Electronic Supplementary Information (ESI)

Efficient multicolour and white circularly polarized luminescence from liquid crystalline polymer networks

*Fengyun Shi, Liting Xu, Jinghua Zhao, Zonglin Li, Wei Zhang, Yonggang Yang and Hongkun Li**

Laboratory of Advanced Optoelectronic Materials, Suzhou Key Laboratory of Novel Semiconductor-Optoelectronics Materials and Devices, State and Local Joint Engineering Laboratory for Novel Functional Polymeric Materials, Jiangsu Engineering Laboratory of Novel Functional Polymeric Materials, College of Chemistry, Chemical Engineering and Materials Science, Soochow University, Suzhou 215123, P. R. China. E-mail: hkli@suda.edu.cn

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Fig. S15 g_{lum} values of ***R/S*-PN-TAE/TPEB** films with different proportions of TAE and TPEB under excitation at 365 nm (A) and 460 nm (B) *versus* wavelength.

Scheme S2 Schematic illustration of visual observation of the pattern.

Movie S1 Visual observation of the pattern

Experimental Section

1. General information

Diphenylmethane, *p*-toluenesulfonic acid (*p*-TsOH), titanium tetrachloride ($TiCl_4$) and *n*-butyllithium (*n*-BuLi) were obtained from Aladdin Chemical Co., Ltd (Shanghai, China). Zinc powder and potassium carbonate (K_2CO_3) were purchased from Sinopharm Chemical Reagent Co., Ltd(Shanghai, China). Ethyl acetate (EA), petroleum ether (PE), dichloromethane (DCM), tetrahydrofuran (THF), ethanol (EtOH), magnesium sulfate ($MgSO_4$), *N,N*-dimethylacetamide (DMAc), cyclopentanone, 1,4-dioxane, sodium carbonate (Na_2CO_3) and anhydrous ether were obtained from Jiangsu Qiangsheng Chemical Reagent Co., Ltd. Palladium(II) acetate [$Pd(OAc)_2$] was obtained from Picasso-e Co., Ltd (Shanghai, China). Sodium, Hydrochloric acid (HCl), trichloromethane ($CHCl_3$), sodium methoxide($NaOCH_3$) and benzil dimethyl ketal (BDK) were obtained from Lingfeng Chemical Reagent Co., Ltd (Shanghai, China). 4-benzoylbiphenyl, 4-bromobenzophenone, 4-(diphenylamino)phenylboronic acid, [1,1'-bis(diphenylphosphino)ferrocene]-dichloropalladium(II) [$Pd(dppf)Cl_2$], bis(pinacolato)diboron, 7-bromobenzo[c][1,2,5] -thiadiazole-4-carbaldehyde, benzophenone, chloroacetonitrile, dicyclohexyl(2',6'-dimethoxy-[1,1'-biphenyl]-2-yl)phosphine and tetrakis(triphenylphosphine)palladium [$Pd(PPh_3)_4$] were purchased from Bide Pharmatech Co., Ltd (Shanghai, China). 2-Methyl-1,4-phenylene bis(4-((6-(acryloyloxy)hexyl)oxy)benzoate) (C6M), 4-methoxyphenyl 4-((6-(acryloyloxy)hexyl)oxy)benzoate (RM105), 2-methyl-1-[4-(methylthio)phenyl]-2-(4-morpholinyl)-1-propanone (907), (13b*R*)-5,6-dihydro-5-(*trans*-4-propylcyclohexyl)-4*H*-dinaphtho[2,1-*f*:1',2'-h] [1,5] dioxonin (*R*5011) and (13b*S*)-5,6-Dihydro-5-(*trans*-4-propylcyclohexyl)-4*H*-dinaphtho[2,1-*f*:1',2'-h][1,5]-dioxonin (*S*5011) were bought from Nanjing Sanjiang Advanced Materials R&d Co., Ltd. THF was dried by distillation from sodium benzophenone ketyprior to use.

^1H NMR spectra were acquired on an Agilent 300MHz spectrometer using $CDCl_3$ as solvent and tetramethylsilane (TMS) as an internal standard. ^1C NMR spectra were performed on an INOVA-400 spectrometer using $CDCl_3$ as solvent and tetramethylsilane (TMS) as an internal standard. Elemental analysis was acquired on an Elementar Vario EL-III instrument. High-resolution mass spectra (HRMS) were recorded on an Ultraflextreme MALDI TOF/TOF spectroscope (Bruker, USA). Fluorescence spectra, lifetime and quantum yields were taken on Edinburgh Instrument FLS980. UV-vis and diffuse reflectance circular dichroism (DRCD) spectra were recorded on a JASCO-815 spectrometer (Tokyo, Japan). CPL spectra were performed on a JASCO CPL-300 spectrometer (Tokyo, Japan). To eliminate the effect of linearly polarized luminescence, CPL spectra of the films were measured by using a plate holder allowing the samples to be rotated through 360° at 90° increments.

