Electronic Supplementary Material (ESI) for Journal of Materials Chemistry C.

Supporting Information

Alkoxy chain regulated stimuli responsive AIE luminogens based on tetraphenylethylene substituted phenanthroimidazole derivatives and non-doped OLEDs with negligible efficiency roll-off

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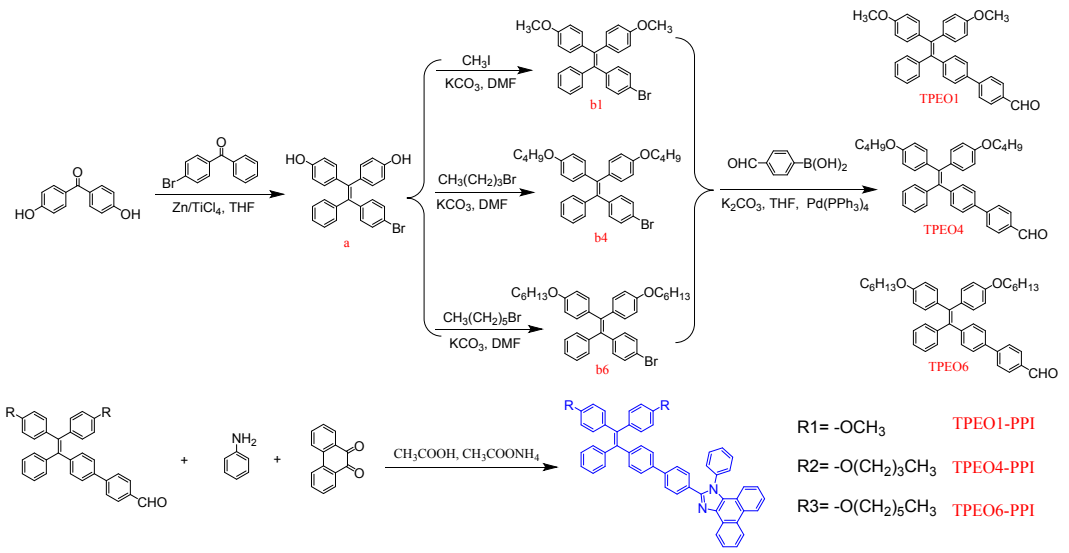
1. Synthesis and characterization



Scheme S1. Synthesis route of **TPEO1-PPI, TPEO4-PPI and TPEO6-PPI.**

Synthesis of 4,4′-(2-(4-bromophenyl)-2-phenylethene-1,1-diyl) -diphenol (a)

Into a 250 mL dry flask 4,4′- dihydroxybenzophenone (2.57 g, 12.00 mmol), 4-bromobenzophenone (6.50 g, 25.00 mmol) and zinc dust (6.53 g, 100 mmol). Next, the flask was vacuumed and purged with nitrogen for three times. Afterward, 150 mL of dried THF was injected into the flask, followed by cooling down to −10 °C . Then, $TiCl_4$ (5.60 mL, 50 mmol) was added into the mixture in a dropwise way. After half an hour, the reaction was then refluxed 12 h under nitrogen conditions. After the solution cooled to room temperature, hydrochloric acid (1 M) was added to the reaction mixture to remove zinc dust. The mixture was then extracted with dichlormethane and dried with anhydrous sodium sulfate. The crude product was purified by column chromatography on silica gel (200-300 mesh) using n-hexane and ethyl acetate (6:1 v/v) as the eluant to give 3.05 g white solid (**a**) in 58 % yield. ^{1}H NMR (400 MHz, DMSO-d6) δ 9.36 (d, *J* = 17.4 Hz, 1H), 7.31 (d, *J* = 8.4 Hz, 1H), 7.11 (dq, *J* = 14.5, 7.1 Hz, 2H), 6.93 (d, *J* = 6.9 Hz, 1H), 6.85 (d, *J* = 8.4 Hz, 1H), 6.74 (t, *J* = 8.2 Hz, 2H), 6.51 (dd, *J* = 18.4, 8.5 Hz, 2H). ^{13}C NMR (101 MHz, DMSO-d6) δ 156.6, 156.5, 144.2, 144.0, 141.8, 136.9, 134.3, 134.2, 133.4, 132.5, 132.5, 131.2, 131.2, 128.4, 126.7, 119.5, 115.2, 115.0. HR-MS m/z calcd for $C_{26}H_{19}BrO_2$ ($[M+H]^+$): 443.06412; found: 443.06423.

Synthesis of 4,4-(2-(4-Bromophenyl)-2-phenylethene-1,1-diyl) bis-((methoxyl) benzene) (b1)

Iodomethane (1.28 g, 9.04 mmol) was added to DMF (40 mL), containing (**a**) (1 g, 2.26 mmol) and K_2CO_3 (1.60 g, 11.30 mmol). Then, the reaction was stirred 15 h under nitrogen conditions at 70 °C. After the mixture cooled to room temperature, it was extracted with dichlormethane, washed with deionized water several times and dried with anhydrous magnesium sulfate. The crude product was purified by column chromatography on silica gel (200-300 mesh) using n-hexane and dichlormethane (10:1 v/v) as the eluant to give 0.9 g pale yellow viscous oil (**b1**) in 85 % yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.29 – 7.19 (m, 2H), 7.10 (d, *J* = 6.6 Hz, 1H), 7.01 (t, *J* = 7.8 Hz, 1H), 6.95 – 6.85 (m, 2H), 6.64 (dd, *J* = 14.2, 8.7 Hz, 1H), 3.80 – 3.65 (m, 2H).

