Supporting Information

Synthesis and Property Modulation of Linearly Polarized Luminescent Side-chain Polymers with Room-temperature Phosphorescence

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Materials

Dibenzofuran (98%), anhydrous aluminum chloride (99%), boron tribromide (99.9%), 4-methoxybenzoyl chloride (97%), methacryloyl chloride (97%), 1, 2-dibromoethane (98%), 1, 4-dibromobutane (98%), 1, 6-dibromohexane (98%), methacrylic acid (99%), potassium bicarbonate (99%, $KHCO_3$), potassium carbonate (99%, K_2CO_3), potassium iodide (99.5%, KI), triethylamine (99.5%), N, N-dimethylformamide (99.9%), 2, 2′-azobis (2-methylpropionitrile) (98%, AIBN) was purchased from Energy Chemical Co., Ltd. Dichloromethane (AR), acetone (AR), ethanol (AR), ethyl acetate (AR), tetrahydrofuran (AR, THF), petroleum ether (AR) and other solvents were purchased from Huihong Reagent Co., Ltd. Among them, AIBN was recrystallized from ethanol before use. THF was refluxed with the addition of sodium metal to remove trace amounts of water.

Measurements and Characterizations

The ^{1}H NMR and ^{13}C NMR spectra of samples were measured by a Bruker ARX 400 MHz spectrometer. The molecular weight of compounds was determined by Bruker Biflex III MALDI-TOF spectrometer. Waters 1515 gel permeation chromatography was applied to measure the number-average molecular weight (Mn) and polymer dispersity index (PDI) of polymers using THF as eluent. Thermogravimetric analysis (TGA) was carried out using TA Q50 instrument with a heating rate of 10 ℃/min under N_2 atmosphere. The Leica DM 4500 P polarizing microscope instrument (POM) was used to record the phase textures and their changes during the cooling process of the polymers. The glass transition temperature of the polymers was measured by a TA Q10 DSC instrument under N_2 atmosphere. The UV-vis absorption spectra of samples were tested by Agilent Cary 100 instrument. The fluorescence spectra of samples were recorded on a PTI Qm 40 luminescence spectrometer. The phosphorescence spectra and phosphorescence lifetime of samples were measured by HORIBA QuantaMater 8000. The photoluminescence quantum yield of polymers was measured by FLS-1000. The micromorphology of polymer films and oriented polymer films was observed by JEOL JSM-6610 scanning electron microscope (SEM).

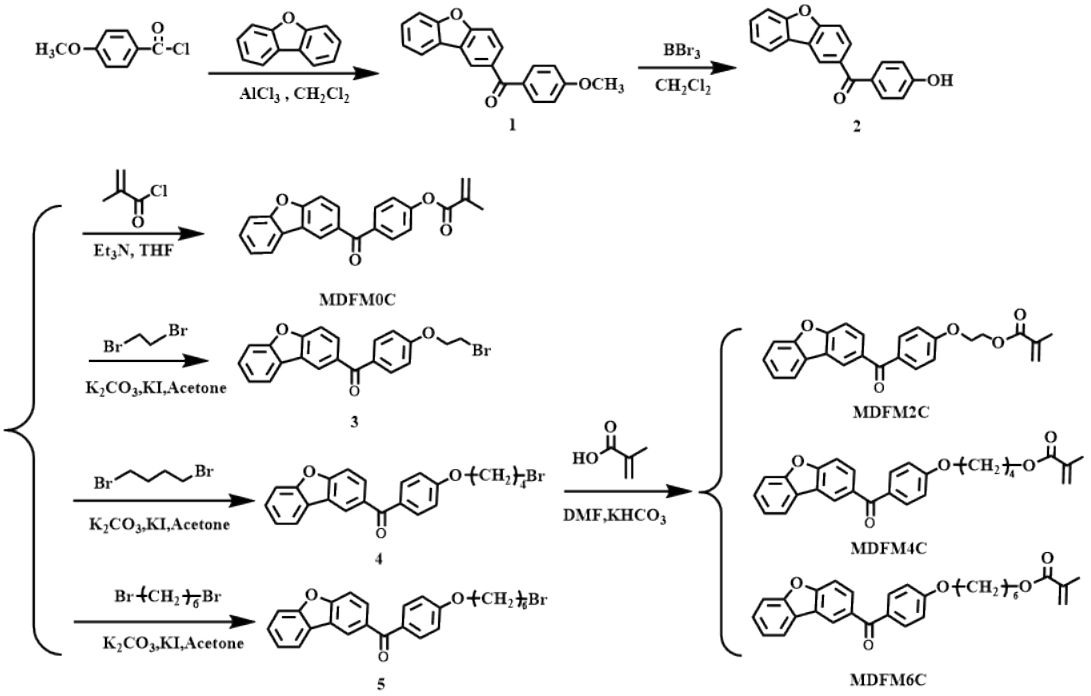

Figure S1. Synthetic routes of momomers MDFMmC (m = 0, 2, 4, 6).

Characterizations of Monomers

MDFM0C: ^{1}H NMR (δ, ppm, DMSO-d_6): 8.56 (s, 1H, Ph-H); 8.24 (d, J=15.6 Hz, 1H, Ph-H); 7.89-7.80 (m, 4H, Ph-H); 7.72 (d, J=13.6 Hz, 1H, Ph-H); 7.54 (t, J=23.6 Hz, 1H, Ph-H); 7.42-7.36 (m, 3H, Ph-H); 6.30 (s, 1H, =CH_2), 5.91 (s, 1H, =CH_2), 1.99 (s, 3H, -CH_3). ^{13}C NMR (δ, ppm, DMSO-d_6): 194.67, 165.38, 158.25, 156.63, 154.28, 135.52, 135.46, 132.83, 131.92, 130.08, 128.86, 128.75, 125.82, 124.28, 124.10, 123.89, 123.55, 122.54, 122.38, 113.38, 112.33, 112.24, 18.46. Mass Spectrometry (MS) (m/z) $[M]^+$ Calcd for $C_{23}H_{16}O_4$, 356.10, found 357.19 $[M+H]^+$.

