

Electronic Supplemental Information

Interfacial Self-Assembly of Chiral Pyrene Exciplex into Superhelix with Enhanced Circularly Polarized Luminescence

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1. Experimental Section

1.1 Chemicals

All chemicals and solvents were used without further purification. Sodium sulfate (Na_2SO_4 , 99.5%, Innochem), Trichloromethane (TCM, AR, Innochem), Milli-Q water (H_2O , 18.2 $\text{M}\Omega\cdot\text{cm}$), *N,N*-Dimethylformamide (DMF, AR, Innochem), Ethyl acetate (EA, AR, Concord Technology), Methanol (MeOH, AR, Concord Technology), Triethylamine (TEA, AR, Innochem), Methylcyclohexane (AR, Concord Technology), 1-hydroxybenzotriazole (HOBt, 98%, Innochem), 1-(3-dimethylaminopropyl)-3-ethylcarbodiimide hydrochloride (EDC·HCl, 98%, Innochem), D-glutamic acid diethyl ester hydrochloride (98%, Aladdin), L-glutamic acid diethyl ester hydrochloride (98%, Aladdin), 1-Pyrenic acid (95%, Innochem), 2-phenanthic acid (PhCA, 95%, Macklin).

1.2 Syntheses

1.2.1 Syntheses of DPyr and LPyr

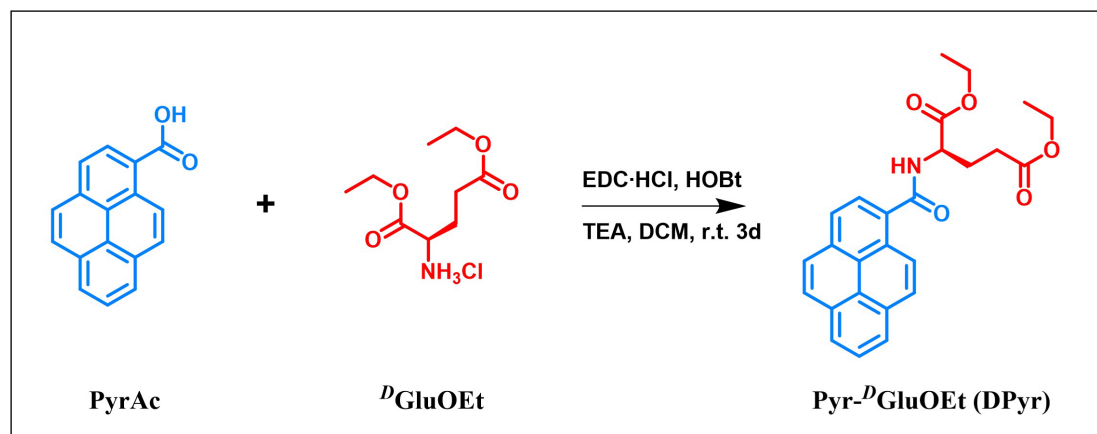


Figure S1. Synthesis of DPyr/LPyr.

As shown in Figure S1, DPyr and LPyr were synthesized according to the literatures^{S1}.

DPyr: D-glutamic acid diethyl ester hydrochloride (1.44 g, 6 mmol) and 1-Pyrenic acid (1.23 g, 5mmol) was dissolved in 100 mL *N,N*-dimethyl-formamide (DMF) in a 250 mL flask. Then, 1-hydroxybenzotriazole (HOBt, 0.68 g, 5 mmol) and 1-(3-dimethylaminopropyl)-3-ethylcarbodiimide hydrochloride (EDC·HCl, 2.88 g, 15 mmol) were added to the solution. Triethylamine (3ml) was then added into the above solution. The mixture was stirred at room temperature overnight.

After that, the organic solvent was removed using rotary evaporator to obtain a residue, which was dissolved in ethyl acetate (EA) and washed with saturated aqueous solution of Na₂SO₄ for three times. The product was a white powder (1.6 g, 3.7 mmol, yield: 74%).

LPyr was synthesized as the same procedure to **DPyr** except L-glutamic acid diethyl ester hydrochloride was used. White powder (yield: 71%).

DPyr:

¹H NMR (400 MHz, CDCl₃) see **Figure S3**: δ 8.71 (d, *J*=9.3 Hz, 1H), 8.27 (d, *J*=7.6 Hz, 2H), 8.24-8.15 (m, 4H), 8.14-8.05 (m, 2H), 6.90 (d, *J*=7.9 Hz, 1H), 5.10-5.01 (m, 1H), 4.33 (t, *J*=7.1 Hz, 2H), 4.21-4.09 (m, 2H), 2.71-2.53 (m, 2H), 2.47 (dq, *J*=13.2, 7.1 Hz, 1H), 2.25 (dd, *J*=14.4, 7.2 Hz, 1H), 1.40 (td, *J*=6.9, 0.8 Hz, 3H), 1.26 (td, *J*=7.2, 1.0 Hz, 3H).

LPyr:

¹H NMR (400 MHz, CDCl₃) see **Figure S4**: δ 8.71 (d, *J*=9.3Hz, 1H), 8.27 (d, *J*=7.6Hz, 2H), 8.23-8.16 (m, 4H), 8.13-8.05 (m, 2H), 6.91 (d, *J*=7.9Hz, 1H), 5.09-5.02 (m, 1H), 4.34 (q, *J*=7.1Hz, 2H), 4.20 -4.10 (m, 2H), 2.71-2.53 (m, 2H), 2.47 (dq, *J*=13.3, 6.8Hz, 1H), 2.25 (dq, *J*=14.8, 7.6Hz, 1H), 1.40 (td, *J*=7.2, 0.9Hz, 3H), 1.26 (td, *J*=7.1, 0.9Hz, 3H).

1.2.2 Syntheses of DPh

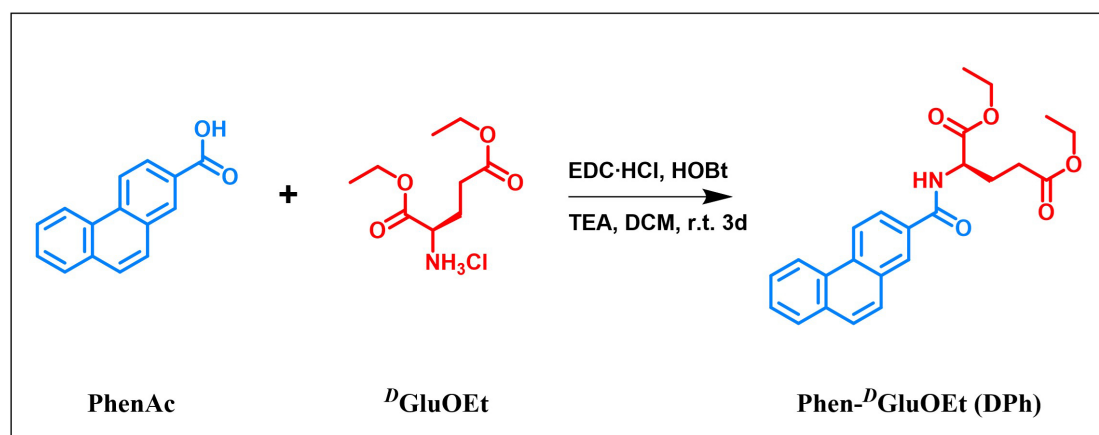


Figure S2. Synthesis of DPh

DPh was synthesized as the same procedure to **DPyr** except 2-phenanthric acid was used. D-glutamic acid diethyl ester hydrochloride (776.6 mg, 3.2 mmol) and 2-phenanthric acid (600 mg, 2.7 mmol) was dissolved in 100 mL *N,N*-dimethyl-formamide (DMF) in a 250 mL flask. Then, 1-hydroxybenzotriazole (HOBt, 365 mg, 2.7 mmol) and 1-(3-dimethylaminopropyl)-3-

ethylcarbodiimide hydrochloride (EDC·HCl, 1.55 g, 8.1 mmol) were added to the solution. Triethylamine (2 ml) was then added into the above solution. The mixture was stirred at room temperature overnight. After that, the organic solvent was removed using rotary evaporator to obtain a residue, which was dissolved in ethyl acetate (EA) and washed with saturated aqueous solution of Na₂SO₄ for three times. The product was a white powder (770 g, 1.9 mmol, yield: 70%).

DPh:

¹H NMR (400 MHz, CDCl₃) see **Figure S5**: δ 8.73 (dd, *J*=14.9, 8.4Hz, 2H), 8.38 (s, 1H), 8.07 (dd, *J*=8.5, 1.8Hz, 1H), 7.93 (d, *J*=7.6Hz, 1H), 7.81 (s, 2H), 7.74-7.63 (m, 2H), 7.22 (s, 1H), 4.93-4.84 (m, 1H), 4.28 (ddd, *J*=8.1, 6.3, 4.8Hz, 2H), 4.12 (tt, *J*=7.2, 3.6Hz, 2H), 2.53 (dtd, *J*=23.7, 16.7, 7.2Hz, 2H), 2.39 (dq, *J*=12.5, 6.8Hz, 1H), 2.23 (dt, *J*=14.4, 7.3Hz, 1H), 1.34 (dd, *J*=7.6, 6.6Hz, 3H), 1.26-1.20 (m, 3H).

1.3 Methods

1.3.1 Procedures of Sample Preparation

1. Preparation of Solution Samples

DPyr/LPyr: 1.724 mg of DPyr (or LPyr) powder was dissolved in 8 mL trichloromethane (TCM) under ultrasonication (1×10^{-4} M).

DPh: 1.628 mg of DPh was dissolved in 8 mL of TCM under ultrasonication (1×10^{-4} M).

The solution samples of **DPyr@DPh**, **LPyr@DPh**, **DPyr@Ph**, **DPyr@PhCA** at equimolar ratios were prepared through similar process.

2. Preparation of Bulk Self-Assembled Samples

DPyr: DPyr (2.15 mg, 0.005 mmol) and methylcyclohexane (250 μL) were mixed in the sample vial. Then, the solution (0.2 M) is obtained after heating. While gel formed after the natural cooling to room temperature.