Synthesis of 4,4-(2-(4-Bromophenyl)-2-phenylethene-1,1-diyl) bis-((butoxy) benzene) (b4)

1-bromobutane (1.51 g, 9.04 mmol) was added to DMF (40 mL), containing (**a**) (1 g, 2.26 mmol) and K_2CO_3 (1.60 g, 11.30 mmol). Then, the reaction was stirred 15 h under nitrogen conditions at 70 °C. After the mixture cooled to room temperature, it was extracted with dichlormethane, washed with deionized water several times and dried with anhydrous magnesium sulfate. The crude product was purified by column chromatography on silica gel (200-300 mesh) using n-hexane and dichlormethane (10:1 v/v) as the eluant to give 1.10 g pale yellow viscous oil (**b4**) in 88 % yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.21 (d, J = 8.4 Hz, 2H), 7.10 (q, J = 6.4 Hz, 3H), 7.00 (dd, J = 7.5, 1.7 Hz,2H), 6.90 (ddd, J = 11.2, 7.0, 3.8 Hz, 6H), 6.63 (dd, J = 14.3, 8.7 Hz, 4H), 3.96 – 3.83 (m, 4H), 1.79 – 1.67 (m, 4H), 1.47 (dp, J = 14.9, 7.6 Hz, 4H), 0.96 (q, J = 7.3 Hz, 6H).

Synthesis of 4,4-(2-(4-Bromophenyl)-2-phenylethene-1,1-diyl) bis-((hexyloxy) benzene) (b6)

1-bromohexane (1.44 g, 9.04 mmol) was added to DMF (50 mL), containing (**a**) (1 g, 2.26 mmol) and K_2CO_3 (1.60 g, 11.30 mmol). Then, the reaction was stirred 15 h under nitrogen conditions at 70 °C. After the mixture cooled to room temperature, it was extracted with dichlormethane, washed with deionized water several times and dried with anhydrous magnesium sulfate. The crude product was purified by column chromatography on silica gel (200-300 mesh) using n-hexane and dichlormethane (10:1 v/v) as the eluant to give 1.27 g pale yellow viscous oil (**b6**) in 92 % yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.21 (d, *J* = 8.4 Hz, 2H), 7.09 (t, J = 6.5 Hz, 3H), 7.03-6.96 (m, 2H), 6.94-6.84 (m, 6H), 6.62 (dd, J = 14.3,8.7 Hz, 4H), 3.87 (dt, *J* = 11.5, 6.6 Hz, 4H), 1.75 (dd, J = 15.4, 4H), 1.48 – 1.20 (m, 12H), 0.90 (q, *J* = 6.7 Hz, 6H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 157.9, 157.8, 143.9, 143.4, 141.0, 137.7, 135.8, 135.8, 133.1, 132.6, 132.5, 131.4, 130.8, 127.8, 126.2, 120.0, 113.7, 113.6, 67.9, 67.8, 31.6, 31.6, 29.3, 25.8, 25.8, 22.6, 14.1. HR-MS m/z

calcd for $C_{38}H_{43}BrO_2$ ([M+H]$^+$): 611.25192; found: 611.25176.

Synthesis of 4′-(1-Phenyl-2,2-bis(4-(methoxyl)phenyl)vinyl)-[1,1 -biphenyl]-4-carbaldehyde (TPEO1).

The product (**b1**) of the last step (0.94 g, 2.00 mmol) was added to mixture of THF (40 mL) and water (10 mL) solution, containing 4-formylphenylboronic acid (0.50 g, 3.50 mmol). The mixture was stirred at room temperature for 30 min and then K_2CO_3 (1.52 g, 11.00 mmol) and $Pd(PPh_3)_4$ (0.12 g, 0.10 mmol) were added to the mixture, followed by refluxing overnight under nitrogen conditions. After the mixture cooled down to room temperature, it was extracted with dichlormethane, washed with distilled water several times and dried with anhydrous magnesium sulfate. The crude product was purified by column chromatography on silica gel (200-300 mesh) using hexane and dichlormethane (5:1 v/v) as the eluant to give 0.75 g yellow viscous solid (**TPEO1**) in 76% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 10.03 (s, 1H), 7.91 (d, J = 8.0 Hz, 2H), 7.72 (d, J = 8.0 Hz, 2H), 7.41 (d, J = 8.0 Hz, 2H), 7.19 – 7.01 (m, 7H), 6.97 (dd, J = 14.7, 8.5 Hz, 4H), 6.65 (t, J = 8.4 Hz, 4H), 3.75 (s, 6H).

Synthesis of 4′-(1-Phenyl-2,2-bis(4-(butoxy)phenyl)vinyl)-[1,1 -biphenyl]-4-carbaldehyde (TPEO4).

The synthetic process is similar with **TPEO1** to yield a yellow powder (**TPEO4**) in 78% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 10.01 (s, 1H), 7.90 (d, J = 15.9 Hz, 2H), 7.72 (d, J = 8.3 Hz, 2H), 7.40 (d, J = 8.4 Hz, 2H), 7.12 (dd, J = 10.9, 4.0 Hz, 4H), 7.05 (dd, J = 7.7, 1.7 Hz, 2H), 6.94 (dd, J = 14.6, 8.8 Hz, 4H), 6.63 (t, J = 8.5 Hz, 4H), 3.88 (t, J = 6.5 Hz, 3H), 1.76 – 1.68 (m, 3H), 1.46 (dqd, J = 14.8, 7.4, 2.1 Hz, 4H), 0.95 (td, J = 7.4, 3.4 Hz, 5H).

Synthesis of 4′-(1-Phenyl-2,2-bis(4-(hexyloxy)phenyl)vinyl)-[1,1 -biphenyl]-4-carbaldehyde (TPEO6).