MDFM2C: ^{1}H NMR (δ, ppm, $CDCl_3$): 8.39 (s, 1H, Ph-H), 7.97 (d, J=13.2 Hz, 1H, Ph-H), 7.91 (d, J=22.4 Hz, 1H, Ph-H), 7.85 (d, J=16.4 Hz, 2H, Ph-H), 7.62 (t, J=26.0 Hz, 2H, Ph-H), 7.53-7.47 (m, 1H, Ph-H), 7.38 (t, J=20.8 Hz, 1H, Ph-H), 6.98 (d, J=18.4 Hz, 2H, Ph-H), 6.10 (s, 1H, =CH_2), 5.56 (s, 1H, =CH_2), 4.24 (t, J=21.6 Hz, 2H, OCH_2-), 4.10 (t, J=38.0 Hz, 2H, OCH_2-), 1.94 (s, 3H, -CH_3). ^{13}C NMR (δ, ppm, $CDCl_3$): 195.08, 167.32, 162.06, 158.40, 156.87, 135.91, 133.16, 132.64, 132.57,

131.02, 129.56, 127.95, 126.31, 124.32, 123.76, 123.34, 123.16, 121.05, 114.22, 113.80, 111.97, 111.42, 66.13, 62.84, 18.35. Mass Spectrometry (MS) (m/z) $[M]^+$ Calcd for $C_{25}H_{20}O_5$, 400.43, found 401.37 $[M+H]^+$.

MDFM4C: ^1H NMR (δ, ppm, $CDCl_3$): 8.39 (s, 1H, Ph-H), 7.97 (d, J=11.6 Hz, 1H, Ph-H), 7.92 (d, J=12.0 Hz, 1H, Ph-H), 7.86 (d, J=12.8 Hz, 2H, Ph-H), 7.62 (t, J=19.2 Hz, 2H, Ph-H), 7.53-7.48 (m, 1H, Ph-H), 7.38 (t, J=19.2 Hz, 1H, Ph-H), 7.02 (d, J=13.2 Hz, 2H, Ph-H), 6.16 (s, 1H, $=CH_2$), 5.61 (s, 1H, $=CH_2$), 4.54 (t, J=12.8 Hz, OCH_2-), 4.32 (t, J=11.6 Hz, 2H, OCH_2-), 1.96 (s, 3H, $-CH_2$-), 1.75-0.72 (m, 4H, $-CH_2$-). ^{13}C NMR (δ, ppm, $CDCl_3$): 195.12, 167.48, 162.63, 162.52, 158.36, 136.39, 133.29, 132.57, 130.57, 130.30, 129.54, 125.49, 124.29, 123.80, 123.46, 123.32, 123.19, 123.13, 114.07, 111.95, 111.38, 67.59, 64.23, 25.86, 25.41, 18.36. Mass Spectrometry (MS) (m/z) $[M]^+$ Calcd for $C_{27}H_{24}O$, 428.48, found 429.47 $[M+H]^+$.

MDFM6C: ^1H NMR (δ, ppm, DMSO-d_6): 8.48 (s, 1H, Ph-H); 8.20 (d, J=20.0 Hz, 1H, Ph-H); 7.82 (d, J=16.0 Hz, 1H, Ph-H); 7.76 (t, J=22.8 Hz, 3H, Ph-H); 7.69 (d, J=16.8 Hz, 1H, Ph-H); 7.52 (t, J=26.8 Hz, 1H, Ph-H); 7.38 (t, J=25.6 Hz, 1H, Ph-H); 7.02 (d, J=24.8 Hz, 2H, Ph-H); 5.97 (s, 1H, $=CH_2$); 5.59 (s, 1H, $=CH_2$); 4.03 (td, J=12.0, 8.0 Hz, OCH_2-); 1.83 (s, 3H, $-CH_3$); 1.73-1.66 (m, 2H, $-CH_2$-); 1.63-1.55 (m, 2H, $-CH_2$-); 1.43-1.31 (m, 4H, $-CH_2$-). ^{13}C NMR (δ, ppm, DMSO-d_6): 194.31, 167.00, 162.78, 157.91, 156.59, 136.44, 133.59, 132.70, 130.74, 130.10, 129.74, 128.72, 125.91, 124.11, 123.99, 123.62, 123.48, 122.22, 114.68, 112.26, 111.99, 68.23, 64.67, 28.88, 28.48, 25.64, 25.58, 18.43. Mass Spectrometry (MS) (m/z) $[M]^+$ Calcd for $C_{29}H_{28}O_5$, 456.19, found 457.35 $[M+H]^+$.