2. Synthesis of TAE and TPEB

2.1. Synthesis of 1,2-di([1,1'-biphenyl]-4-yl)-1,2-diphenylethene (TAE)

4-Benzoylbiphenyl (2.58 g, 10 mmol) and Zn dust (3.95 g, 40 mmol) were added into two-necked round flask, and freshly distilled THF (100 mL) was injected under nitrogen atmosphere. Then $TiCl_4$ (2.2 mL, 20 mmol) was added dropwise at 0 °C in an ice-water bath. The reaction mixture was refluxed at 80 °C under nitrogen atmosphere for 8 h. After cooling to room temperature, the reaction mixture was quenched by addition of K_2CO_3 aqueous solution. Then, an appropriate amount of hydrochloric acid was slowly added dropwise. After stirring for half an hour, the solution was extracted with 50 mL of DCM. The combined organic layers were dried over anhydrous $MgSO_4$. After filtration and solvent evaporation, the crude product was purified by a silica gel column using the PE as eluent. A white solid of TAE was obtained in 82.6% yield (2.00 g). ^1H NMR (300 MHz, $CDCl_3$), δ (TMS, ppm): 7.49 (d, J = 8.1 Hz, 4H), 7.29 (d, J = 8.2 Hz, 5H), 7.21 (d, J = 12.3 Hz, 5H), 7.04 (t, J = 8.3 Hz, 14H). ^{13}C NMR (101 MHz, $CDCl_3$), δ (ppm): ^{13}C NMR (101 MHz, $CDCl_3$), δ (ppm): 143.6, 140.4, 138.8,131.6, 131.2, 128.5, 127.5, 126.95, 126.6, 125.9. Elemental analysis calcd (%) for $C_{38}H_{28}$: C, 94.18; H, 5.82. Found: C, 94.37; H, 5.89.

2.2. Synthesis of 2-(4-(diphenylamino)phenyl)-3-(7-(4-(1,2,2-triphenylvinyl)phenyl)-benzo[c] [1,2,5] thiadiazol-4-yl)acrylonitrile (TPEB)

TPEB was prepared according to the published procedures.[1] ^1H NMR (300 MHz, $CDCl_3$), δ (TMS, ppm): 8.65 (d, J = 7.7 Hz, 1H), 8.40 (s, 1H), 7.81 (dd, J = 7.9, 4.9 Hz, 3H), 7.66 (d, J = 8.4Hz, 2H), 7.31 (t, J = 7.6 Hz, 4H), 7.15 (d, J = 11.6 Hz, 25H).

^{13}C NMR (101 MHz, $CDCl_3$), δ (ppm): 153.0, 150.9, 147.3, 144.8, 142.2, 141.6, 139.5, 138.3, 132.6, 132.4, 130.2, 129.4, 129.2, 127.6, 126.1, 125.6, 125.2, 124.9, 124.5, 123.7, 123.1, 121.8, 120.1, 116.0, 110.4. HRMS (MALDI-TOF), *m/z* 760.131, (*m/z*, calcd 760.266).

3. Preparation of liquid crystalline polymer network (LCPN) films

Molecular structures of the compounds used in the polymerizable liquid crystal system are shown in **Chart 1**.

*3.1. Preparation of LCPN films doped with **TAE***

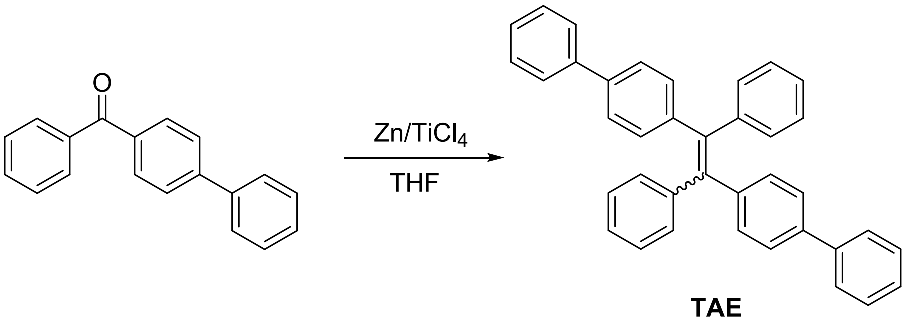
C6M (0.476 g), *R*/*S*5011 (0.018 g), RM105 (0.476 g), TAE (0.02 g) and BDK (0.01 g) were dissolved in anhydrous CH_2Cl_2. Then, the solvent was evaporated on the surface of a glassed plate at 80 °C for 5 min. The thickness of the obtained films was always kept at 11μm by sandwich structures (glassed plates with 11μm spacer in the middle). After the temperature cooled down to room temperature, photopolymerization was carried out under UV irradiation using a 365 nm lamp for 10 seconds. Then the LCPN films were obtained. Free-standing films can be obtained by peeling the films off the glassed plates with a blade.

3.2. Preparation of LCPN films doped with different mass ratios of TAE and TPEB

The preparation procedure of the liquid crystalline polymer network films doped with TAE and TPEB was the same as above. The total mass fraction of TAE and TPEB maintained at 2 wt% (Table S1).

3.3. Preparation of LCPN-coated PET film

The mixtures of C6M, *S*5011, RM105, 907, TAE and TPEB were dissolved in DMAc and cyclopentanone (4:6, m:m) to keep the solid content of 30% (the weight ratios shown in Table S2). A pattern would be printed out on transparent PET films by adding the mixtures to printer cartridges and setting programs (A4UV). The solvent was evaporated by heating. After the film was cooled down to room temperature, the photopolymerization was carried out under mercury lamp (1000W) for 10 s. Then, a pattern was obtained.