The bulk self-assembly samples of **DPh** and **DPyr@DPh** were prepared through similar process, with the total concentration is kept at 0.2 M.

3. Preparation of the LS films

The Langmuir-Blodgett (LB) and Langmuir-Schaefer (LS) experiments were carried out as documented referecne^{S2}. Each above prepared samples of chloroform solutions (1×10^{-4} M, pure or mixture combinations) were uniformly dropped on the water surface ($18.2 \text{ M}\Omega \cdot \text{cm}$, $25 \text{ }^\circ\text{C}$), respectively. After the solvent evaporates for 15 minutes, the film pressing speed was set to $5 \text{ cm}^2 \cdot \text{min}^{-1}$, and the surface pressure-molecular area (π -A) isotherm curves were obtained at this compression speed. When the surface pressure reached 10 mN/m , the pulling speed was set to $1 \text{ mm} \cdot \text{min}^{-1}$, and the horizontal transfer (LS) method was adopted. The multilayered LS films were transferred to a clean and hydrophobic treated quartz or silicon wafers, and the samples were characterized after drying at ambient conditions.

4. Preparation of Single Crystals

DPyr: The methylcyclohexane solution of **DPyr** and filtered using $0.22 \text{ }\mu\text{m}$ filters to give a clear solution (1×10^{-4} M). After slow evaporation for 3 ~ 5 days, White transparent cristas were obtained.

The tries on the composite cocystal samples of **DPyr@DPh**, **LPyr@DPh**, **DPyr@Ph**, **DPyr@PhCA** were prepared through similar process. However, only the single crystal of **DPyr** alone were found in these samples.

1.3.2 Characterization

UV-Vis: UV-visible absorption spectra were recorded on U-3900 (Hitachi) with the solution and aggregation samples put into 1 mm and 0.1 mm quartz cuvettes, respectively.

ECD: ECD were recorded on CD spectrometer J-1500 (JASCO) with the solution and aggregation samples put into 1 mm and 0.1 mm quartz cuvettes, respectively.

FL: Fluorescence (FL) spectra were performed on F-4500 fluorescence spectrophotometer (Hitachi) with a voltage 400 V and 5 nm slit on both the excitation and emission sides. The wavelength scanning rate was 1200 nm/min . The excitation wavelength was 360 nm unless otherwise stated. The fluorescence decay curves were recorded on FLS 980 (Edinburgh Instruments). The wavelength of the excitation laser was 358.4 nm. IRF measurement was performed when the

lift time less than 5 ns. The photoluminescence quantum yields were measured by FluoroMax+ (HORIBA).

CPL: Circularly polarized luminescence (CPL) spectra of all samples in 1 mm quartz cuvette were measured on a CPL-300 spectrophotometer (JASCO) in the range of 320 ~ 800 nm with a scanning rate of 500 nm min⁻¹. And the DC value was adjusted to about 0.5 V. The CPL spectra were tested at least 5 times to ensure the accuracy of the measurements. The g_{lum} spectra were transferred from CD spectra using the Spectra Manager software of JASCO.

SEM: The LS film samples were spread onto the single-crystal silica plates, vacuum dried and coated by a thin layer of Au and Pt, and then tested by scanning electron microscope (SEM, Hitachi S-4800) with an accelerating voltage of 10 kV and an operating current of 10 μ A.

FT-IR: The LS film samples were spread onto the single-crystal silica plates, And then separated by vacuum-dried. Then perform FT-IR spectroscopy measurements on the Bruker tensor27 with the test wavenumber range from 400 to 4000 cm⁻¹.

PXRD: Deposit the sample on a silicon wafer, and dried in vacuum. Powder X-ray diffraction spectra of samples were recorded on EmpyreanX (PANalytical B.V.) with Cu/K α eadiation ($\lambda=1.5406\text{\AA}$) at 40 kV and 40 mA with the scanning range was from 1~30 $^\circ$.

TEM: TEM images were obtained on a HT-7700 electron microscope at an accelerating voltage of 100 kV. The suspension of Dpyr@DPh was spread onto carbon-coated Cu grids (unstained), which was vacuum dried for transmission electron microscopy observation.

¹H NMR: ¹H NMR were recorded on a Bruker Avance 400 spectrometer, TMS as internal standard, 298 K. The powders were dissolved in d- Chloroform.

Single-Crystal XRD: A suitable crystal was selected and recorded on a XtaLAB AFC10 (RCD3): fixed-chi single diffractometer (Rigaku MM007HF single crystal X-ray diffractometer). The crystal was kept at 100.00(10) K or 170.01(14) during data collection. Using Olex2 (Dolomanov, O. V.; Bourhis, L. J.; Gildea, R. J.; Howard, J. A. K.; Puschmann, H. *J. Appl. Cryst.* **2009**, *42*, 339-341), the structure was solved with the ShelXT structure solution program using Intrinsic Phasing and refined with the ShelXL refinement package using Least Squares minimization (Sheldrick, G. M. *Acta Cryst.* **2015**, *A71*, 3-8).

1.4 Instruments

¹H NMR spectra were measured on a Bruker Avance spectrometer (Bruker BioSpin). Electrospray ionization mass spectrometry (ESI-MS) were performed on Bruker-Autoflex III. The surface pressure-area (π -A) isotherm and Langmuir-Schaefer (LS) film was recorded on a computer-controlled KSV-minitrough system with a surface area of 273 cm² (L = 364 mm and W = 75 mm) (KSV Instruments, Helsinki, Finland). UV-Vis spectra were recorded on U-3900 (Hitachi). ECD and LD spectra were measured by CD spectrometer J-1500 (JASCO). CPL spectra were recorded on CPL-300 spectrophotometer (JASCO). FL spectra were performed on F-4500 fluorescence spectrophotometer (Hitachi) and the fluorescence decay curves was measured by FLS 980 (Edinburgh Instruments). Photoluminescence quantum yield was measured by FluoroMax⁺ (HORIBA). FT-IR spectra were measured by Bruker Tensor-27. Powder XRD and single crystal analysis were performed on an X-ray diffractometer of EmpyreanX (PANalytical B.V.) and single crystal X-ray diffractometer (Rigaku MM007HF), respectively. Scanning electron microscopy (SEM) was performed on S4800 (Hitachi).

2. Figures and Tables

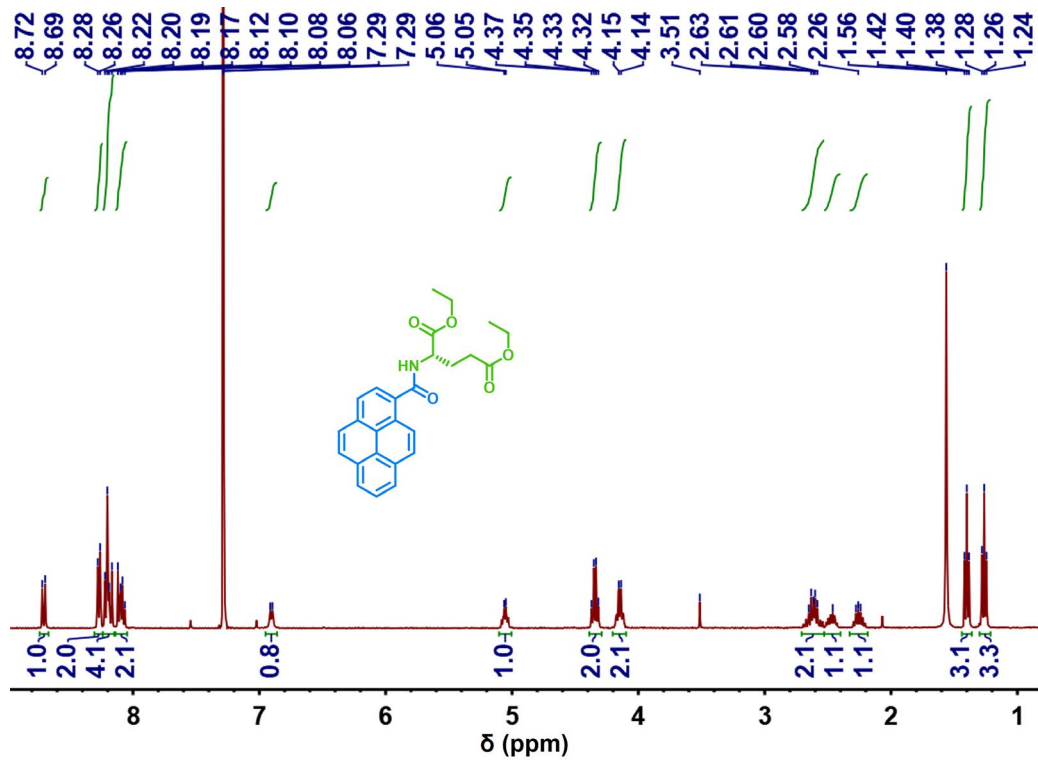


Figure S3. ¹H NMR (400 MHz, CDCl₃) spectra of DPyr.