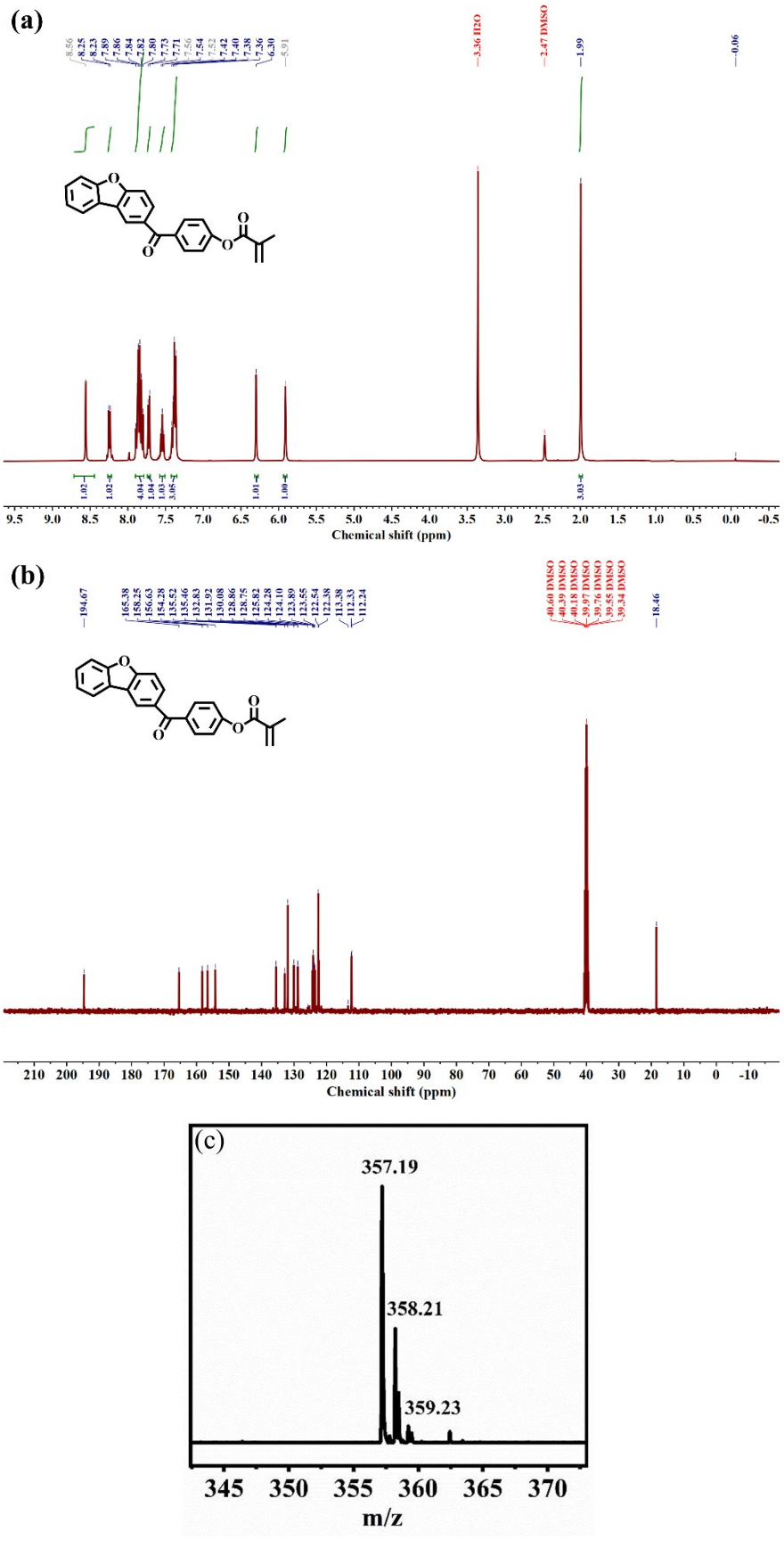

Figure S2. (a) ^{1}H NMR, (b) ^{13}C NMR and (c) MS spectra of MDFM0C in DMSO-d_6.

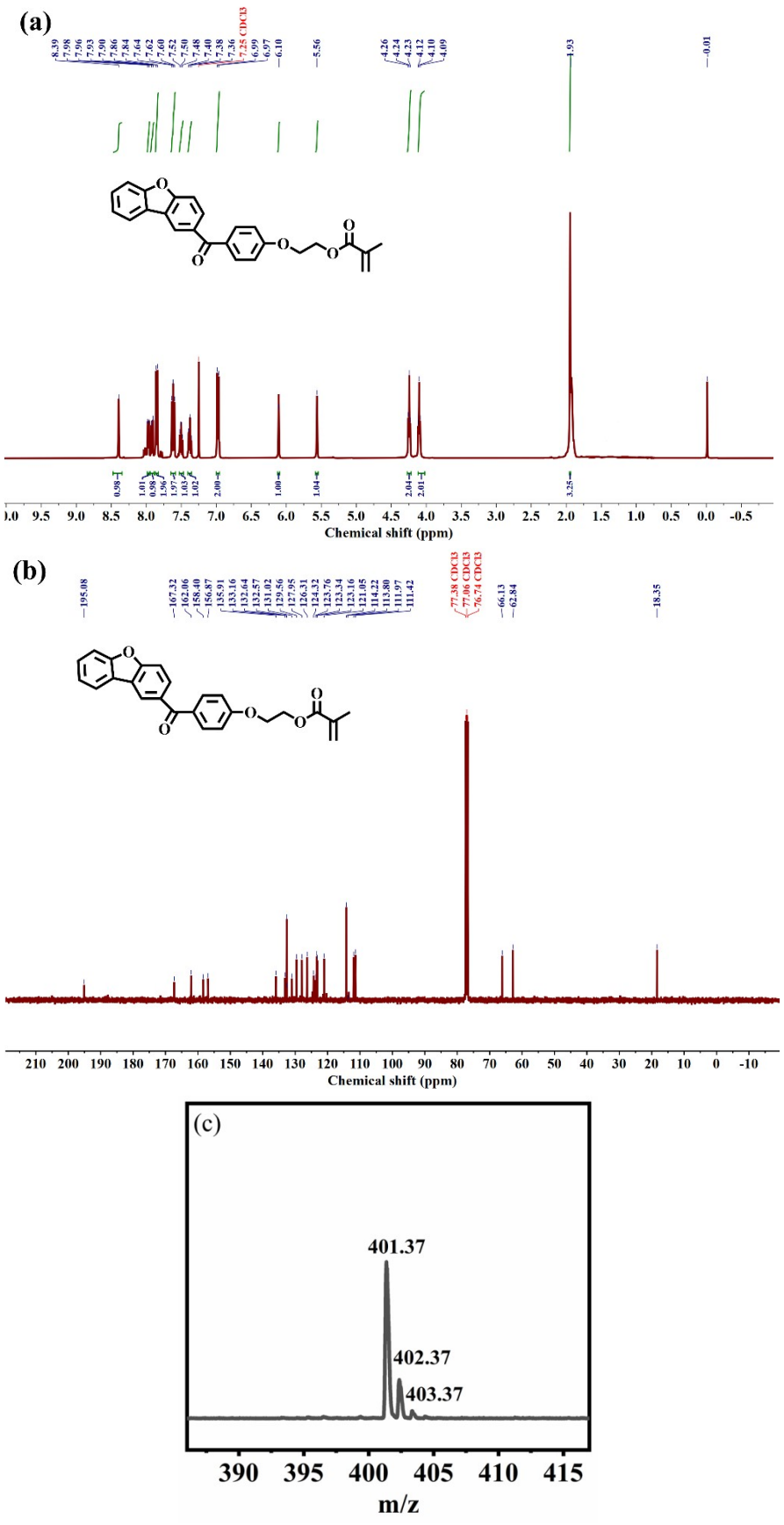

Figure S3. (a) ^{1}H NMR, (b) ^{13}C NMR and (c) MS spectra of MDFM2C in $CDCl_3$.