The synthetic process is similar with **TPEO1** to yield a yellow powder (**TPEO6**) in 75% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 10.03 (s, 1H), 7.91 (d, *J* = 8.3 Hz, 2H), 7.72 (d, *J* = 8.2 Hz, 2H), 7.40 (d, *J* = 8.3 Hz, 2H), 7.16 – 7.08 (m, 5H), 7.06 (dd, *J* = 7.6, 5.7 Hz, 2H), 6.95 (dt, *J* = 11.8, 8.2 Hz, 4H), 6.63 (t, *J* = 8.5 Hz, 4H), 3.87 (t, *J* = 6.5 Hz, 4H), 1.78 – 1.66 (m, 4H), 1.49 – 1.23 (m, 12H), 0.89 (q, *J* = 6.7 Hz, 6H).^{13}C NMR (101 MHz, $CDCl_3$) δ 192.0, 157.9, 157.8, 146.8, 145.0, 144.2, 141.1, 138.2, 136.8, 136.0, 135.0, 132.6, 132.6, 132.1, 131.5, 130.2, 127.8, 127.3, 126.5, 126.2,

113.7, 113.6, 67.9, 31.6, 29.3, 25.8, 22.6, 14.0. HR-MS m/z calcd for $C_{45}H_{48}O_3$ ($[M+H]^+$): 637.36762; found：637.36751.

Synthesis of TPEO1-PPI

TPEO1 (0.99 g, 2.00 mmol), 9,10-phenanthrenequinone (0.42 g, 2.00 mmol), aniline (0.93 g, 10.00 mmol), and ammonium acetate (0.62 g, 8.00 mmol) were refluxed in 20 ml acetic acid solution under an argon atmosphere for 2 h. After cooling to room temperature, an brown mixture was obtained and poured into methanol under stirring. The raw product was separated by filtration and washed with methanol, and then dried under vacuum. The crude product was purified by column chromatography on silica gel (200-300 mesh) using dichlormethane as the eluant to give 1.10 g yellow solid with a 73 % yield. ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.94 (s, 1H), 8.77 (d, *J* = 8.3 Hz, 1H), 8.71 (d, *J* = 8.4 Hz, 1H), 7.76 (t, *J* = 7.4 Hz, 1H), 7.70 – 7.59 (m, 6H), 7.57 – 7.47 (m, 5H), 7.34 (d, *J* = 8.3 Hz, 2H), 7.27 (d, *J* = 7.3 Hz, 1H), 7.18 (d, *J* = 7.8 Hz, 1H), 7.15 – 7.02 (m, 7H), 6.96 (dd, *J* = 19.3, 8.8 Hz, 4H), 6.64 (dd, *J* = 10.5, 8.8 Hz, 4H), 3.74 (d, *J* = 4.8 Hz, 6H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 158.19, 150.61, 144.20, 143.86, 140.91, 140.46, 138.80, 138.68, 137.41, 136.32, 132.60, 131.87, 131.45, 130.20, 129.68, 129.58, 129.15, 128.25, 127.74, 127.31, 126.47, 126.28, 126.13, 125.67, 124.91, 124.12, 123.06, 122.86, 120.87, 113.07, 55.09. HR-MS m/z calcd for $C_{55}H_{40}N_2O_2$ ($[M+H]^+$): 761.31; found: 761.289.

Synthesis of TPEO4-PPI

The synthetic process is similar with **TPEO1-PPI** to yield a yellow powder (77%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.93 (s, 1H), 8.77 (d, J = 8.3 Hz, 1H), 8.71 (d, J = 8.3 Hz, 1H), 7.75 (t, J = 7.4 Hz, 1H), 7.65 (dd, J = 19.8, 7.7 Hz, 6H), 7.52 (dd, J = 17.9, 7.6 Hz, 5H), 7.34 (d, J = 8.1 Hz, 2H), 7.27 (d, J = 11.5 Hz, 2H), 7.18 (d, J = 8.2 Hz, 1H), 7.14 – 7.01 (m, 7H), 6.94 (dd, J = 12.8, 8.6 Hz, 4H), 6.63 (t, J = 7.6 Hz, 4H), 3.88 (td, J = 6.3, 2.9 Hz, 4H), 1.76 – 1.68 (m, 4H), 1.46 (dd, J = 14.7, 7.4 Hz, 4H), 0.95 (t, J = 7.4 Hz, 6H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 157.76, 150.65, 144.30, 143.97, 140.92, 140.65, 138.83, 138.45, 137.35, 136.13, 132.60, 131.89, 131.47, 130.20, 129.66, 129.57, 129.16, 128.25, 127.72, 127.23, 126.46, 126.27, 126.09, 125.64, 124.89, 124.12, 123.07, 122.84, 120.87, 113.60, 67.52, 31.40, 19.27, 13.90. HR-MS m/z calcd for $C_{61}H_{52}N_2O_2$ ($[M+H]^+$): 845.40; found: 845.489.

Synthesis of TPEO6-PPI

The synthetic process is similar with **TPEO1-PPI** to yield a yellow powder (80%). ^{1}H NMR

(600 MHz, $CDCl_3$) δ 8.90 (s, 1H), 8.77 (d, *J* = 8.4 Hz, 1H), 8.71 (d, *J* = 8.3 Hz, 1H), 7.75 (t, *J* = 7.4 Hz, 1H), 7.63 (dt, *J* = 13.4, 6.9 Hz, 6H), 7.57 – 7.46 (m, 5H), 7.34 (d, *J* = 8.2 Hz, 2H), 7.29 – 7.24 (m, 1H), 7.19 (d, *J* = 8.2 Hz, 1H), 7.13 – 7.02 (m, 7H), 6.94 (dd, *J* = 20.2, 8.6 Hz, 4H), 6.66 – 6.59 (m, 4H), 3.87 (dd, *J* = 10.9, 6.5 Hz, 4H), 1.78 – 1.67 (m, 4H), 1.48 – 1.39 (m, 4H), 1.38 – 1.29 (m, 8H), 0.90 (t, *J* = 6.5 Hz, 6H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 157.74, 150.65, 144.31, 143.99, 140.96, 140.64, 138.73, 138.42, 137.27, 136.12, 132.61, 131.90, 131.48, 130.22, 129.70, 129.59, 129.15, 128.24, 127.73, 127.20, 126.47, 126.30, 126.09, 125.70, 124.95, 124.13, 123.05, 122.85, 120.88, 113.58, 67.84, 31.64, 29.30, 25.76, 22.62, 14.07. HR-MS m/z calcd for $C_{65}H_{60}N_2O_2$ ($[M+H]^+$): 901.47; found: 901.508