Scheme S1. Synthetic route to TAE.

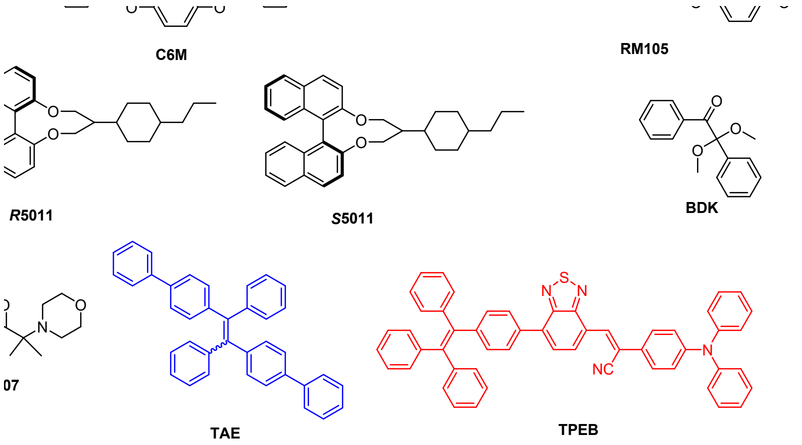


Chart S1. Molecular structures of the compounds in the reactive CLC mixtures

Table S1. Mass percentages of compounds for preparation of LCPN films

Sample / Compound	***R*-/*S*-PN-TAE**	*R*-/*S*-200:1	*R*-/*S*-100:1	*R*-/*S*-50:1	*R*-/*S*-20:1	*R*-/*S*-10:1
C6M (%)	47.60	47.60	47.60	47.60	47.60	47.60
RM105 (%)	47.60	47.60	47.60	47.60	47.60	47.60
BDK (%)	1.00	1.00	1.00	1.00	1.00	1.00
R/*S*5011 (%)	1.80	1.80	1.80	1.80	1.80	0.80
TAE (%)	2.00	1.99	1.98	1.96	1.90	1.82
TPEB (%)	0	0.01	0.02	0.04	0.10	0.18

Table S2. Mass percentages of compounds for preparation of LCPN-coated PET film

Color of fluorescent pattern	C6M (wt%)	RM105 (wt%)	*S*5011 (wt%)	907 (wt%)	TAE (wt%)	TPEB (wt%)
blue	45.10	45.10	1.80	6.00	2.00	0.00
white	45.10	45.10	1.80	6.00	1.98	0.02
red	45.10	45.10	1.80	6.00	1.82	0.18

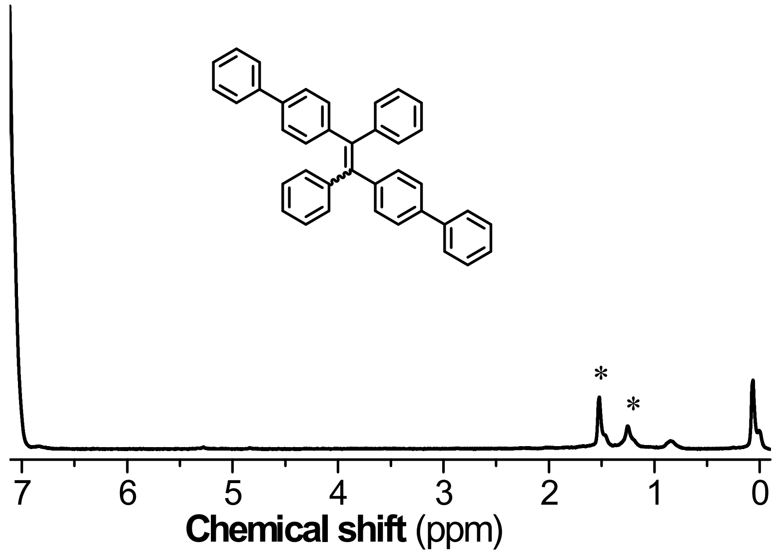


Fig. S1 ^{1}H NMR spectrum of TAE in $CDCl_3$. The solvent peaks are labeled with asterisks.

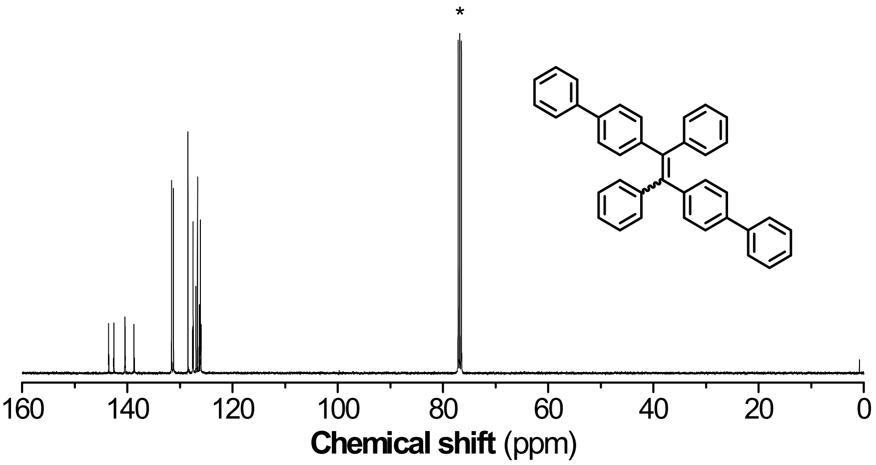


Fig. S2 ^{13}C NMR spectrum of TAE in $CDCl_3$. The solvent peak is labeled with asterisk.