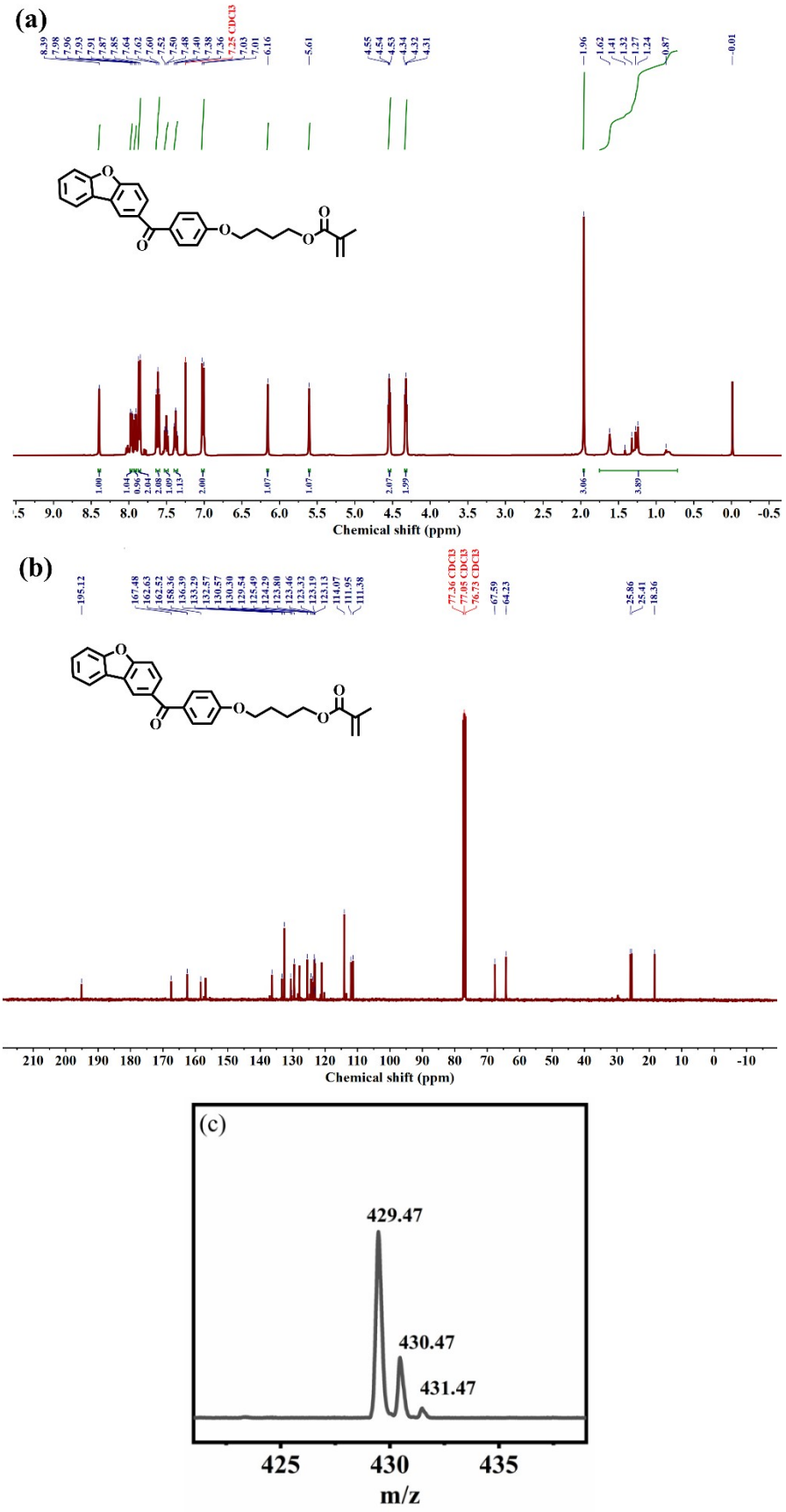

Figure S4. (a) ^{1}H NMR, (b) ^{13}C NMR and (c) MS spectra of MDFM4C in $CDCl_3$.