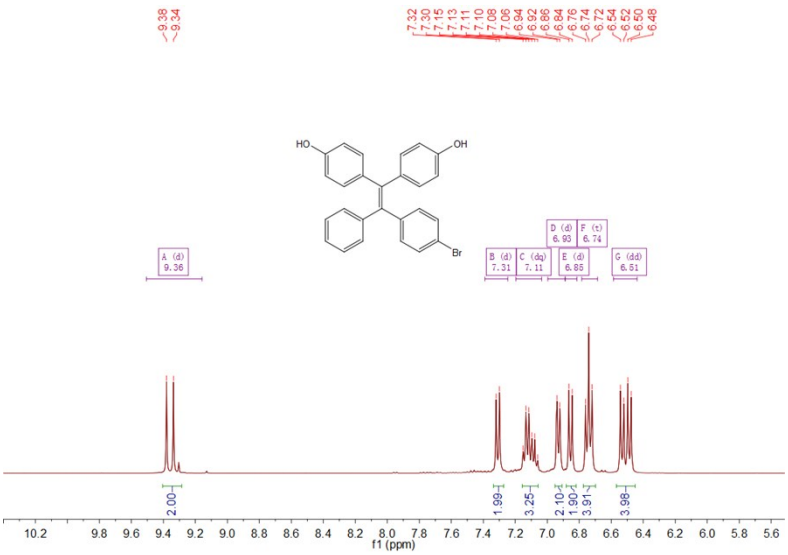


Fig. S1. ^{1}H-NMR spectrum of **a**

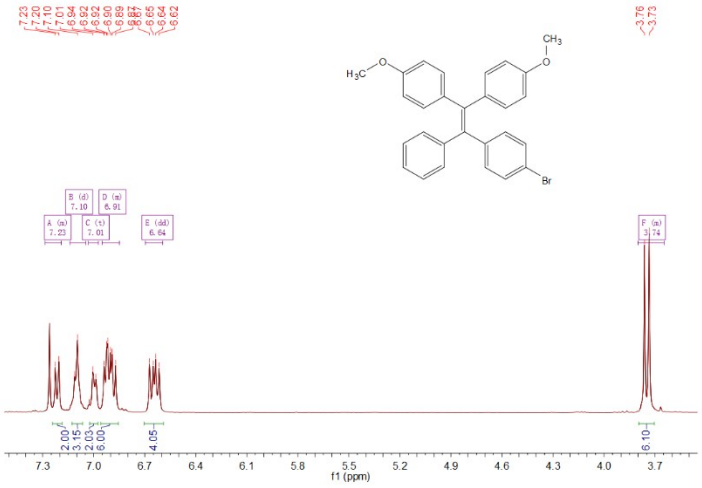


Fig. S2. ^{1}H-NMR spectrum of **b1**

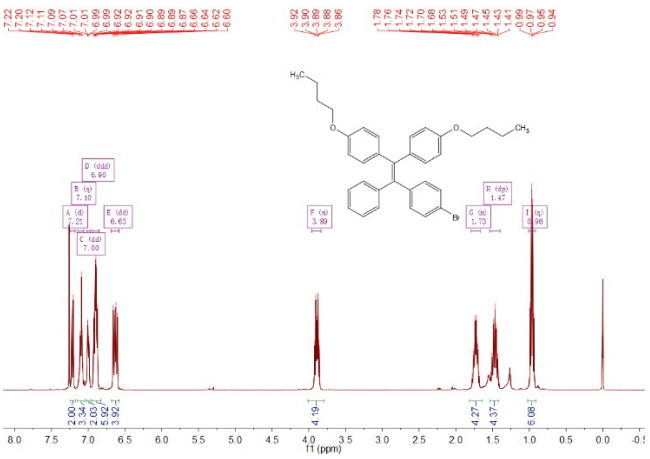


Fig. S3. [1]H-NMR spectrum of **b4**

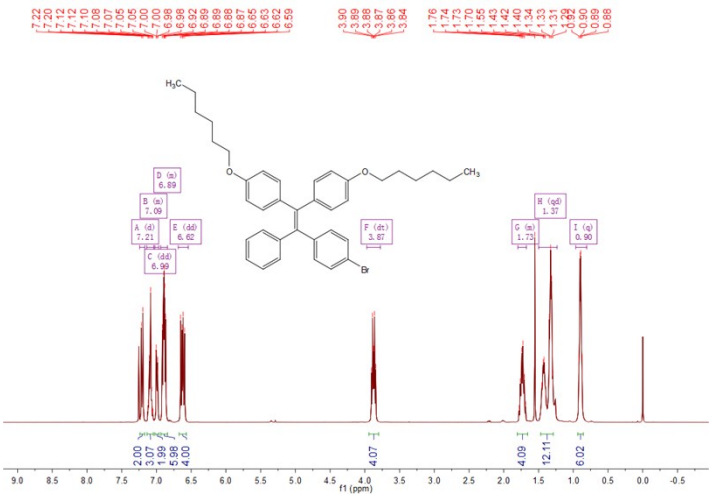


Fig. S4. [1]H-NMR spectrum of **b6**

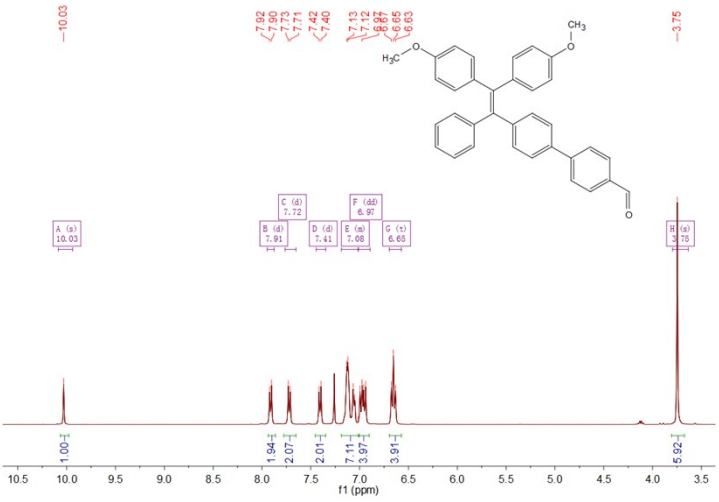


Fig. S5. [1]H-NMR spectrum of **TPEO1**