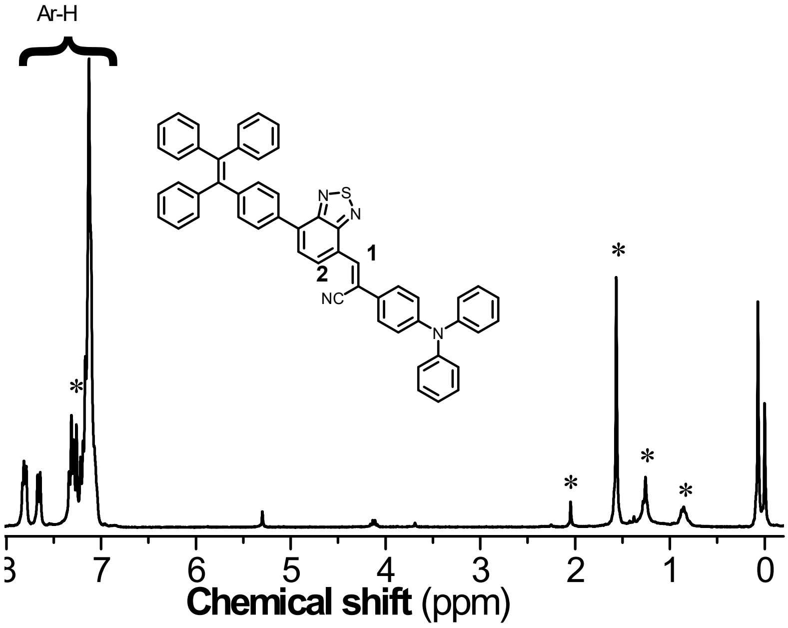


Fig. S3 ^{1}H NMR spectrum of TPEB in $CDCl_3$. The solvent peaks are labeled with asterisks.

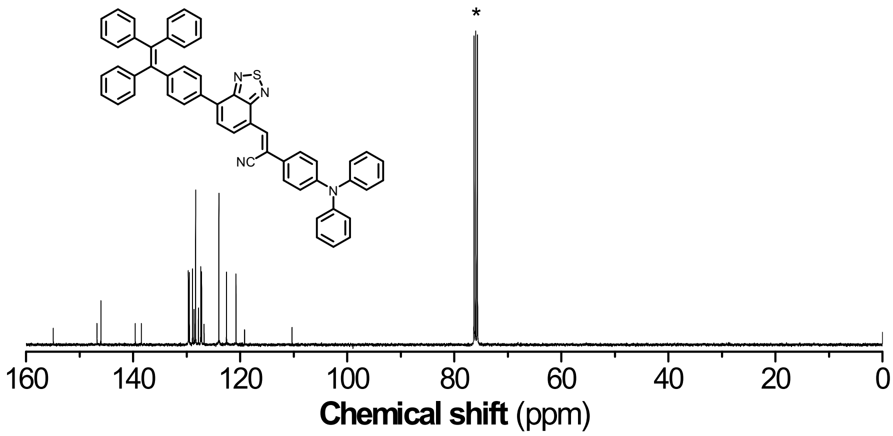


Fig. S4 ^{13}C NMR spectrum of TPEB in $CDCl_3$. The solvent peak is labeled with asterisk.

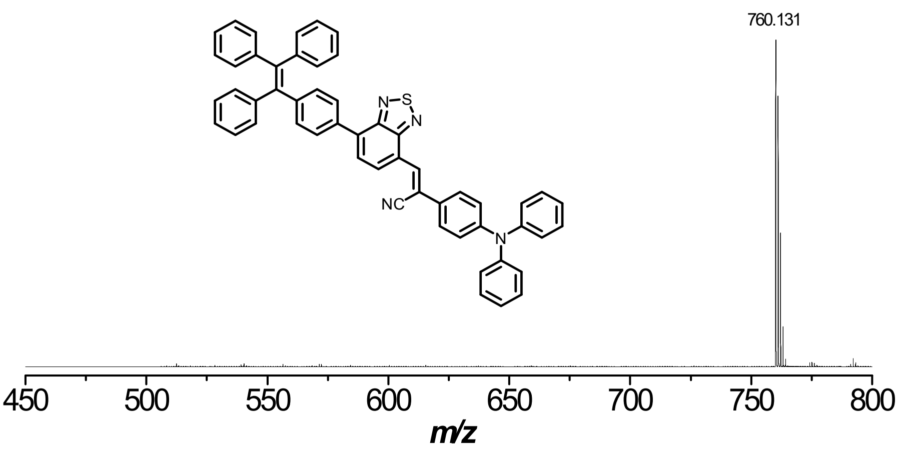


Fig. S5 Mass spectrum of TPEB.