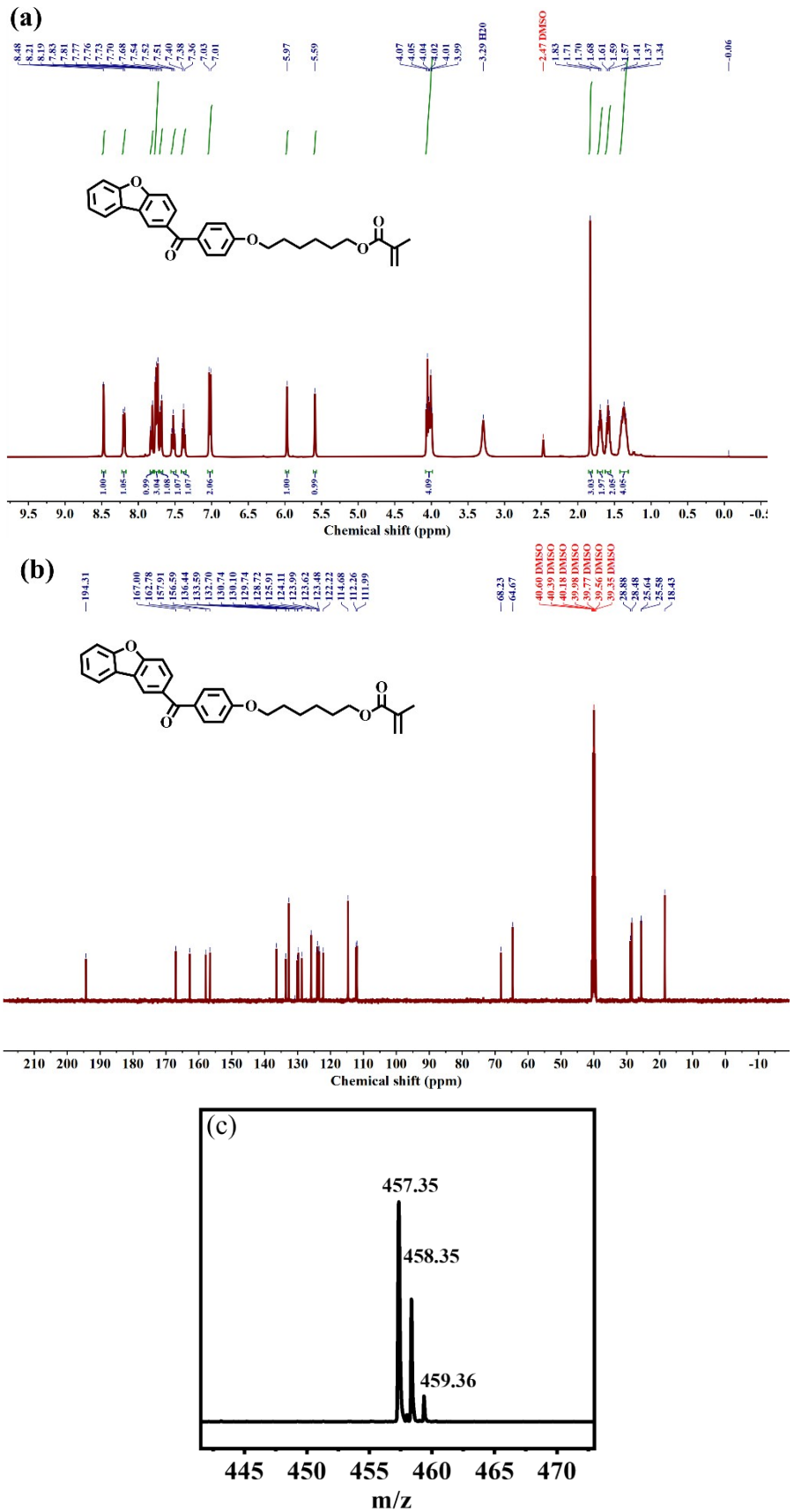

Figure S5. (a) ^{1}H NMR, (b) ^{13}C NMR and (c) MS spectra of MDFM6C in DMSO-d_6.

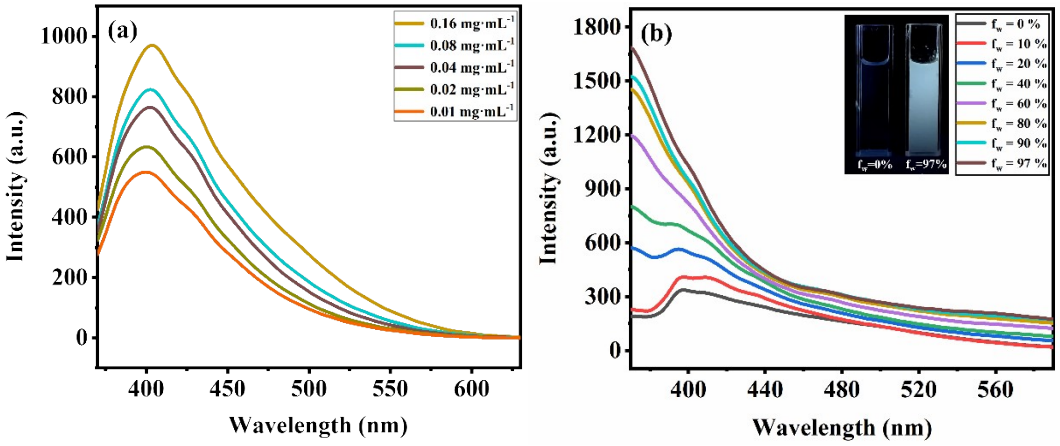

Figure S6. (a) Emission spectra of PMDFM4C in THF solutions with different polymer concentration (λ_{ex}=350 nm) and (b) in THF/H_2O mixtures with different volume fractions of H_2O (c=0.2 mg/mL, λ_{ex}=350 nm). The inserted pictures were taken under 365 nm UV light.

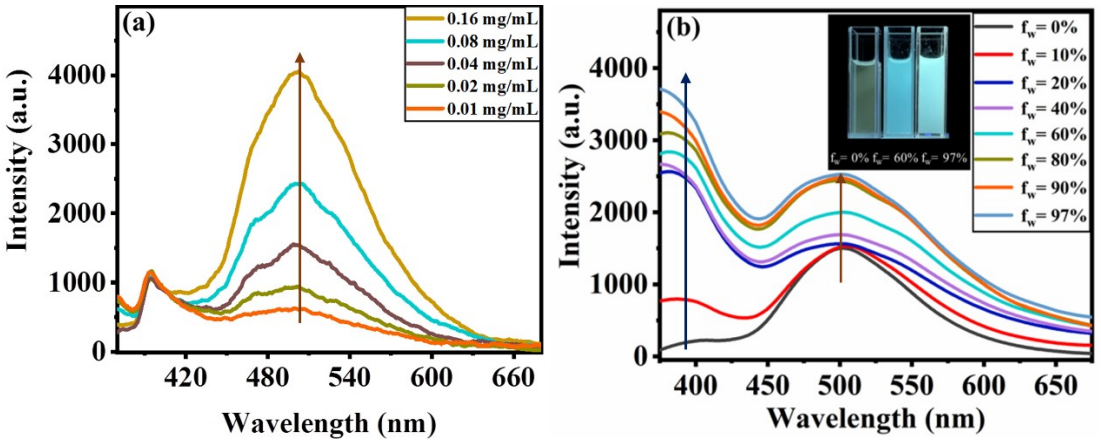

Figure S7. (a) Emission spectra of PMDFM0C in THF solutions with different polymer concentrations (λ_{ex}=350 nm) and (b) in THF/H_2O mixtures with different volume fractions of H_2O (c=0.2 mg/mL, λ_{ex}=350 nm). The inserted pictures were taken under 365 nm UV light.

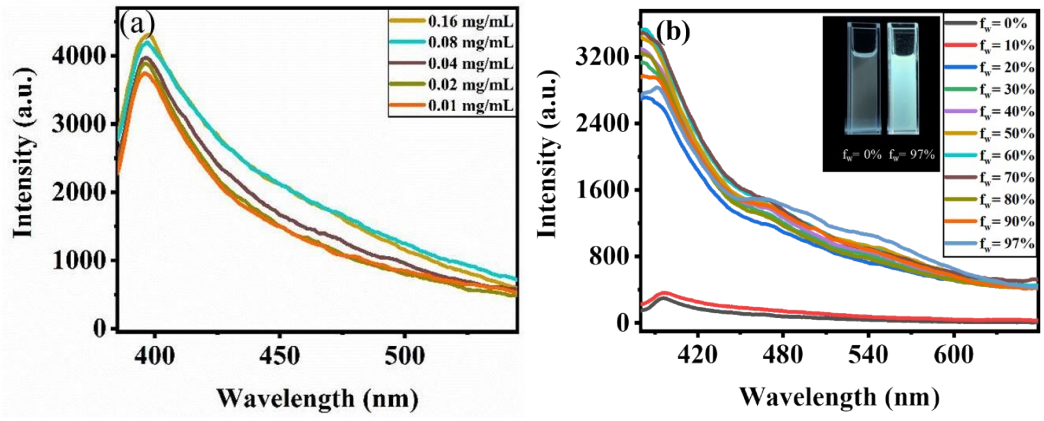

Figure S8. (a) Emission spectra of PMDFM6C in THF solutions with different polymer concentrations (λ_{ex}=350 nm) and (b) in THF/H_2O mixtures with different volume fractions of H_2O (c=0.2 mg/mL, λ_{ex}=350 nm). The inserted pictures were taken under 365 nm UV light.