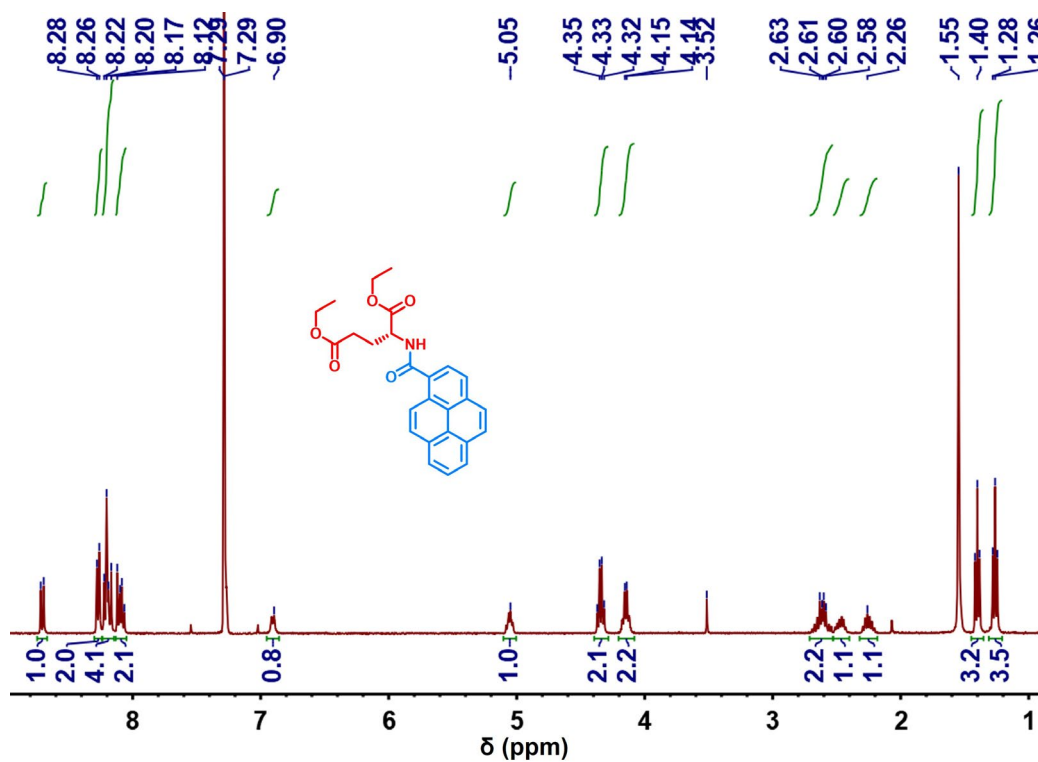


Figure S4. ¹H NMR (400 MHz, CDCl₃) spectra of LPyr.

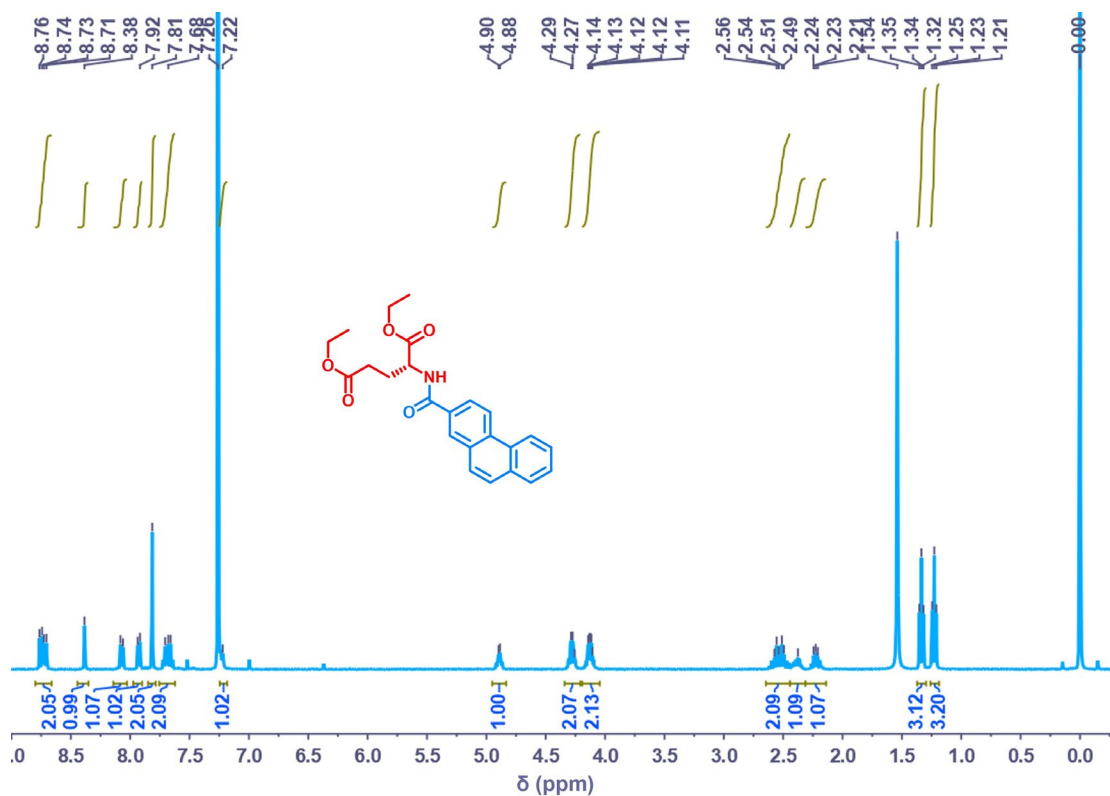


Figure S5. ^1H NMR (400 MHz, CDCl_3) spectra of **DPh**.

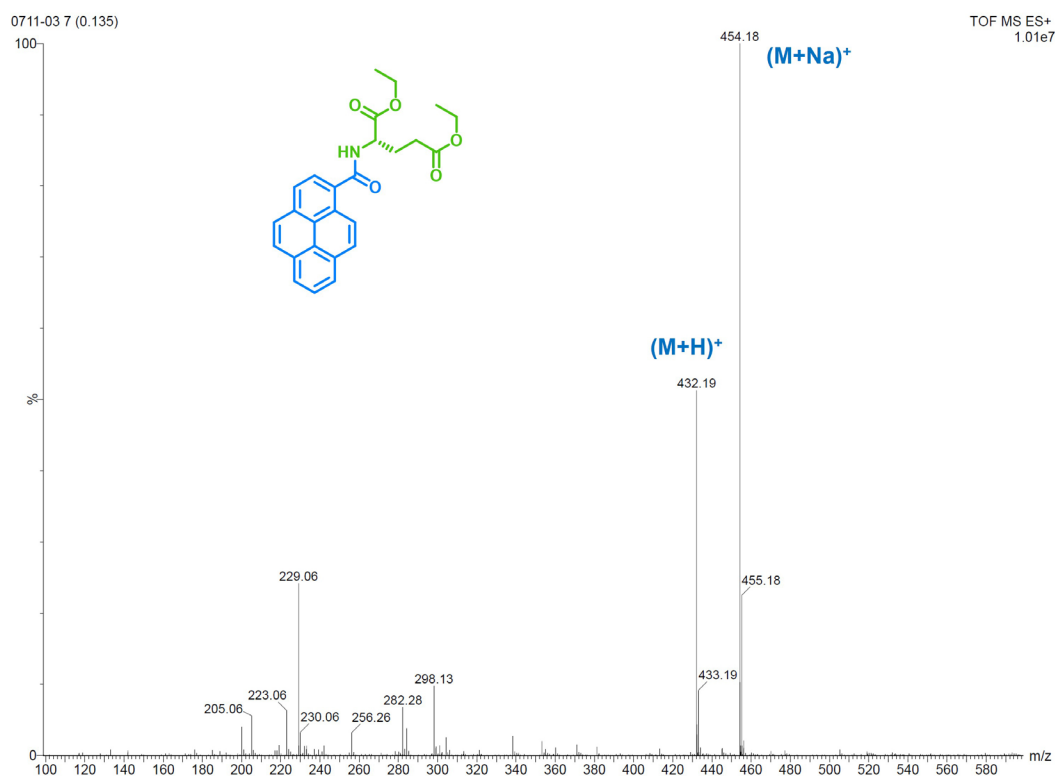


Figure S6. ESI-MS spectra of **DPyr**, Calc: $\text{C}_{26}\text{H}_{25}\text{NO}_5 = 431.49$, found: 432.19 ($\text{M}+\text{H}$) $^+$, 454.18 ($\text{M}+\text{Na}$) $^+$.

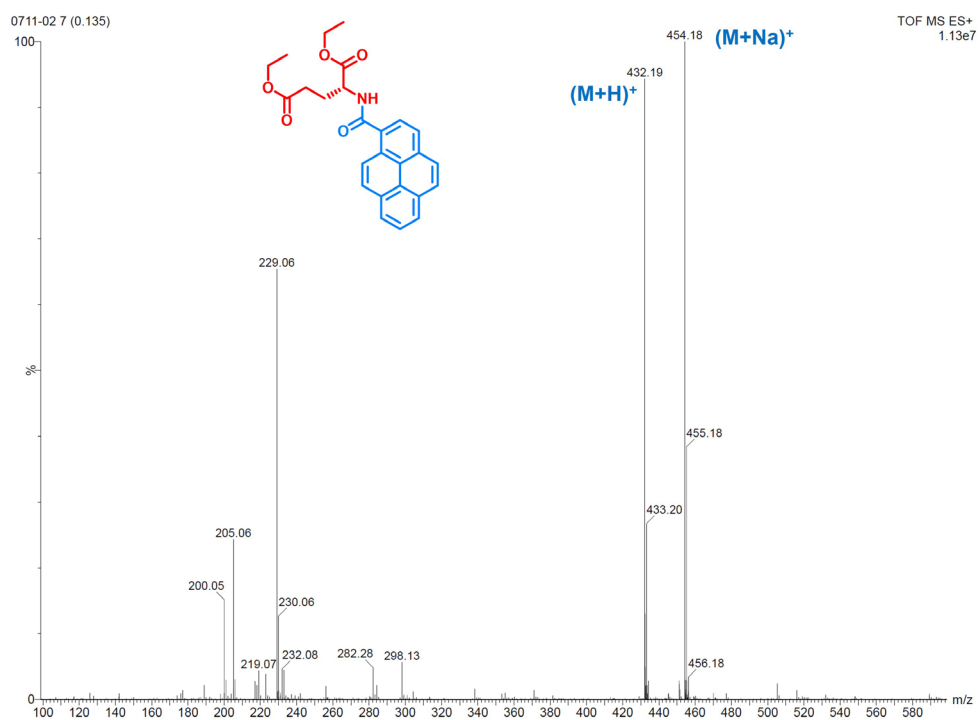


Figure S7. ESI-MS spectra of **LPyr**, Calc: $C_{26}H_{25}NO_5 = 431.49$, found: $432.19 (M+H)^+$, $454.18 (M+Na)^+$.