Fig. S6. [1]H-NMR spectrum of **TPEO4**

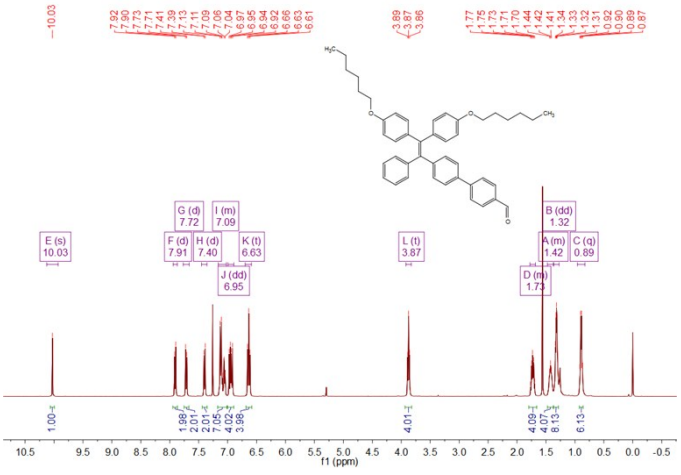


Fig. S7. [1]H-NMR spectrum of **TPEO6**

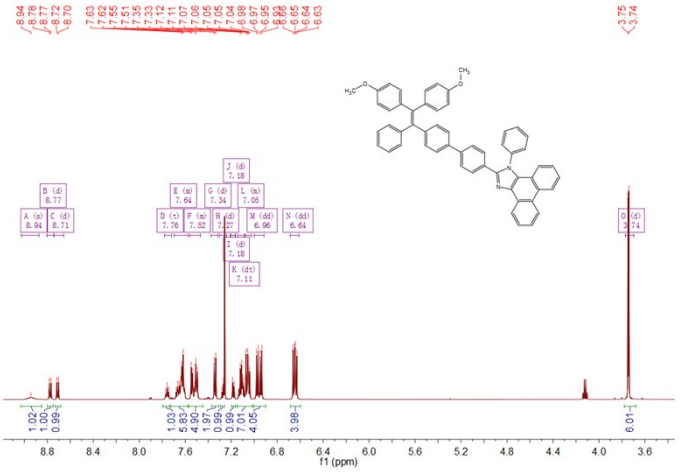


Fig. S8. [1]H-NMR spectrum of **TPEO1-PPI**

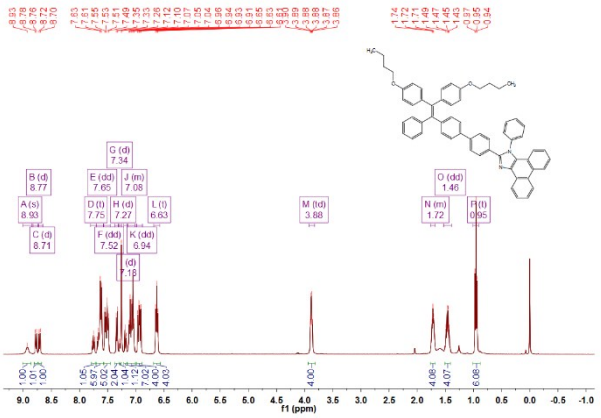


Fig. S9. [1]H-NMR spectrum of **TPEO4-PPI**

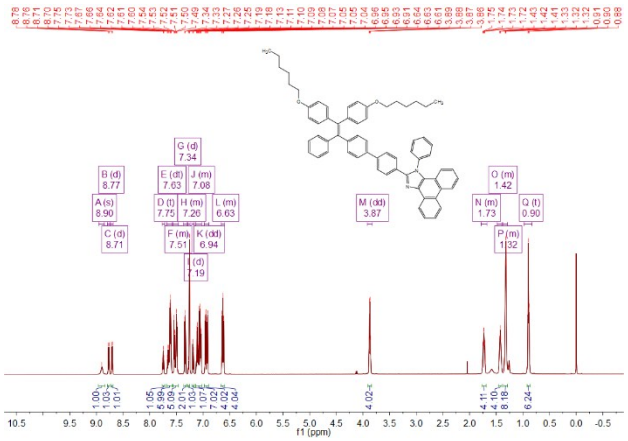
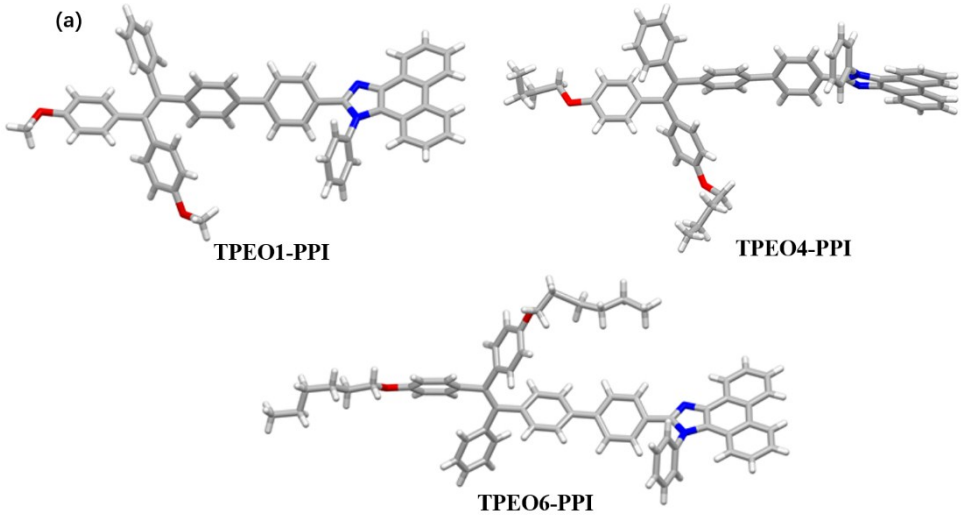