Table S1. Photo-physical properties of PMDFM6C.

Polymers	**τ_{Phos}(ms)** [a]	**Φ(%)** [b]	**Φ_F(%)** [b]	**Φ_{Phos}(%)** [b]	**K_p (s^{-1})** [c]	**k_{nr}^{Phos} (s^{-1})** [d]
PMDFM6C	476.8	6.5	1.5	5.0	0.1	2.0

[a] Phosphorescence lifetime at 541 nm. [b] Measured by FLS 1000.

[c] Calculated by $k_p = \Phi_{Phos}/\tau_{Phos}$. [d] Calculated by $k_{nr}^{Phos} = (1 - \Phi_{Phos})/\tau_{Phos}$.

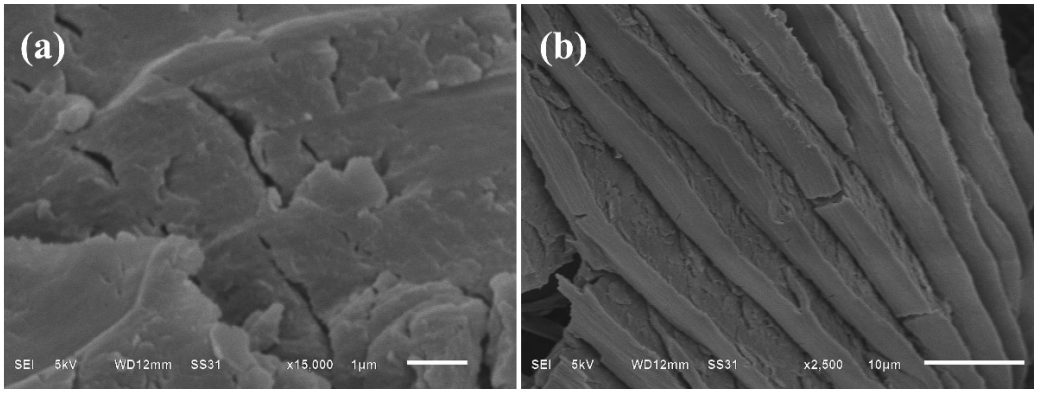

Figure S9. The SEM images of the unoriented (a) and (b) oriented PMDFM6C films.

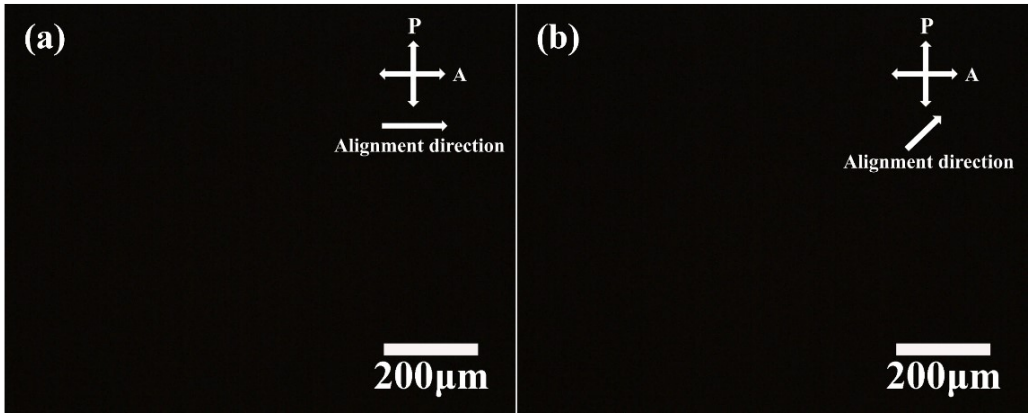

Figure S10. POM images of the oriented PMDFM0C film at room temperature. The alignment direction is parallel (a) and 45° (b) to the crossed polarizer.

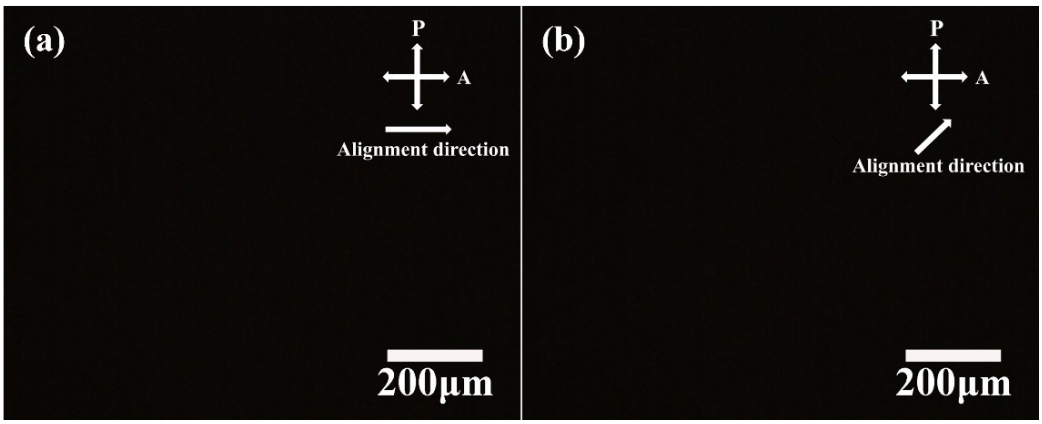

Figure S11. POM images of the oriented PMDFM2C film at room temperature. The alignment direction is parallel (a) and 45° (b) to the crossed polarizer.

Figure S12. POM images of the oriented PMDFM4C film at room temperature. The alignment direction is parallel (a) and 45° (b) to the crossed polarizer.