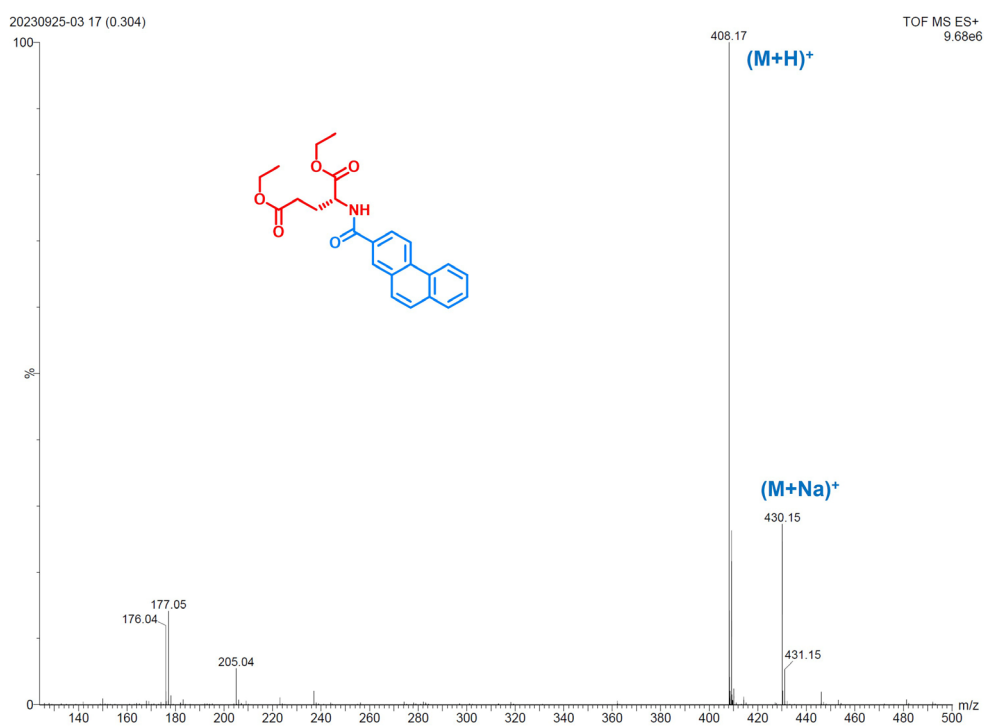


Figure S8. ESI-MS spectra of **DPh**, Calc: $C_{24}H_{25}NO_5 = 407.47$, found: $408.17 (M+H)^+$, $430.15 (M+Na)^+$.

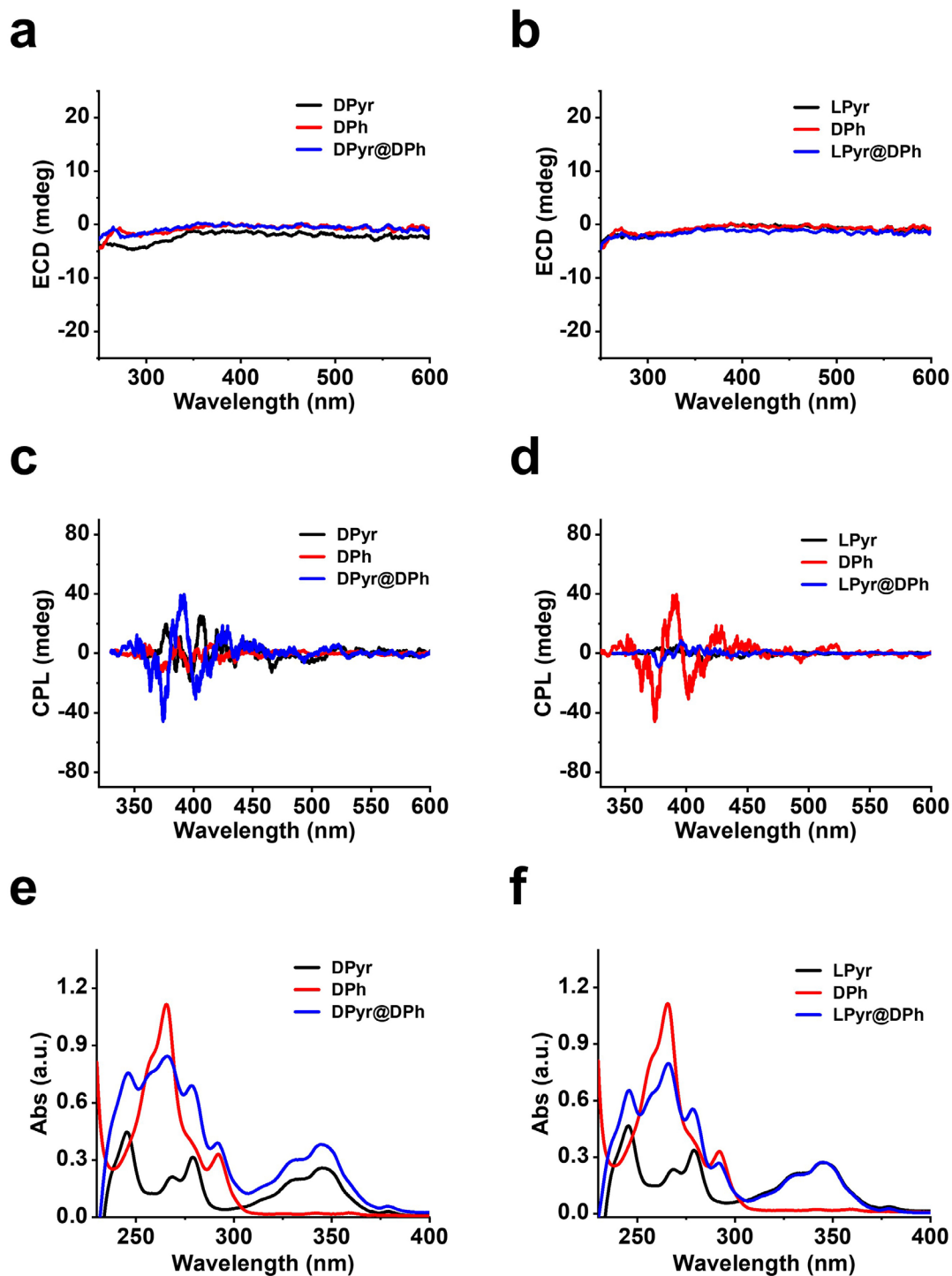


Figure S9. (a,b) ECD, (c,d) CPL, and (e,f) UV-Vis spectra of DPyr, LPyr, DPh and DPyr/LPy & DPh complex solutions in TCM solution (1×10^{-4} M). (Note: λ_{ex} : 320 nm, slit: 3000 μm for CPL and 2 nm for FL at both excitation and emission sides)

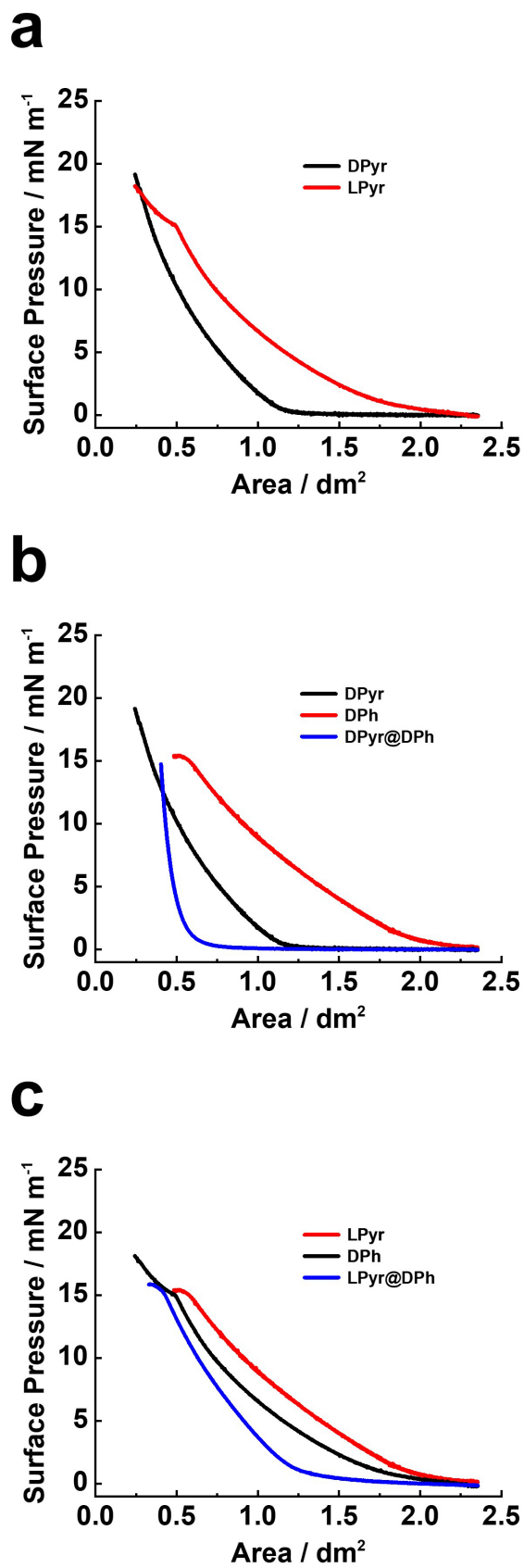


Figure S10. (a-c) The π -A isotherms curves of DPyr, LPyr, DPh, DPyr@DPh and LPyr@DPh at the air/water interface (pure water subphase, $18.2 \text{ M}\Omega \cdot \text{cm}$, $25 \text{ }^\circ\text{C}$).