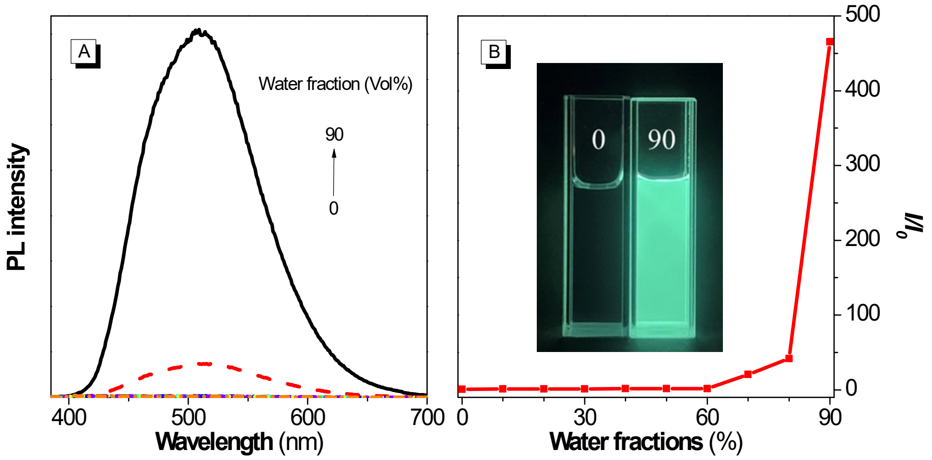


Fig. S6 (A) PL spectra of TAE in the mixtures of THF and water with different water fractions (f_w) and a concentration of 10 µM, λ_{ex}: 365 nm; (B) Plot of relative emission peak intensity (I/I_0) of TAE at 500 nm versus f_w; Inset: Pictures of TAE in THF and water mixtures with f_w of 0 and 90% taken under excitation at 365 nm.

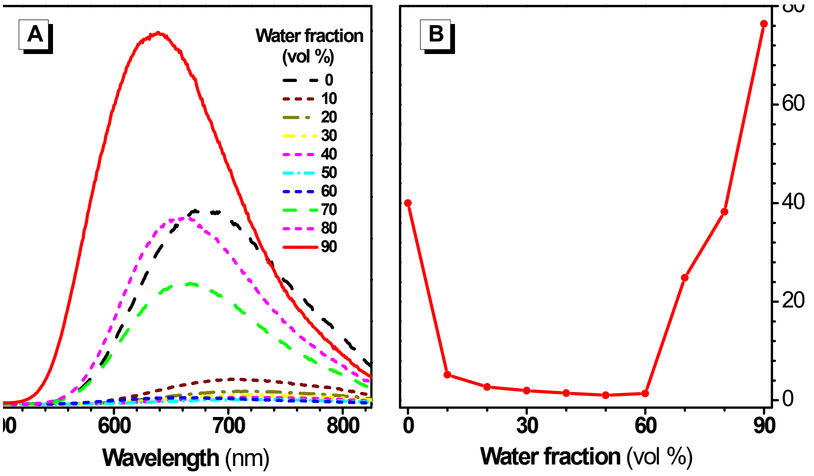


Fig. S7 (A) PL spectra of TPEB in THF and water mixtures with a concentration of 10 μM, λ_{ex}: 480 nm; (B) Plot of relative emission peak intensity (I/I_0) of TPEB at 650 nm versus water fractions.

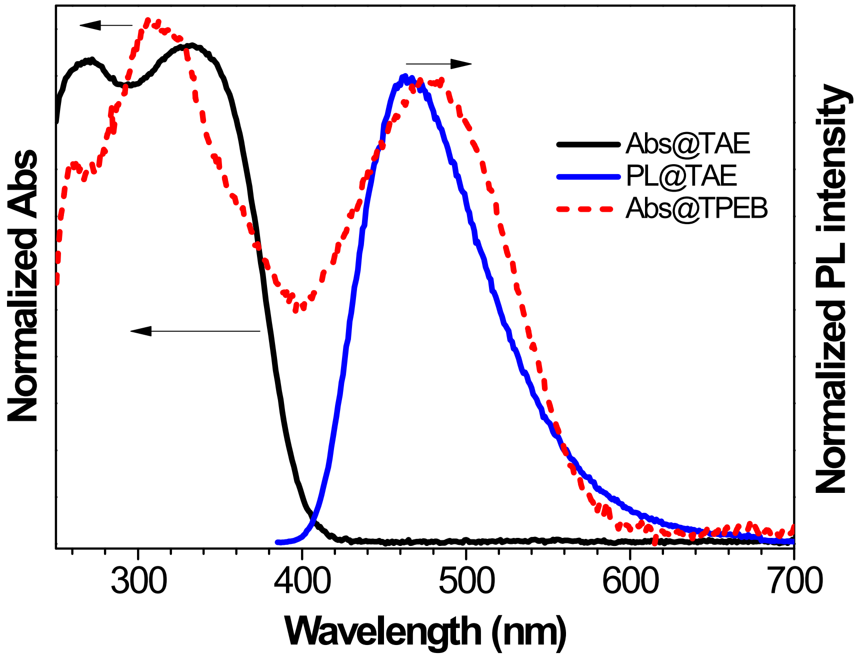


Fig. S8 Normalized absorption spectra of TAE- and TPEB-doped PMMA films and normalized PL spectrum of TAE powder.