Figure S13. POM images of the oriented PMDFM6C film at room temperature. The alignment direction is parallel (a) and 45° (b) to the crossed polarizer.

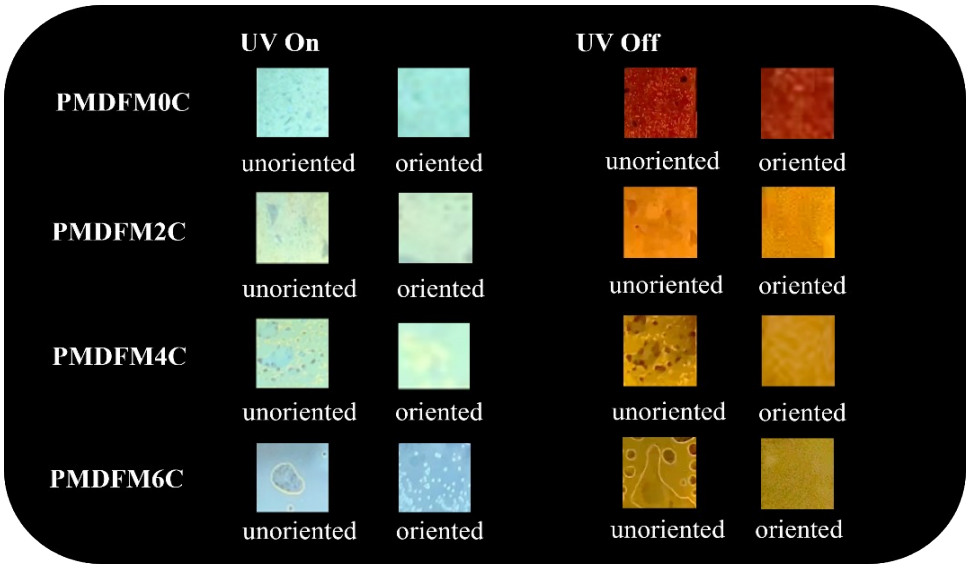

Figure S14. Photographs of unoriented and oriented polymer films under 365 nm UV light and after removing the excitation light source.

Table S2. The luminescent quantum yield of PMDFM6C films before and after orientation.

	Φ(%)	**Φ_F(%)**	**Φ_{Phos}(%)**
unoriented	6.5	1.5	5.0
oriented	5.1	1.2	3.9

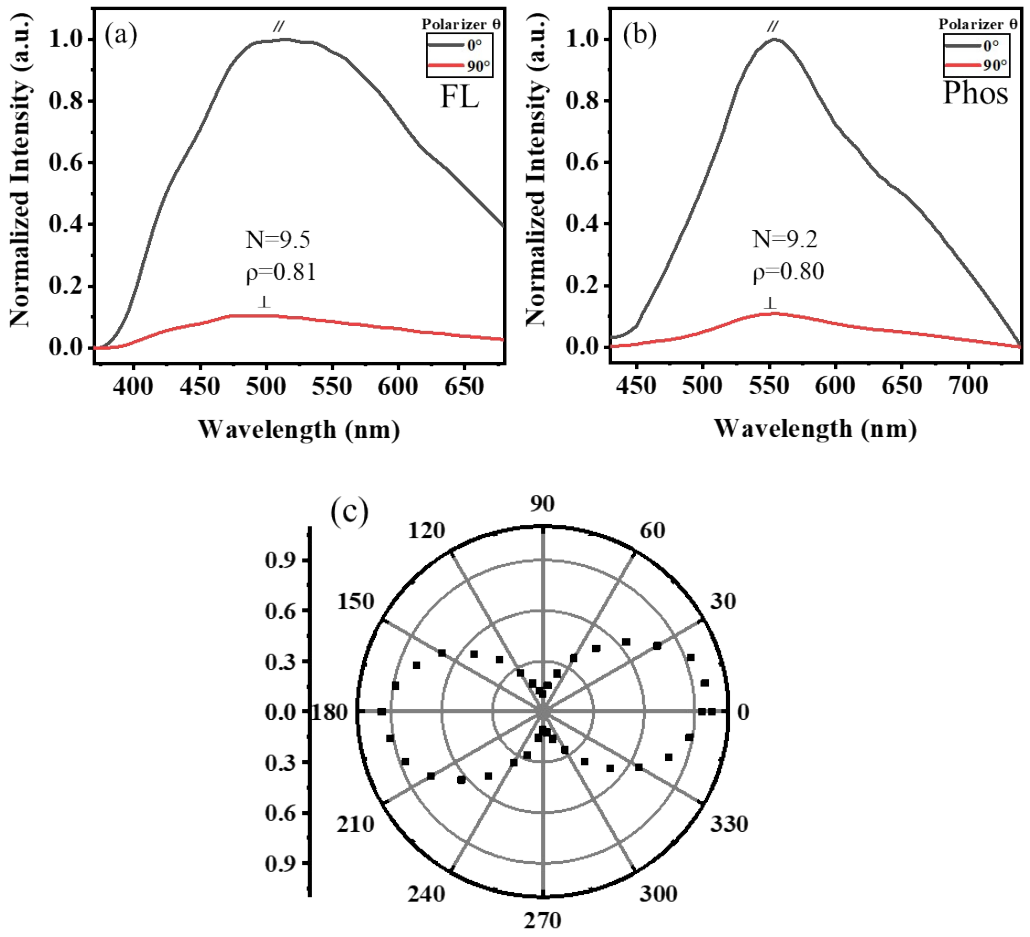

Figure S15. (a) Linearly polarized fluorescence spectra (λ_{ex}=350 nm) and (b) linearly polarized phosphorescence spectra (λ_{ex}=380 nm, T_d=0.2 ms) of the oriented PMDFM0C film. (c) Normalized fluorescence intensity of the oriented PMDFM0C film with different polarization angles (λ_{ex}=350 nm).