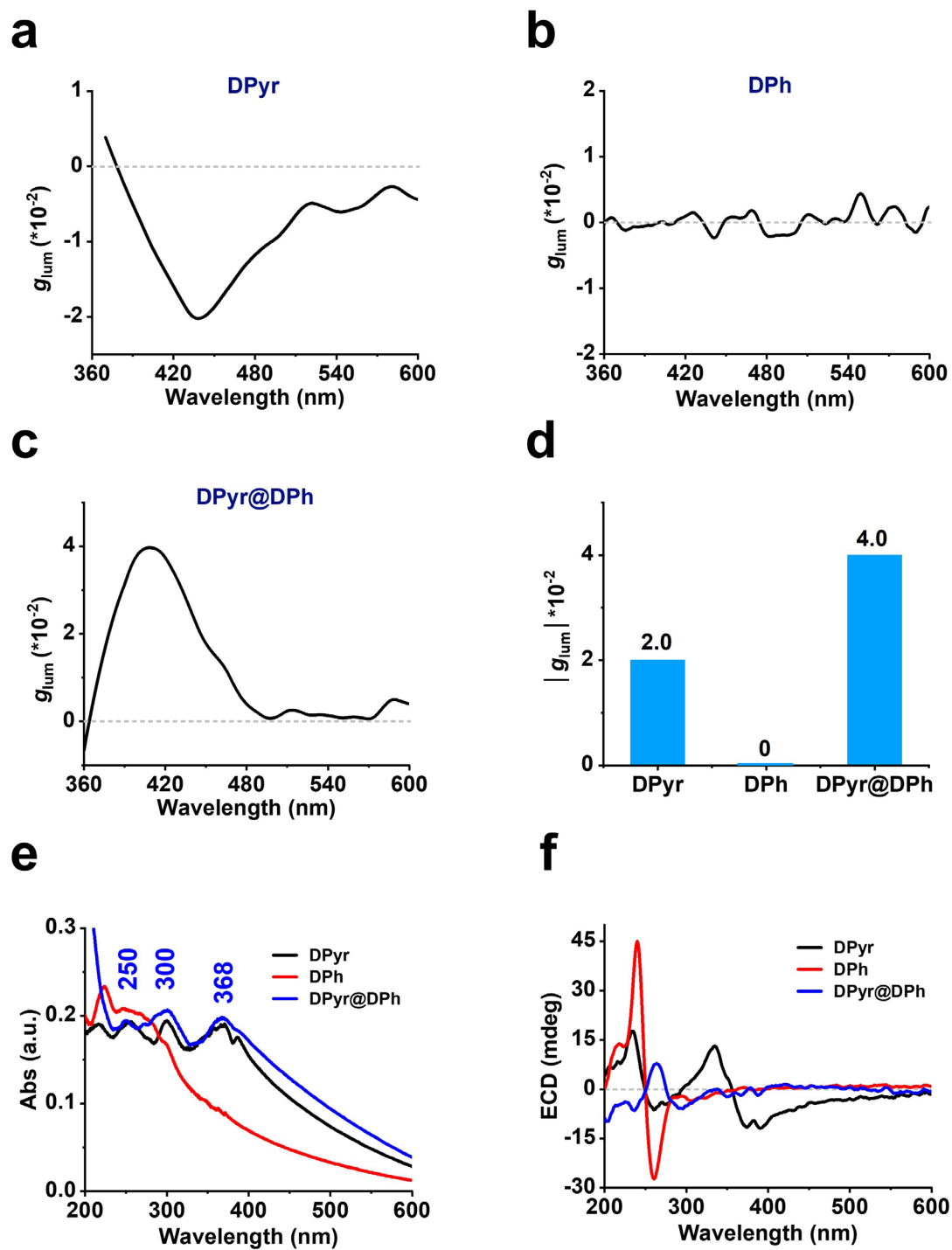


Figure S11. The (a-c) g_{lum} , (e) UV-Vis and (f) ECD spectra of (a) DPyr and (b) DPh and (c) DPyr@DPh LS films (75 layers at 10 mN/m). (d) The comparison of the absolute values of the maximum g_{lum} of DPyr and DPh and DPyr@DPh LS films from pure water subphases at 25 °C. (Note: λ_{ex} : 320 nm, slit: 3000 μ m for both excitation and emission sides).

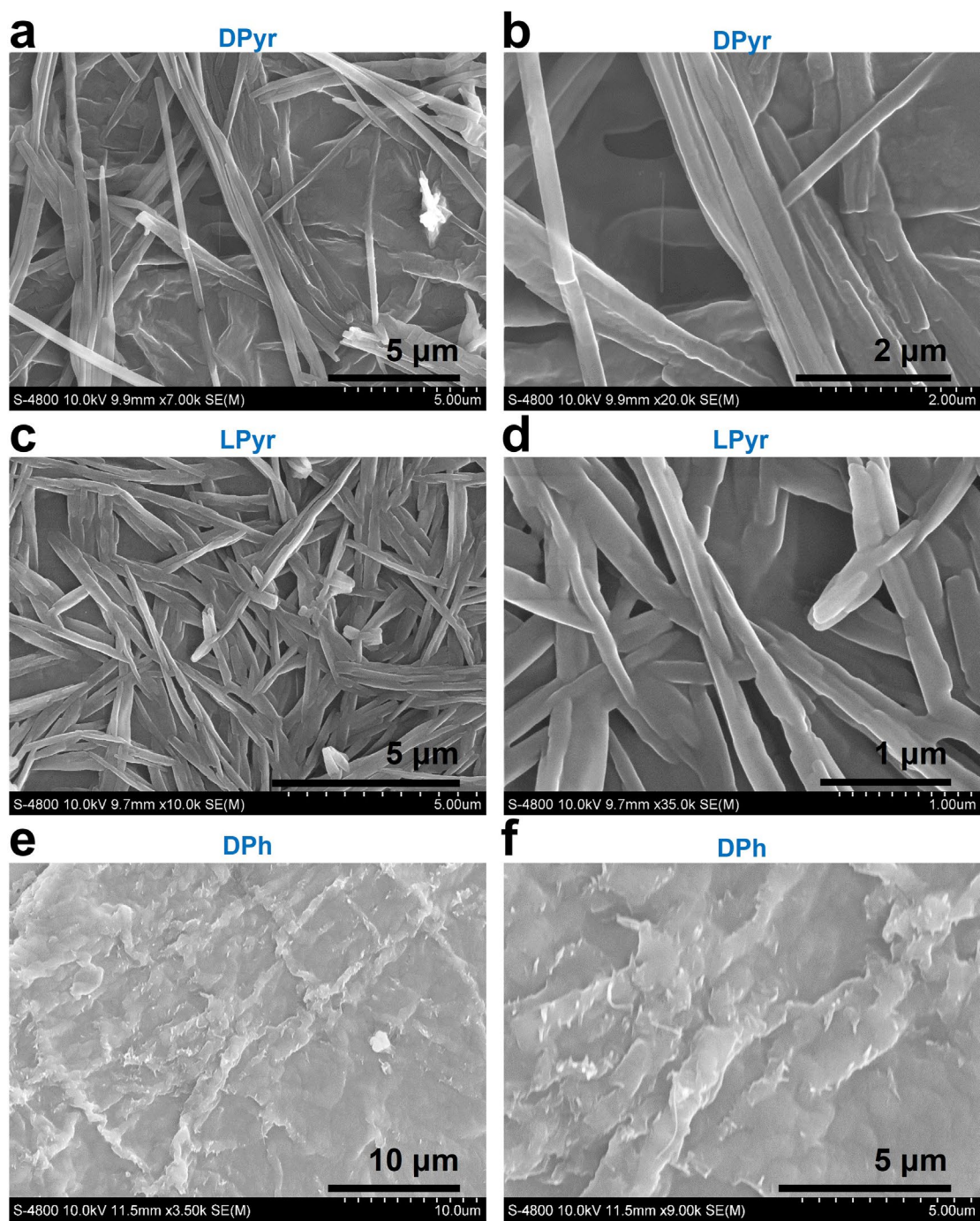


Figure S12. the low-resolution SEM and TEM pictures of (a,b) DPyr, (c,d) LPyr, (e,f) DPh LS films (310 layers at 10 mN/m).