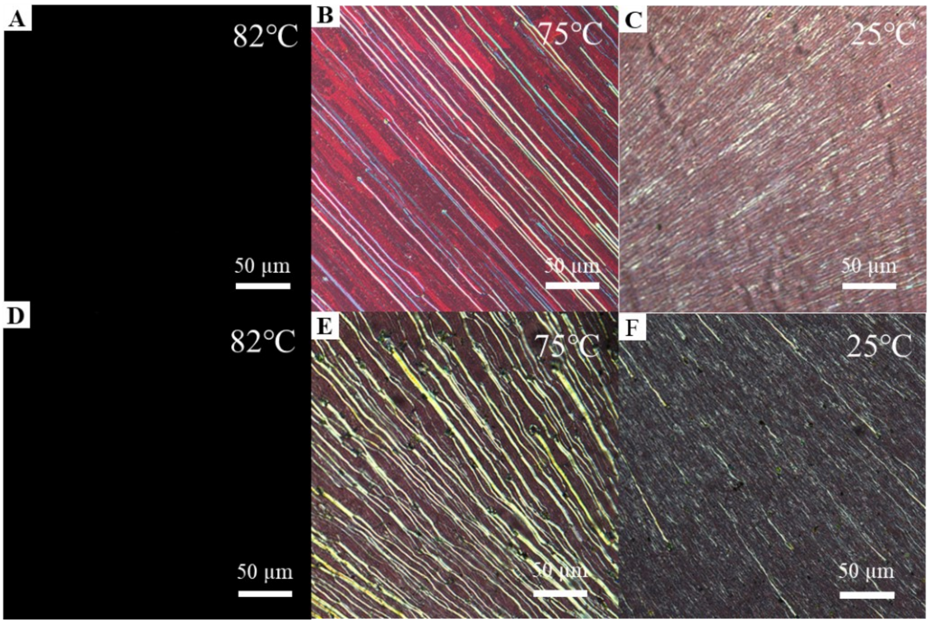


Fig. S9 POM images of the mixtures of C6M and RM105 (1:1, mass ratio), TAE, BDK, *R*5011 (A, B, C) and *S*5011 (D, E, F) at different temperatures.

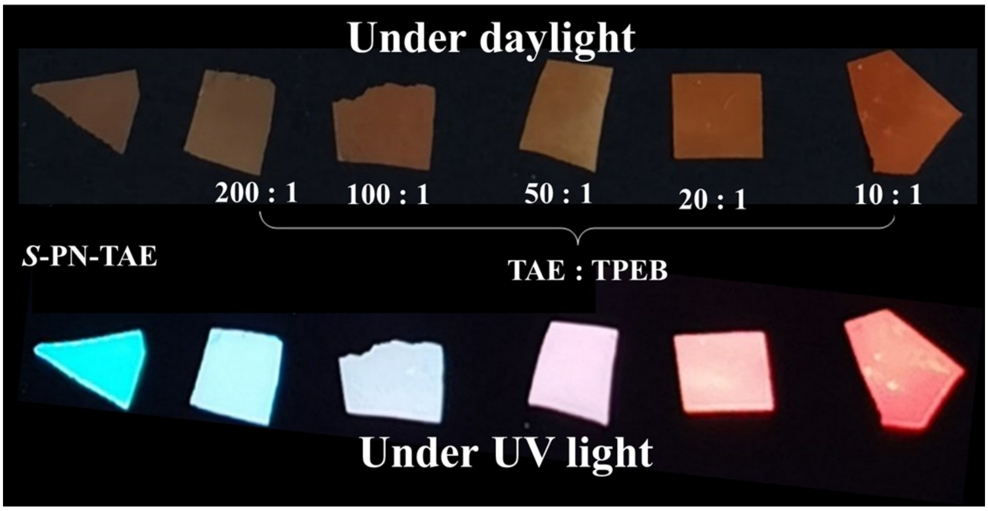


Fig. S10 Photographs of ***S*-PN-TAE** and ***S*-PN-TAE/TPEB** films with different proportions of TAE and TPEB under day light (top) and UV light (down).

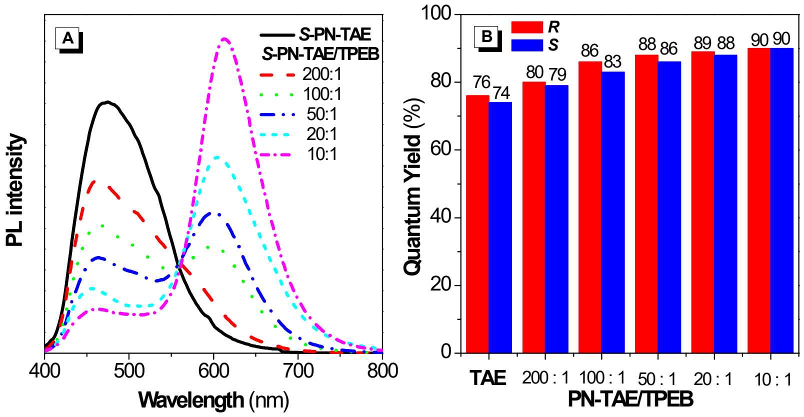


Fig. S11 PL spectra of ***S*-PN-TAE** and ***S*-PN-TAE/TPEB** films with different proportions of TAE and TPEB films. (B) Fluorescence quantum yields of ***R/S*-PN-TAE** and ***R/S*-PN-TAE/TPEB** films.