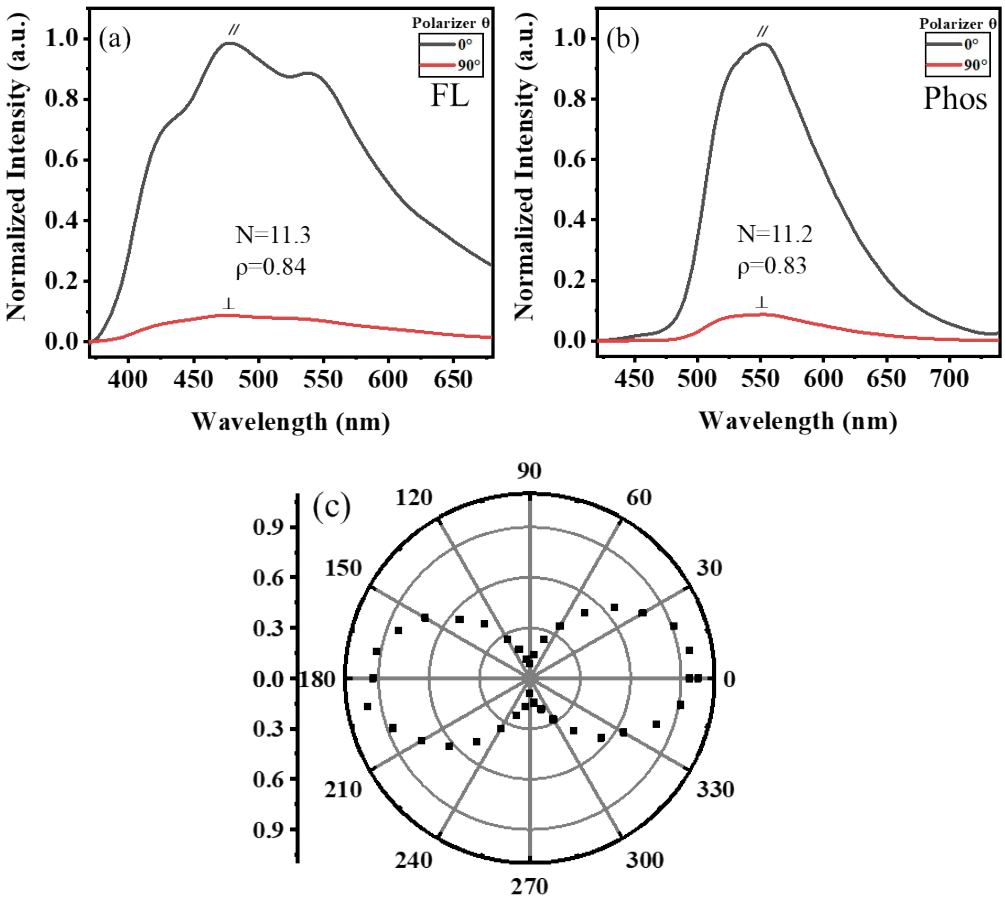

Figure S16. (a) Linearly polarized fluorescence spectra (λ_{ex}=350 nm) and (b) linearly polarized phosphorescence spectra (λ_{ex}=380 nm, T_d=0.2 ms) of the oriented PMDFM2C film. (c) Normalized fluorescence intensity of the oriented PMDFM2C film with different polarization angles (λ_{ex}=350 nm).

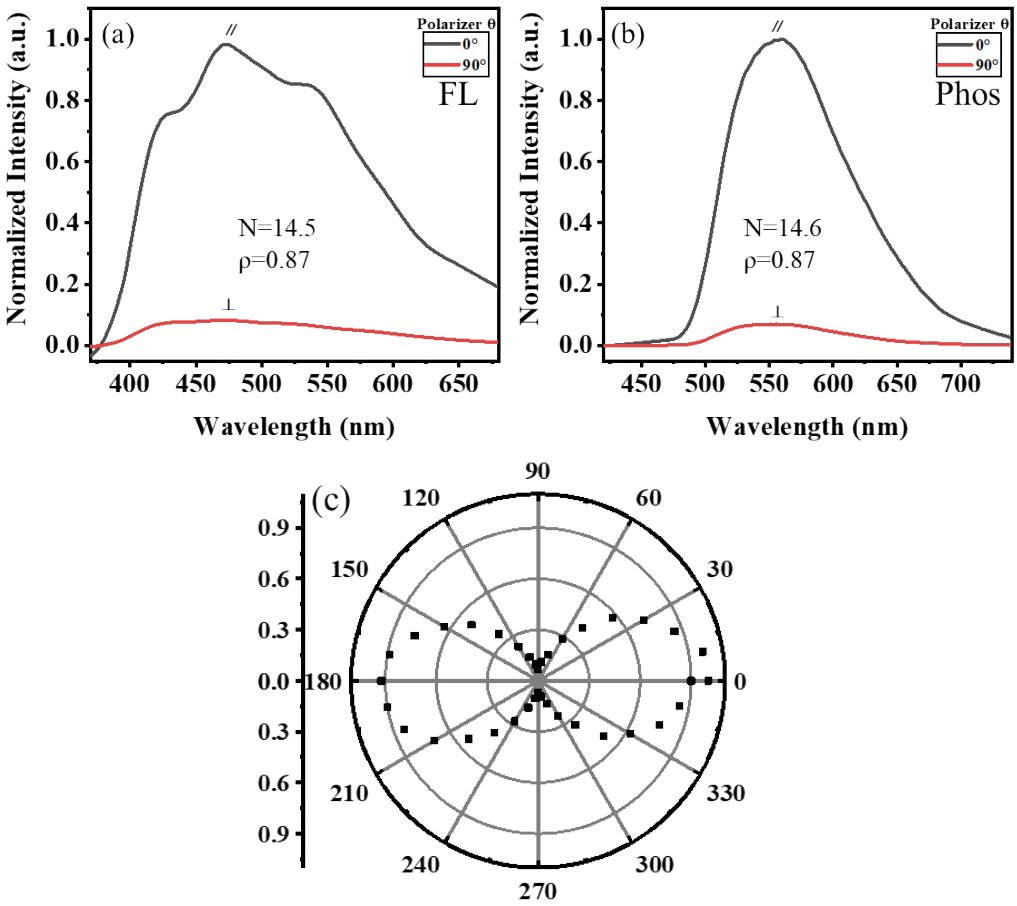

Figure S17. (a) Linearly polarized fluorescence spectra (λ_{ex}=350 nm) and (b) linearly polarized phosphorescence spectra (λ_{ex}=380 nm, T_d=0.2 ms) of the oriented PMDFM4C film. (c) Normalized fluorescence intensity of the oriented PMDFM4C film with different polarization angles (λ_{ex}=350 nm).