Fig. S10. [1]H-NMR spectrum of **TPEO6-PPI**



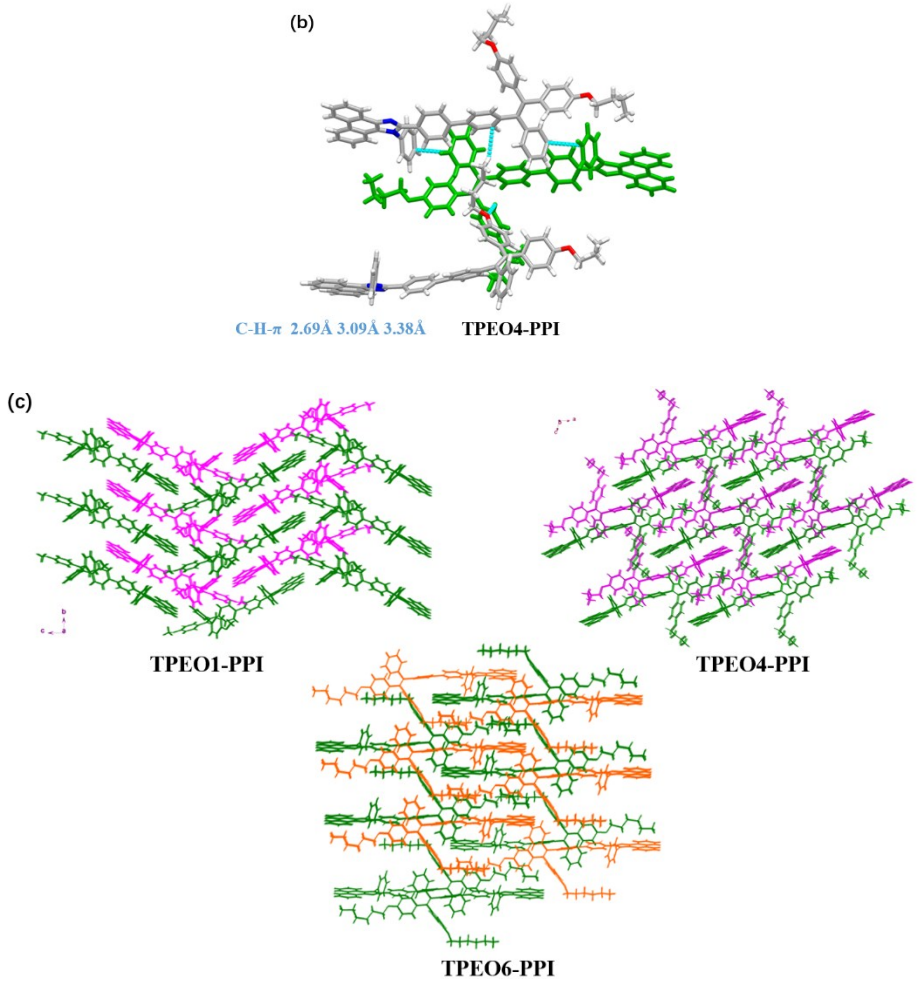
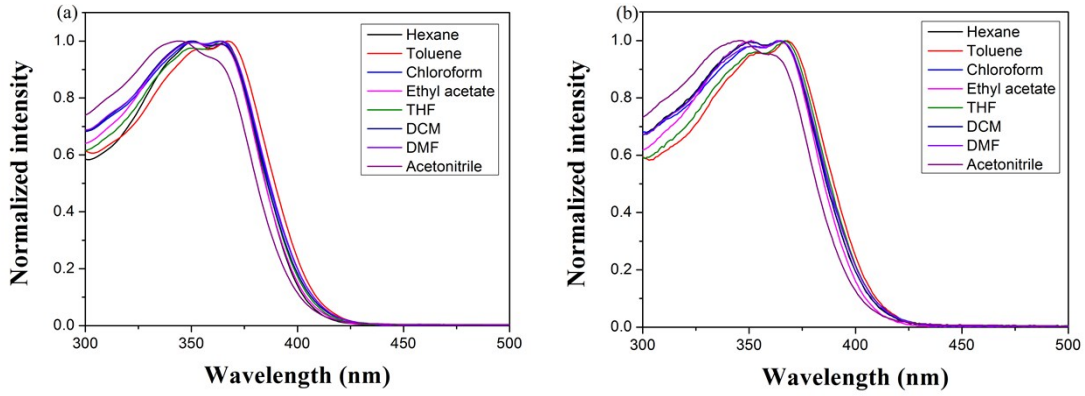


Fig. S11. Single crystal (a) and molecular packing(c) of **TPEO1-PPI**, **TPEO4-PPI** and **TPEO6-PPI**.