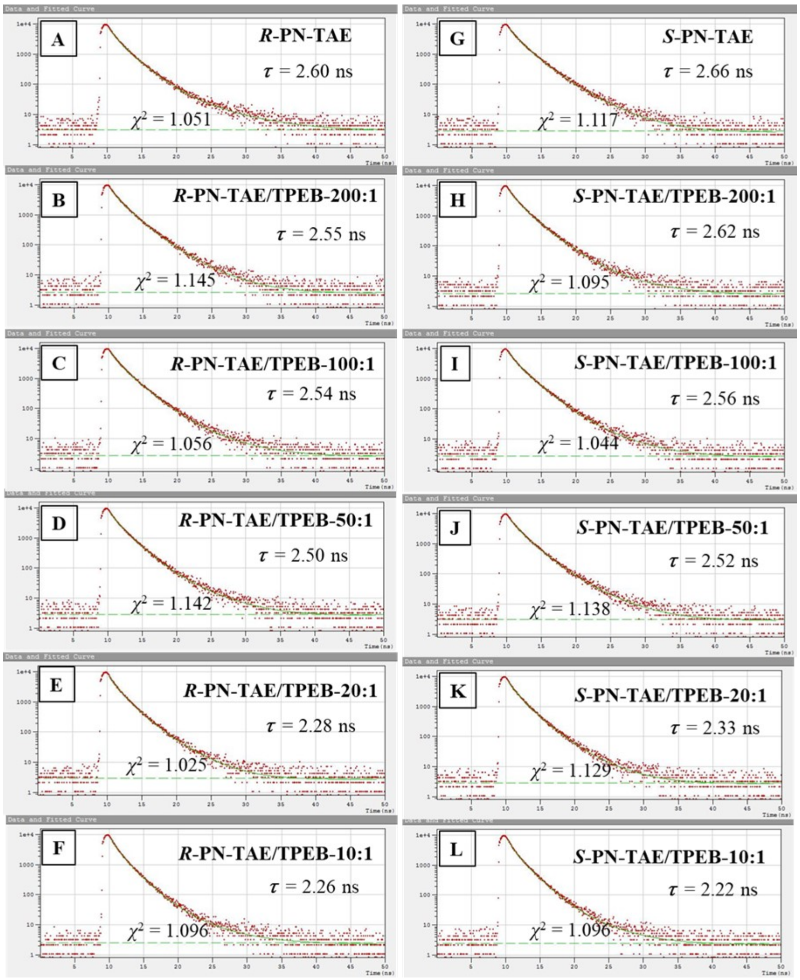


Fig. S12 Time-resolved fluorescence decay curves of ***R*-PN-TAE** and ***R*-PN-TAE/TPEB** (A-F) and ***S*-PN-TAE** and ***S*-PN-TAE/TPEB** (G-L) at 460 nm; the fluorescence lifetime was calculated according to the below equation

$$\tau = \frac{\sum f_i \tau_i^2}{\sum f_i \tau_i}$$

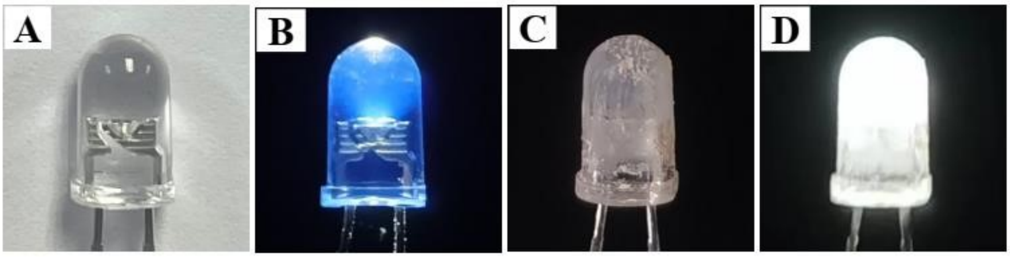


Fig. S13 Photographs of the WLED: (A) a 365-nm ultraviolet LED is turned off; (B) the same ultraviolet LED is turned on; (C) the LED is coated with TAE and TPEB when the LED is turned off; (D) the coated LED emits WL when it is turned on.

