Electronic Supplementary Information for

Circularly polarized luminescence of achiral open-shell π-radicals

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Materials and Methods

Materials: Commercial room-temperature liquid crystal, R811，S811，5CB, was bought from the Chengzhi Yonghua Display Material Co., Ltd. The π-radicals of TTM-1Cz ，PTM-PCz，TTM-3PCz were synthesized according to previous reports.

Instrumentation: UV-vis spectra were recorded on Hitachi U-3900 spectrophotometer. Fluorescence spectra were measured on F-4500 fluorescence spectrophotometer. CD and CPL spectra were measured on JASCO J-1500 and JASCO CPL-200 spectrophotometers, respectively. The MCD and MCPL test were both performed using a magnetic attachment with a magnetic field strength of 1.6 T. A longitudinal uniform magnetic field can be obtained by putting the sample into a magnetic attachment. POM images were recorded on Leica DM2700M upright materials microscope.

Characterizations and methods: The sample used to test the spectra of UV-vis, fluorescence, was fabricated in the following method. Firstly, 1.3 mg TTM-1Cz, 1.9 mg PTM-PCz, 1.5 mg TTM-3PCz were added into the 5mL centrifuge tube respectively, and then mixing with 2mL hexane. After that, the resulting solution was sonicated for about 1 min to achieve good solution. Finally, transferred 200 μL solution into the quartz cuvette. The UV-vis spectra were recorded from 250 nm to 750 nm. Emission spectra were recorded with excitation wavelength of 380 nm. The free-standing thin film the TTM-3PCz doped into PMMA 10 wt% (toluene) put in magnetic field was fabricated in the following method. The solution of TTM-3PCz (10 mM) in toluene 10 μL was added into PMMA 10 wt% (toluene) 300 μL, then, transferred 200 μL solution on quartz plate, natural volatile solvent. MCD spectra were recorded from 250 nm to 750 nm. Spectra of MCPL were measured with excitation wavelength of 420 nm. The change of magnetic field direction is realized by adjusting the direction of magnetic accessories. The free-standing thin film of the π-radical emitter and LGAm/DGAm co-dispersed in PMMA 10 wt% (toluene) was fabricated in the following method. Prepare 2mL radicals cyclohexane solution (1 mM), divide into two parts, and then add 10mg LGAm and DGAm respectively. Take 100 μL of the above solution and mix it with PMMA 10 wt% (toluene) 200 μL, drop it on the quartz plates and volatilize the solvent. CD spectra were recorded from 250 nm to 750 nm. Spectra of CPL were measured with excitation wavelength of 380 nm. The sample of π-radicals induced by chiral liquid crystal was fabricated in the following method. 1 mg R811/S811 and 100 mg 5CB were added into the 5mL centrifuge tube, and then mixing with 50 μL solution of TTM-1Cz (5 mM) in toluene. After that, the resulting solution was sonicated for about 1 min to achieve good solution, evaporated toluene slowly by the vacuum pump. Finally, transferred 50 μL solution into the quartz cell. The thin chiral nematic liquid crystal film was generated in the inner face of the quartz cell. CD spectra were recorded from 250 nm to 750 nm, integrating sphere been used. Spectra of CPL were measured with excitation wavelength of 380 nm. The sample of TTM-1Cz induced by chiral liquid crystal in electric field was fabricated same as the method of induced by chiral liquid crystal. The difference is that the sample was put into an ITO liquid crystal cells for CPL testing, when a DC electric field (10 V) was applied to the liquid crystal cell, excited at 380 nm. The sample used POM measurement was prepared by the following method. Casting the solution of TTM-1Cz/R811(S811)/5CB on a quartz plate, uniform film could be formed after evaporating the solvent. The film sample could be used for POM measurement.

