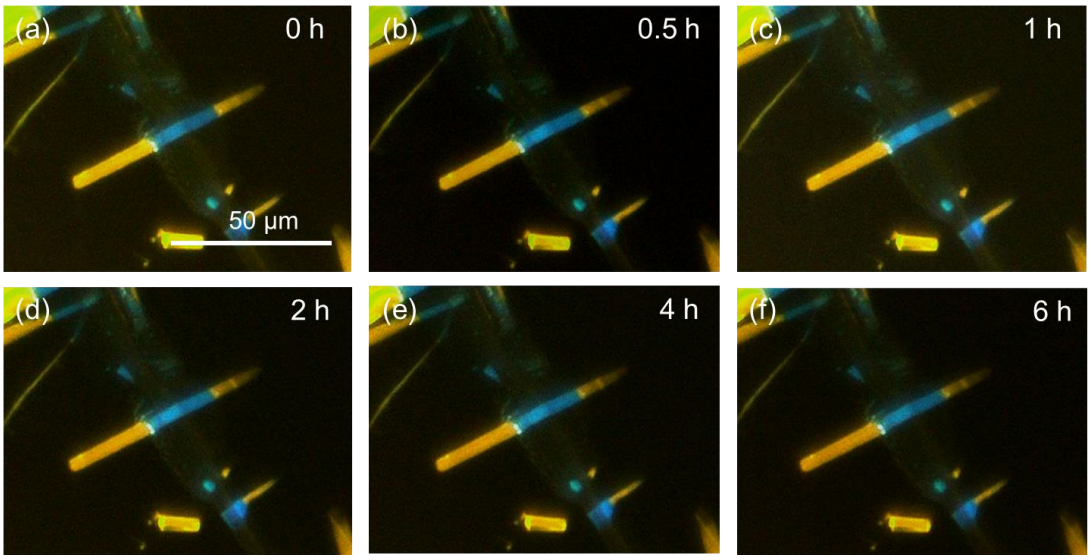

Fig. S12 (a-f) Fluorescence microscopy images of TPPE-H microcrystals after heating at 100 ℃ for 6 h.

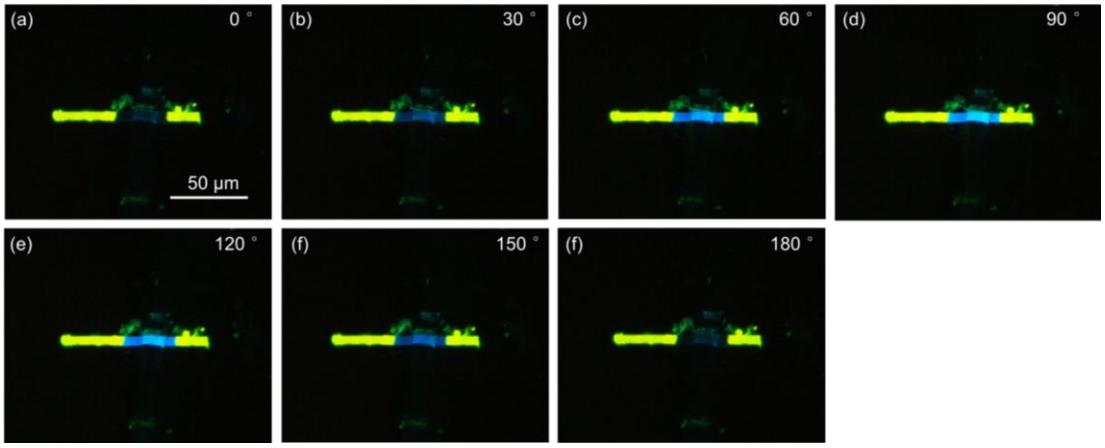

Fig. S13 (a,f) Fluorescence microscopy images recorded during the angle-resolved polarized luminescence measurement under UV excitation of the triblock heterostructure after 7 days of storage at room temperature. The indicated degrees refer to the angle between the linear polarizer relative to the crystal orientation.

Table S1 Photophysics data of TPPE and TPPE-H micrycrystals.

crystals	λ_{ex}/nm[a]	$\lambda_{em,max}$/nm	τ/ns	Φ_{FL}/%[b]
TPPE	300	470	1.43	43.9
TPPE-H	365	554	3.81	77.1

[a]Excitation wavelength. [a]Absolute emission yield.

Table S2 Crystallographic data and parameters.

compound	TPPE
CCDC number	2257690
empirical formula	$C_{46}H_{32}N_4$
formula weight	640.75
Temperature (K)	170.15
crystal system	monoclinic
Space group	*I*2
a (Å)	16.6067(7)
b (Å)	5.4254(3)
c (Å)	20.6546(10)
α (°)	90
β (°)	93.326(4)
γ (°)	90
V ($Å^3$)	1857.79(15)
Z value	2
Density (g/cm^3)	1.145
R1 (final)	0.0740
wR2 (final)	0.2158
R1 (all)	0.0991
wR2 (all)	0.2447

References

1. T. Lu and F. Chen, *J. Comput. Chem.*, 2012, **33**, 580-592.
2. C. Mu, Z. Zhang, Y. Hou, H. Liu, L. Ma, X. Li, S. Ling, G. He and M. Zhang, *Angew. Chem., Int. Ed.,* 2021, **60**, 12293-12297.
3. Z.-Q. Li, D.-X. Ma, F.-F. Xu, T.-X. Dan, Z.-L. Gong, J.-Y. Shao, Y. S. Zhao, J. Yao and Y.-W. Zhong, *Angew. Chem., Int. Ed.*, 2022, **61**, e202205033.