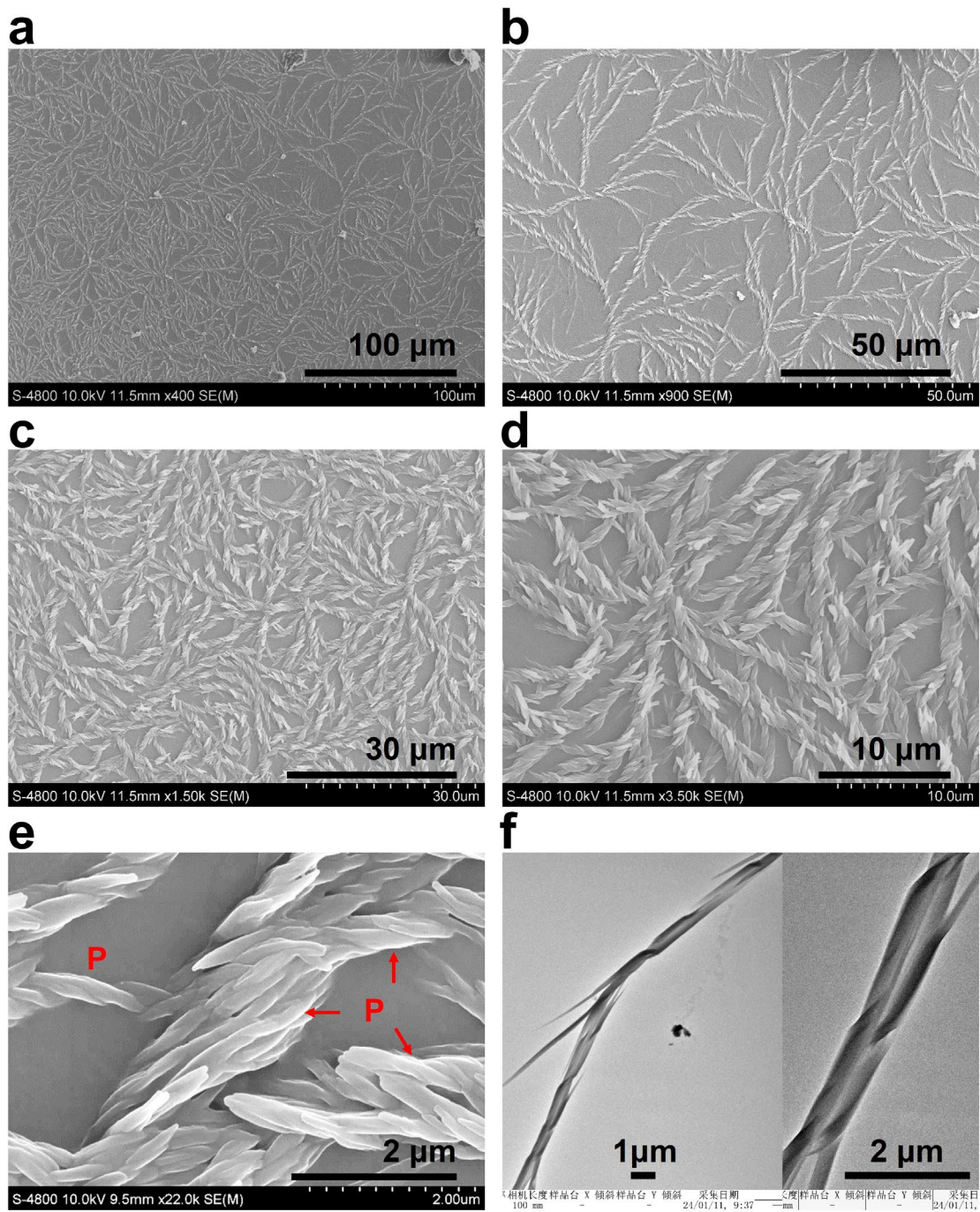


Figure S13. the low-resolution SEM and TEM pictures of Dpyr@DPh LS films (310 layers at 10 mN/m).

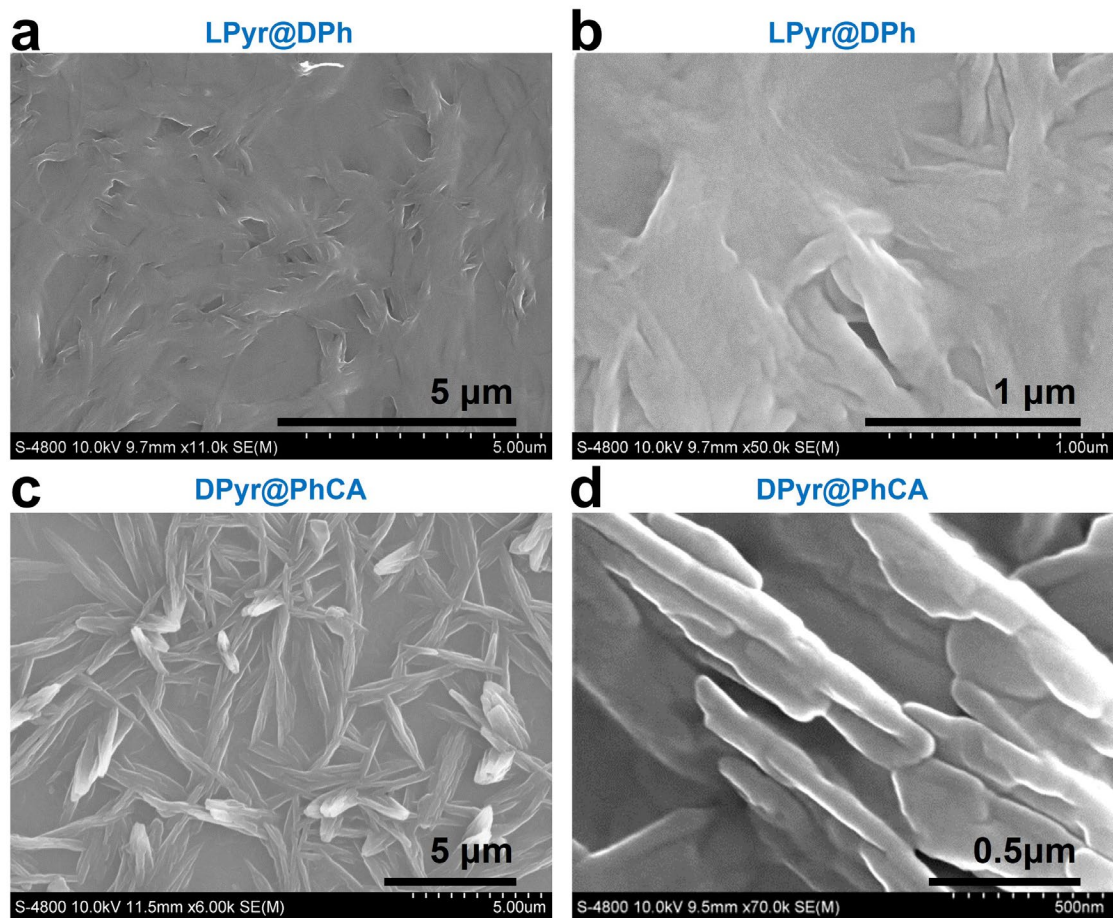


Figure S14. the low-resolution SEM pictures of (a,b) LPyr@DPh, (c,d) DPyr@PhCA LS films (310 layers at 10 mN/m).

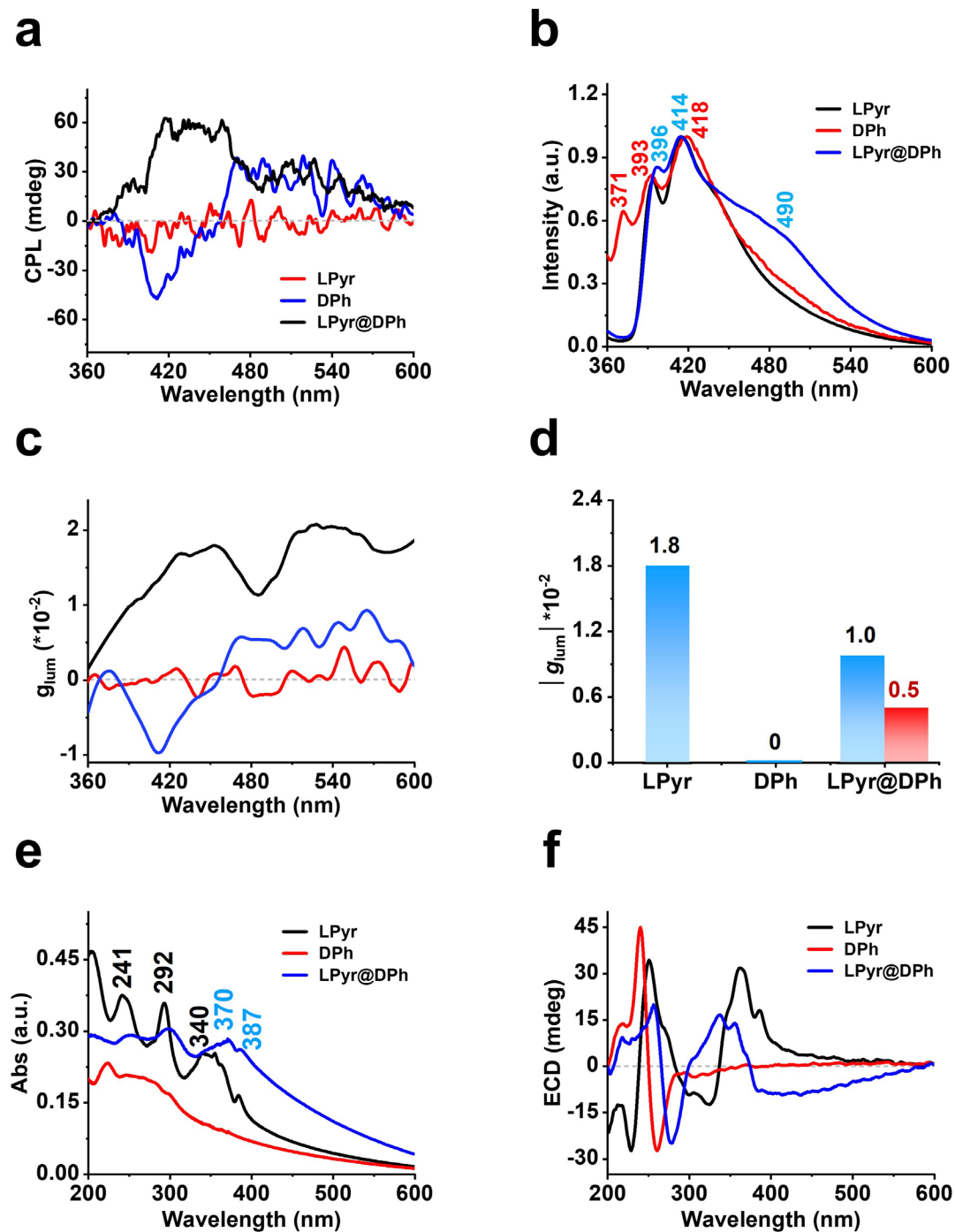


Figure S15. The (a) CPL, (b) FL, (c) g_{lum} , (e) UV-Vis and (f) ECD spectra of LPyr and LPyr@DPh LS films (75 layers at 10 mN/m). (d) The comparison of the absolute values of the maximum g_{lum} of LPyr and DPh and LPyr@DPh LS films from pure water subphases at 25 °C. (Note: λ_{ex} : 320 nm, slit: 3000 μm for both excitation and emission sides).