2. Photophysical properties



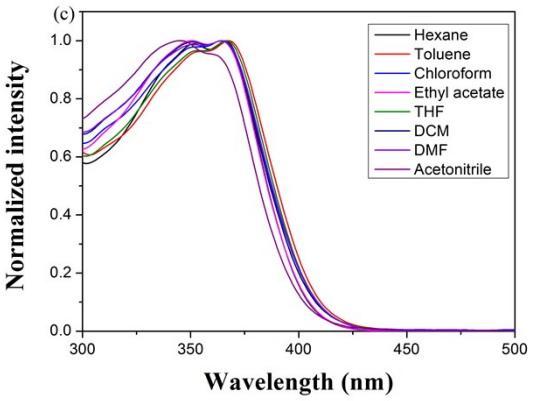


Fig. S12. UV–vis absorption of (a) **TPEO1-PPI**, (b) **TPEO4-PPI**, (c) **TPEO6-PPI** in different solution.

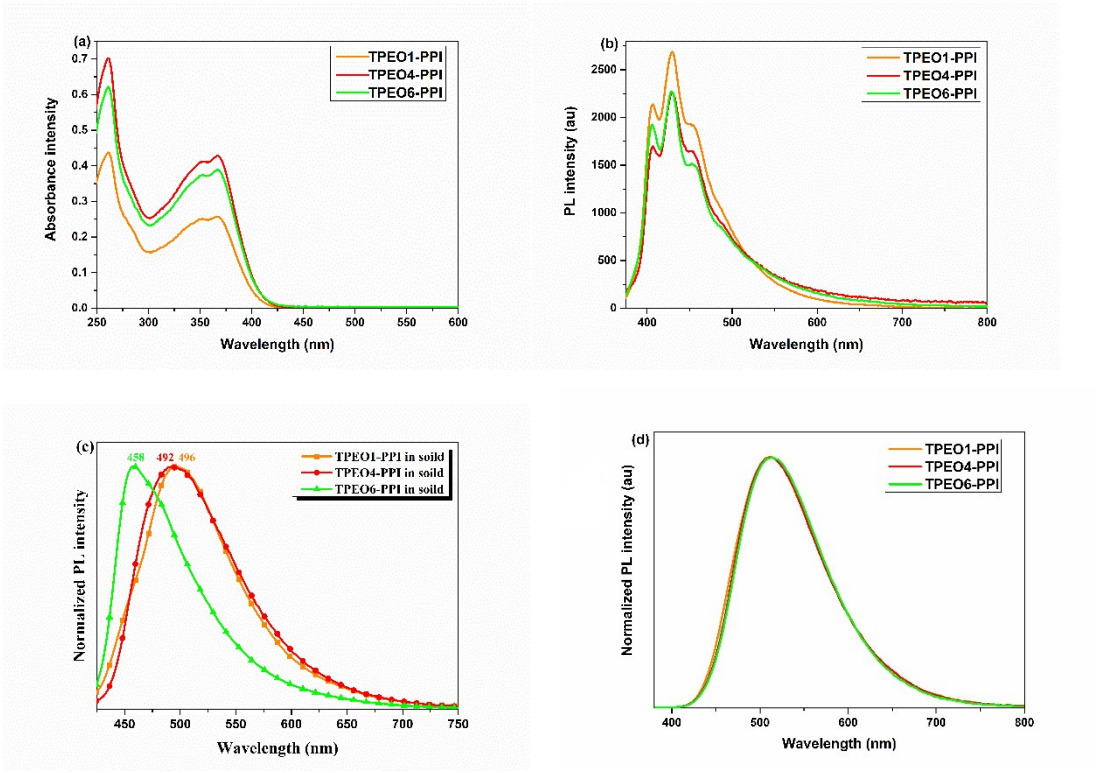
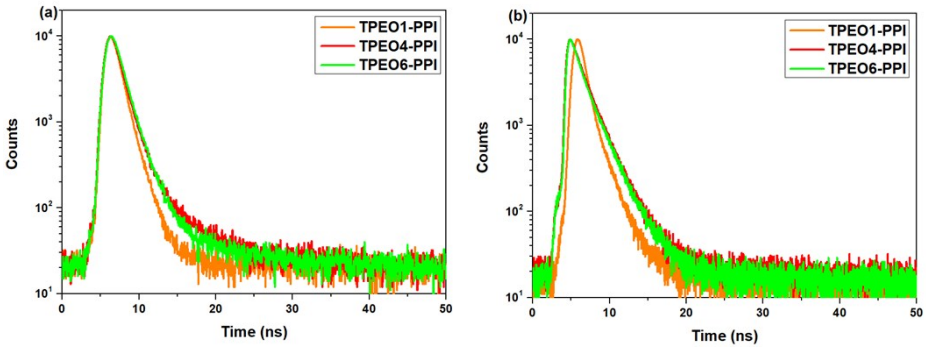


Fig. S13. UV–vis absorption (a) and fluorescence spectra of **TPEO1-PPI**, **TPEO4-PPI** and **TPEO6-PPI** in (b)THF solution, (c) solid powder and (d) neat films.



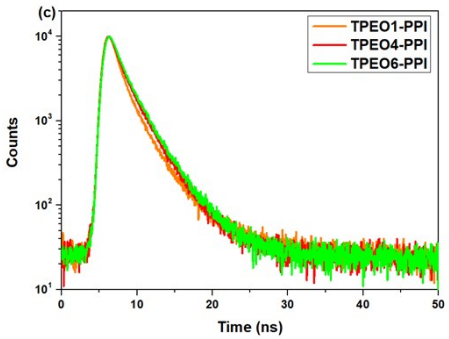


Fig. S14. Fluorescence decay curves of the **TPEO1-PPI**, **TPEO4-PPI**, **TPEO6-PPI** in (a) THF solutions (10^{-5} M), (b) solid powder and (c) solid films.