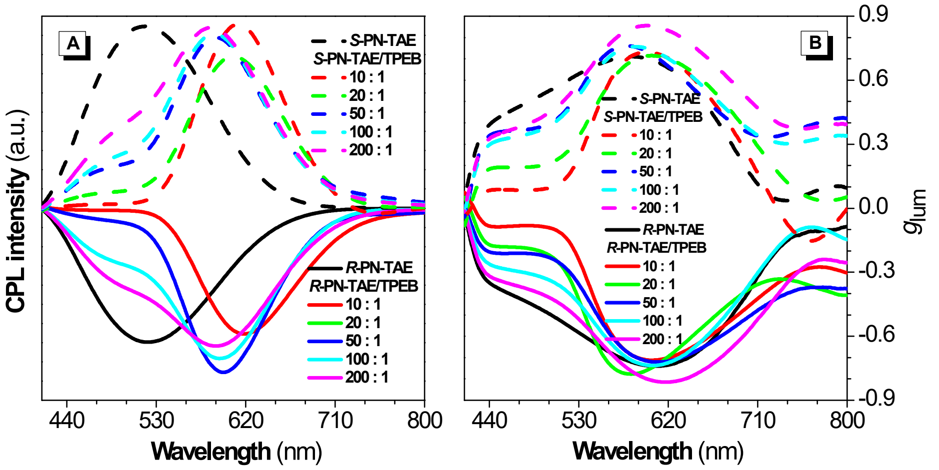


Fig. S14 (A) CPL spectra and (B) g_{lum} values of ***R/S*-PN-TAE** and ***R/S*-PN-TAE/TPEB** films after more than one year of storage. λ_{ex}: 365 nm.

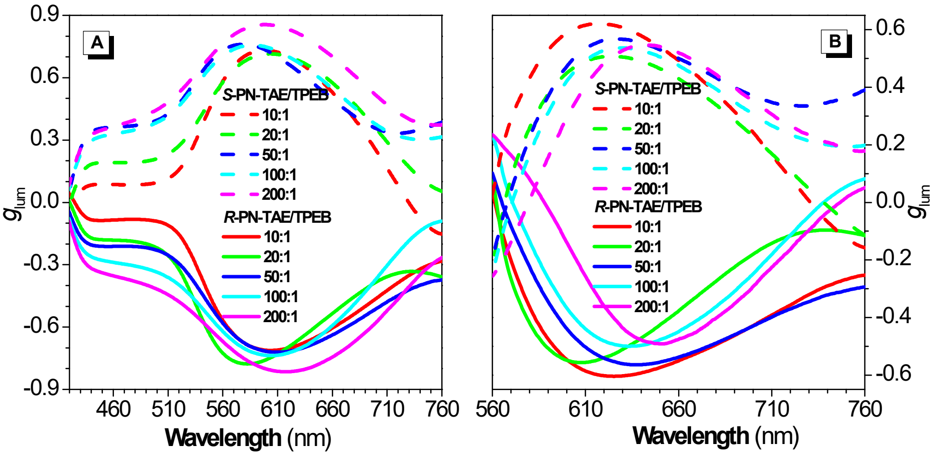
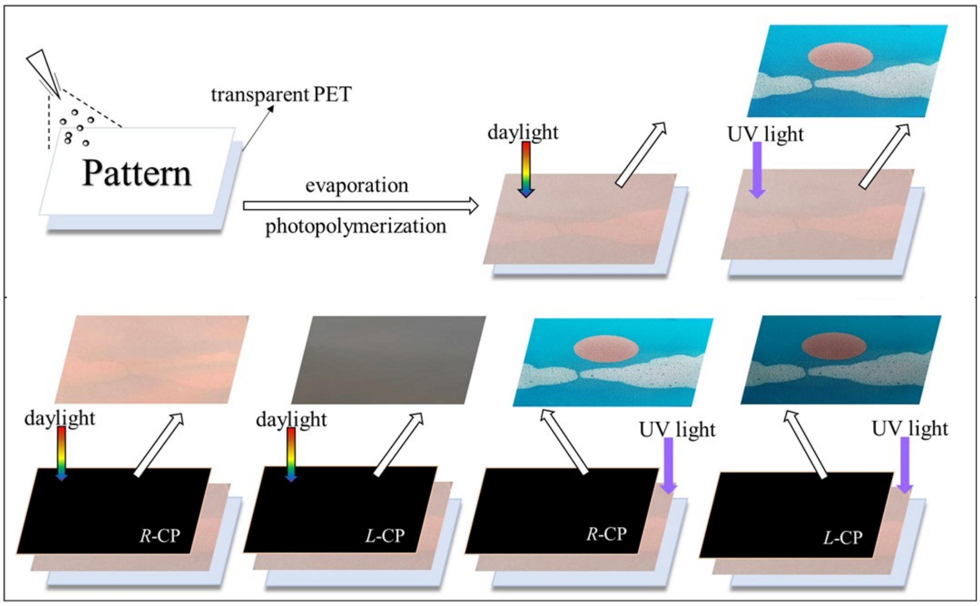


Fig. S15 g_{lum} values of ***R/S*-PN-TAE/TPEB** films with different proportions of TAE and TPEB under excitation at 365 nm (A) and 460 nm (B) *versus* wavelength.



Scheme S2 Schematic illustration of the observation of the pattern.

References

[1] Q. Luo, C. Lv, H. Sheng, F. Cao, J. Sun, C. Zhang, M. Ouyang, B. Zou and Y. Zhang, *Adv. Opt. Mater.*, 2020, **8**, 1901836.