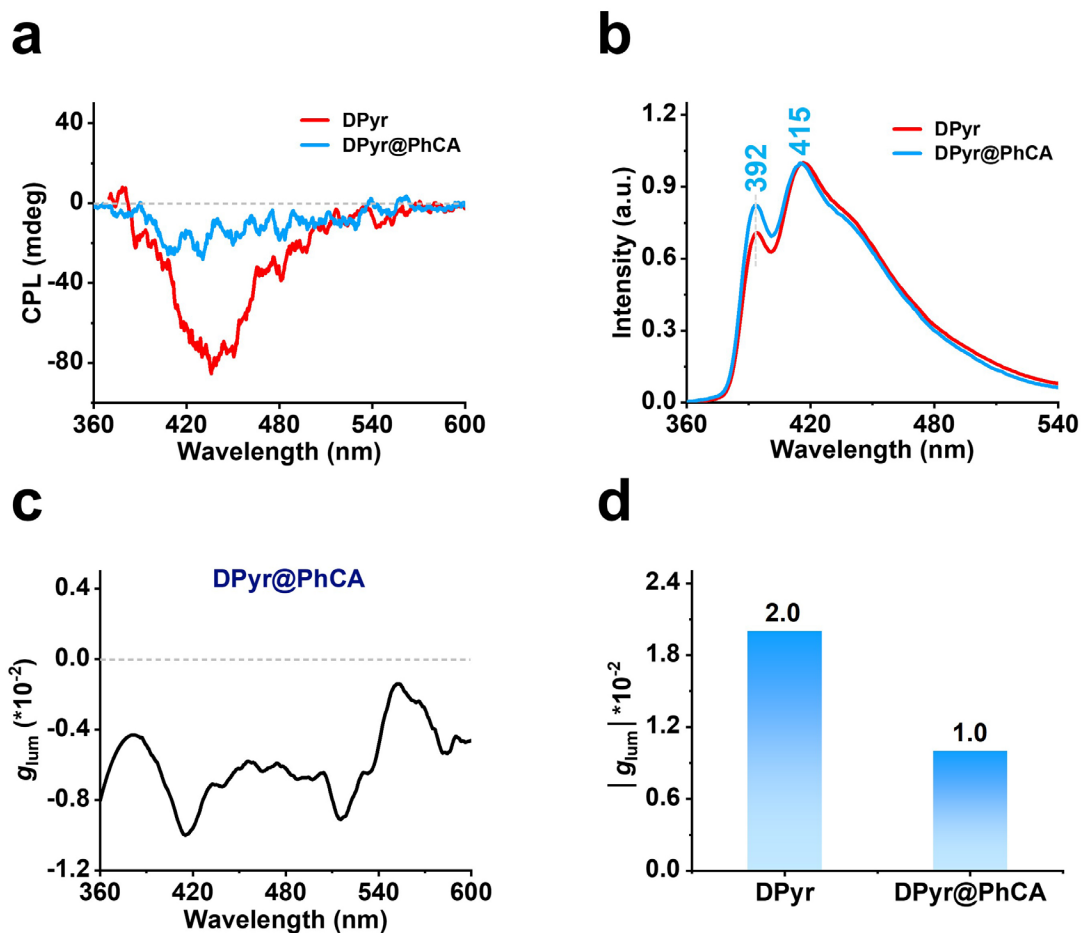


Figure S16. The (a) CPL, (b) FL and (c) g_{lum} spectra of DPyr and DPyr@PhCA LS films (75 layers at 10 mN/m). (d) The comparison of the absolute values of the maximum g_{lum} of DPyr and DPyr@PhCA LS films from pure water subphases at 25 °C. (Note: λ_{ex} : 320 nm, slit: 3000 μm for both excitation and emission sides)

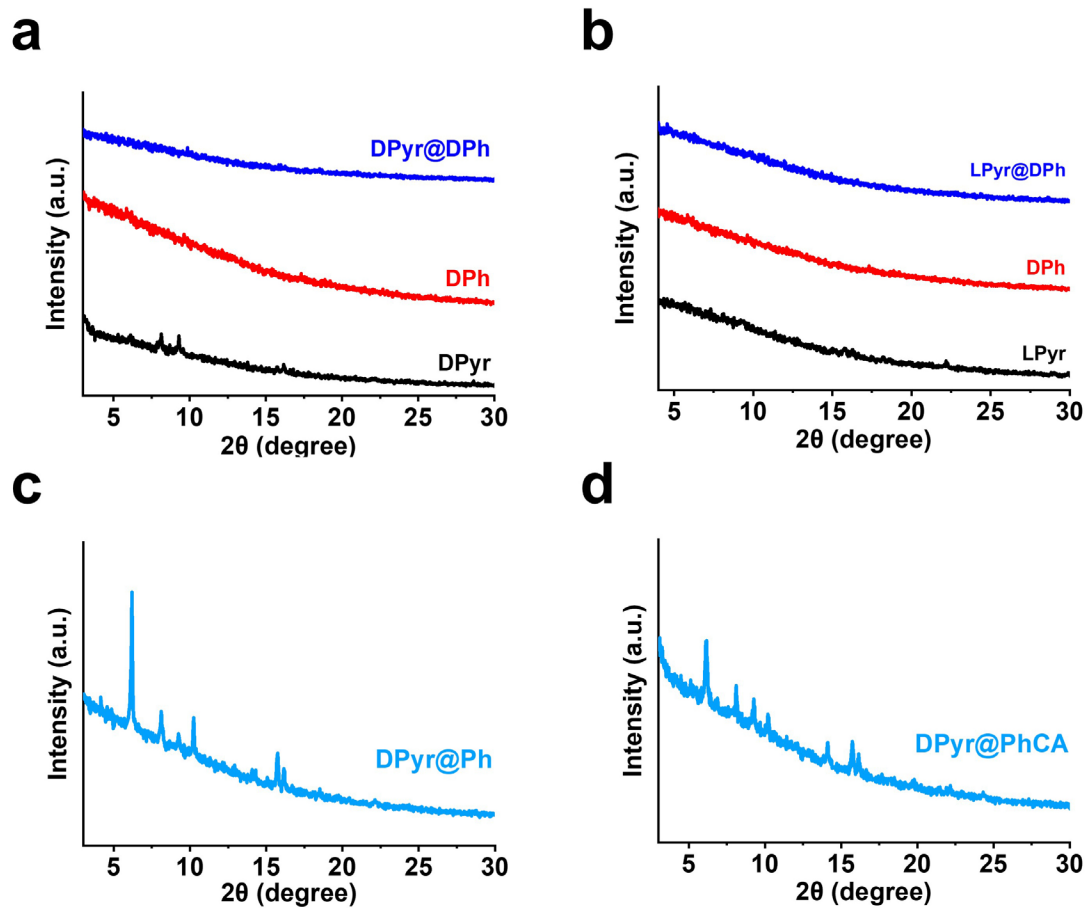


Figure S17. the XRD spectra of DPyr, DPh, LPyr, DPyr@DPh, LPyr@DPh and DPyr@Ph, DPyr@PhCA LS films (310 layers at 10 mN/m).

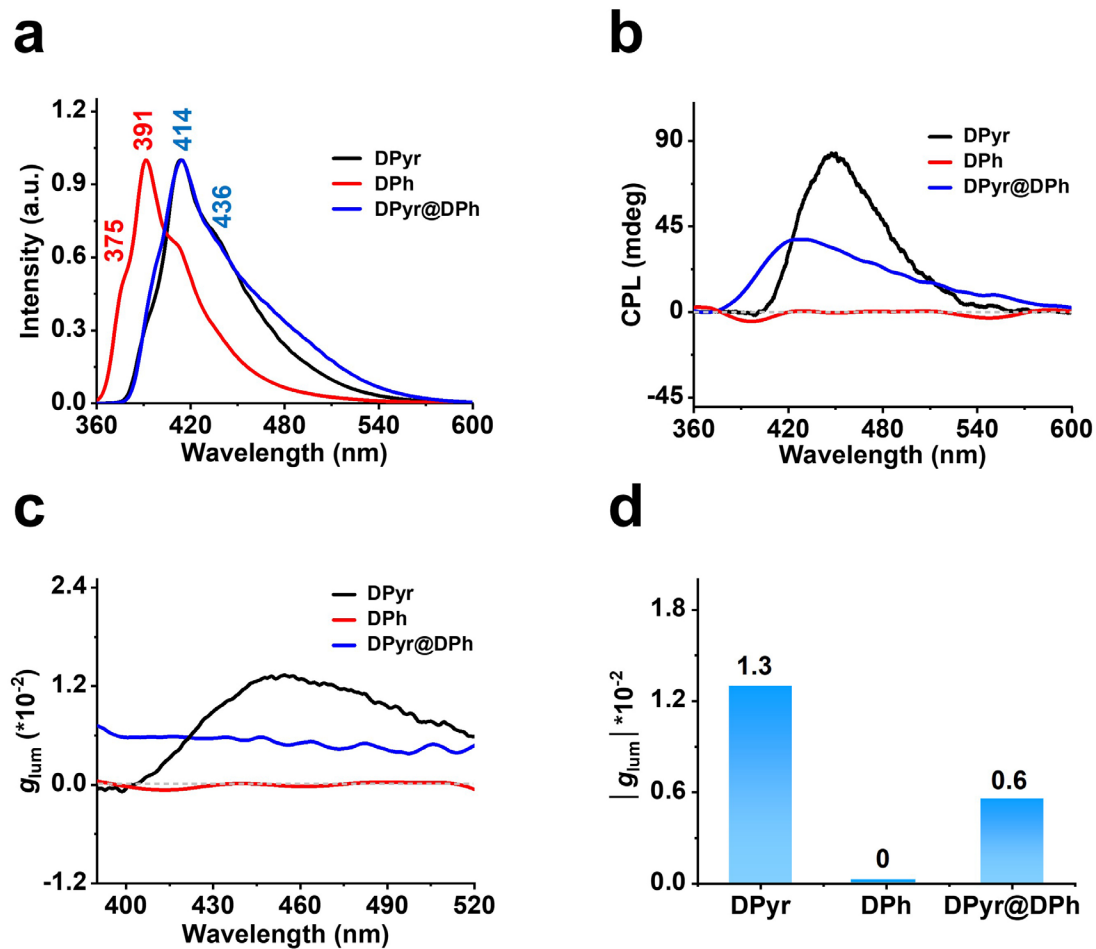


Figure S18. The g_{lum} spectra of (a) DPyr and (b) DPh and (c) DPyr@DPh gels from bulk self-assembly. (Note: λ_{ex} : 320 nm, slit: 3000 μm for both excitation and emission sides).