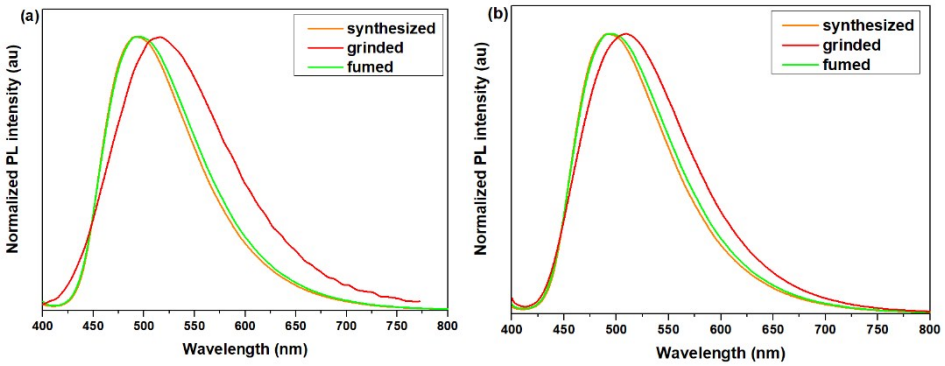


Fig. S15. Normalized fluorescent spectra of **TPEO1-PPI** (a), **TPEO4-PPI** (b) in different solid-states: synthesized, grinded and re-steamed (λ_{ex}=365 nm)

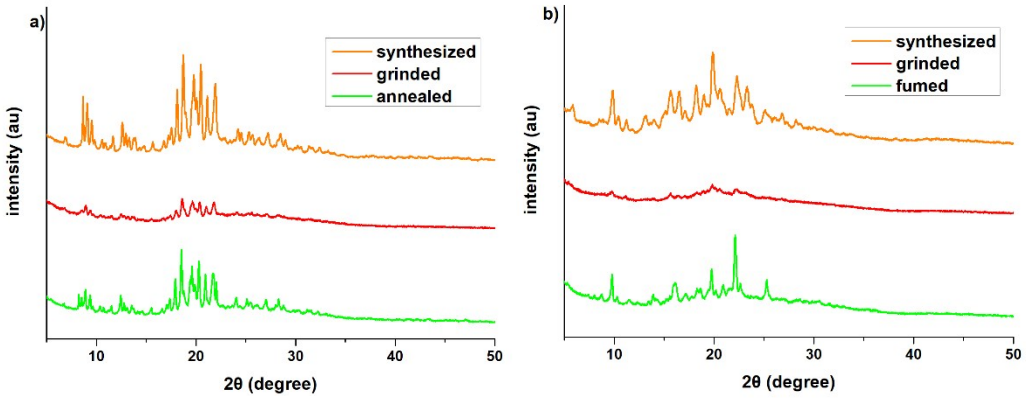


Fig. S16. XRD patterns of **TPEO1-PPI** a) and **TPEO4-PPI** b) in different solid-states: synthesized, grinded and fumed.

Table S1. Peak Emission Wavelengths of **TPEO1-PPI**, **TPEO4-PPI** and **TPEO6-PPI** under Various External Stimuli.

Compound	$\lambda_{synthesized}$ (nm)	$\lambda_{grinded}$ (nm)	λ_{fumed} (nm)
TPEO1-PPI	496	511	498
TPEO4-PPI	492	512	495
TPEO6-PPI	459	512	462

5. Electrochemical measurements

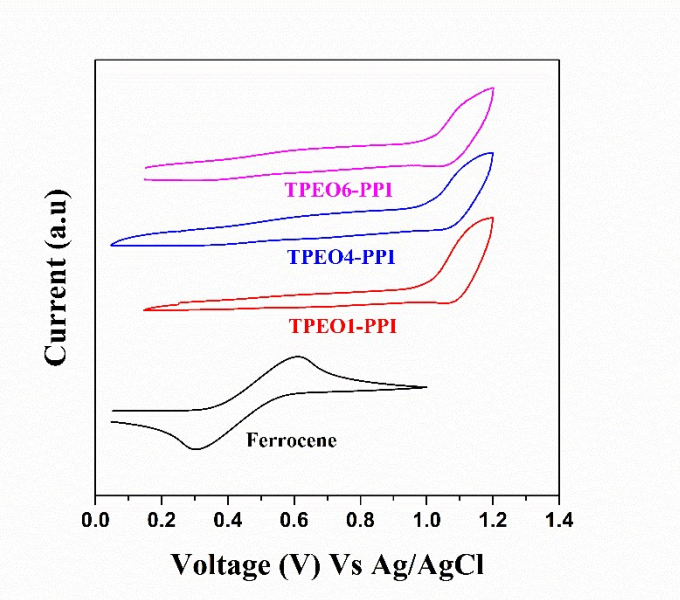


Fig. S17. Cyclic voltammetry curves of **TPEO1-PPI**, **TPEO4-PPI**, **TPEO6-PPI** in THF.

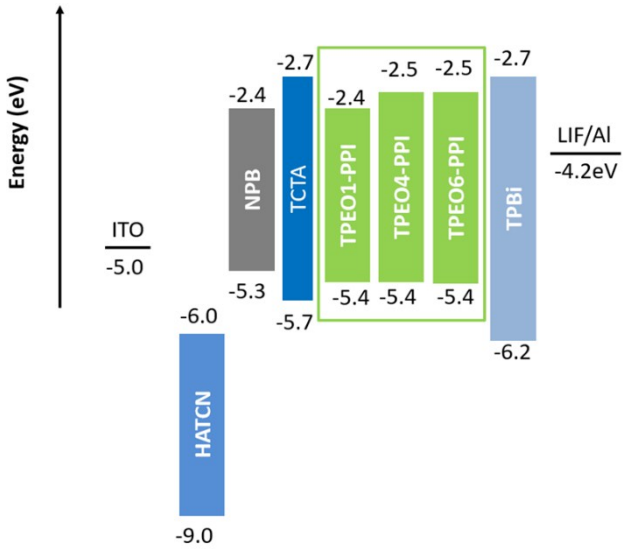


Fig. S18. Schematic diagram of material level and structure of the device.