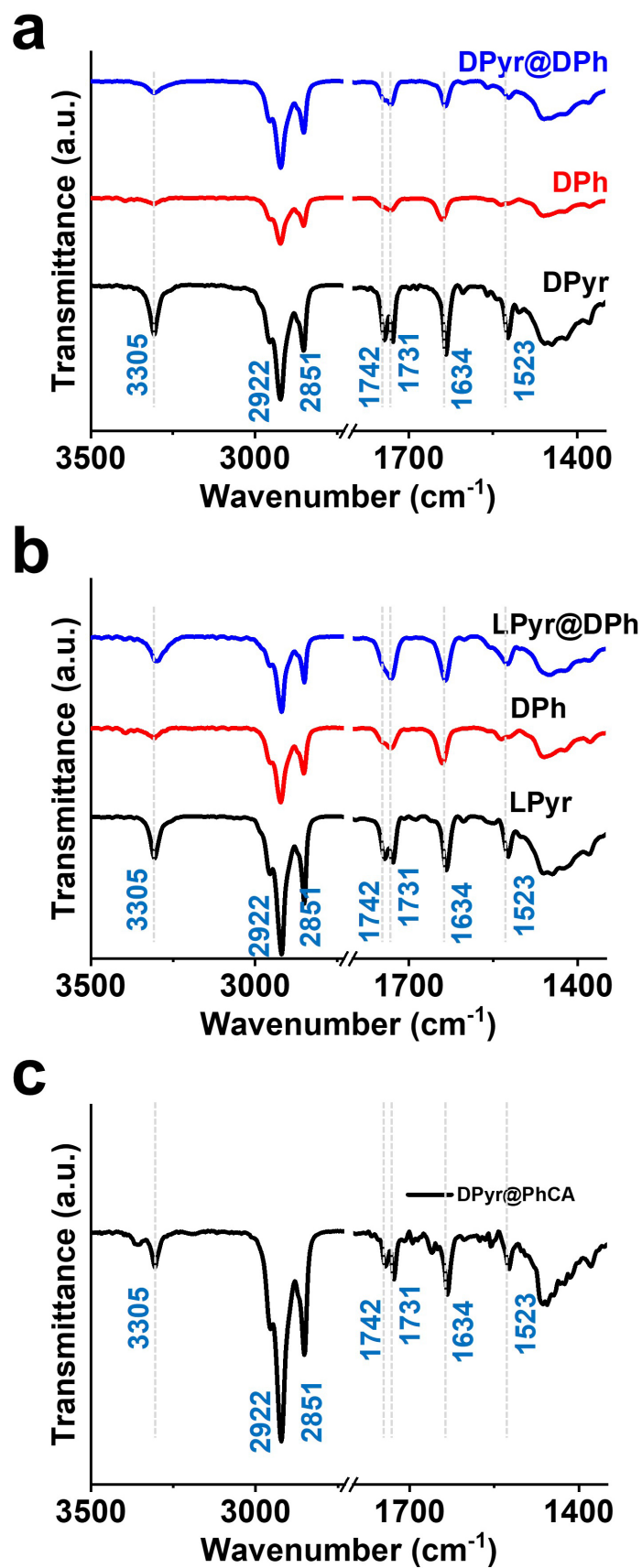


Figure S19. the FT-IR spectra of DPyr, DPh, LPyr, DPyr@DPh, LPyr@DPh and DPyr@PhCA LS films (310 layers at 10 mN/m).

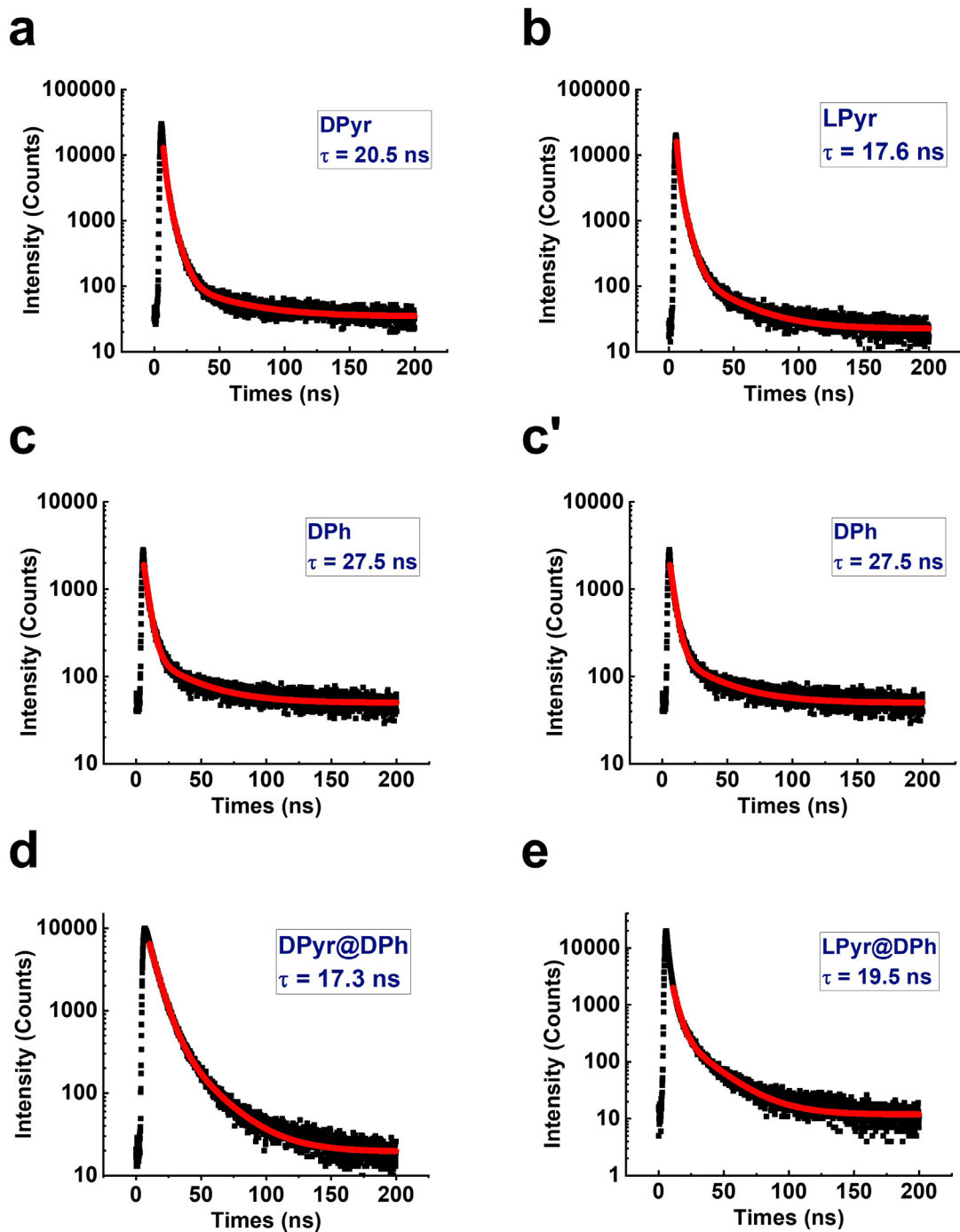


Figure S20. the lifetime spectra (a-e) of DPyr, LPyr, DPh, DPyr@DPh, LPyr@DPh LS films (75 layers at 10 mN/m).

Table S1. the photoluminescent QYs and lifetimes.

	LS films			Solution (1×10^{-4} M)		
	DPyr	DPh	DPyr@DPh	DPyr	DPh	DPyr@DPh
QY (%)	4.4	0.5	10.5	47.2	<1	41.1
lifetime (ns)	20.5	27.5	17.3	12.8	1.6	12.4

Table S2. Crystal data and structure refinement for DPyr

Identification code	TX15307 (DPyr)
Empirical formula	C ₂₆ H ₂₅ NO ₅
Formula weight	431.47
Temperature/K	169.99(10)
Crystal system	orthorhombic
Space group	P2 ₁ 2 ₁ 2 ₁
a/Å	5.0705(2)
b/Å	19.7168(7)
c/Å	21.8610(10)
α/°	90
β/°	90
γ/°	90
Volume/Å ³	2185.53(15)
Z	4
ρ _{calc} /g/cm ³	1.311
μ/mm ⁻¹	0.741
F(000)	912.0
Crystal size/mm ³	0.35 × 0.02 × 0.01
Radiation	Cu Kα (λ = 1.54184)
2θ range for data collection/°	6.036 to 163.932
Index ranges	-6 ≤ h ≤ 6, -16 ≤ k ≤ 24, -27 ≤ l ≤ 24
Reflections collected	12326
Independent reflections	4400 [R _{int} = 0.0650, R _{sigma} = 0.0717]
Data/restraints/parameters	4400/0/291
Goodness-of-fit on F ²	1.088
Final R indexes [I ≥ 2σ (I)]	R ₁ = 0.0646, wR ₂ = 0.1630
Final R indexes [all data]	R ₁ = 0.0799, wR ₂ = 0.1788
Largest diff. peak/hole / e Å ⁻³	0.38/-0.29
Flack parameter	-0.1(2)

3. References

(S1) P. F. Duan and M. H. Liu, *Langmuir* 2009, **25**, 8706-8713.

(S2) C. C. Yang, D. Yang, X. F. Zhu, Y. Meng and M. H. Liu, *Langmuir* 2020, **36**, 12366-12374.