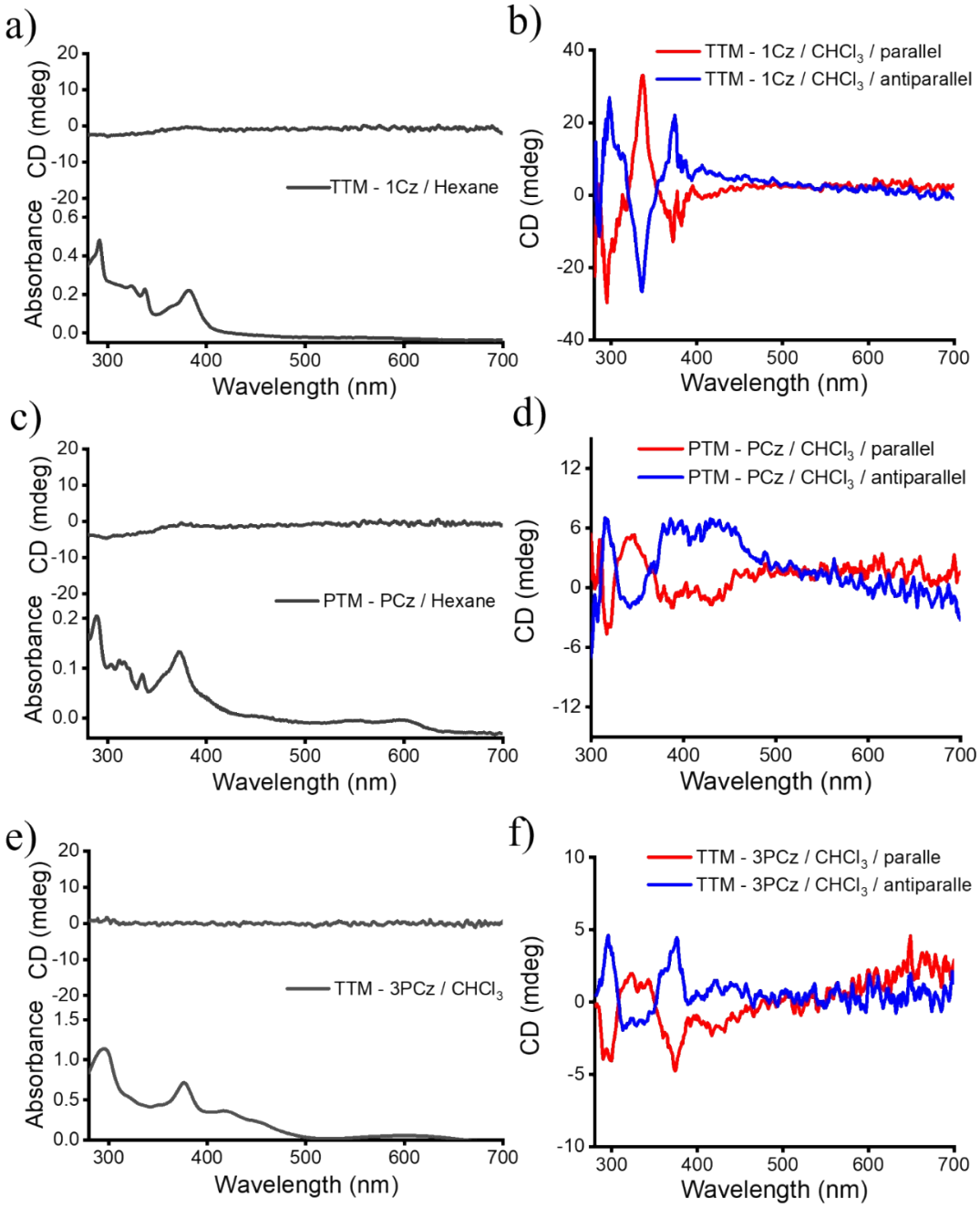

Fig. S1 (a), (c), (e) CD and absorption spectra of TTM-1Cz in hexane (0.01 mM), PTM-PCz in hexane (0.01 mM), TTM-3PCz in $CHCl_3$ (0.1 mM) and the test optical path was 2 mm, respectively. (b), (d), (f) MCD and UV-vis spectra of TTM-1Cz in $CHCl_3$ (1 mM), PTM-PCz hexane (1 mM), TTM-3PCz in $CHCl_3$ (0.5 mM) and the test optical path was 2 mm, respectively. MCD spectra were recorded from 250 nm to 750 nm. The change of magnetic field direction is realized by adjusting the direction of magnetic accessories. The blue line indicates that the test results of magnetic accessories placed in a way where the magnetic inductance line is antiparallel to the light ray. The red line indicates the test results of magnetic accessories placed in a way where the magnetic inductance line is parallel to the light ray.

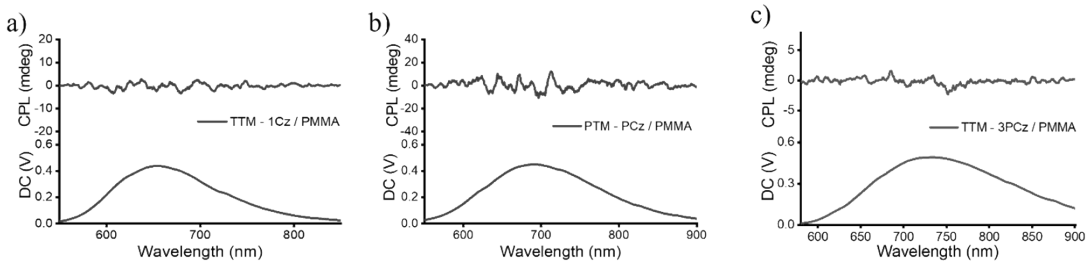

Fig. S2 CPL spectra of PMMA free-standing films made from TTM-1Cz, PTM-PCz, TTM-3PCz, doping into PMMA 10 wt% respectively, excited at 380 nm.

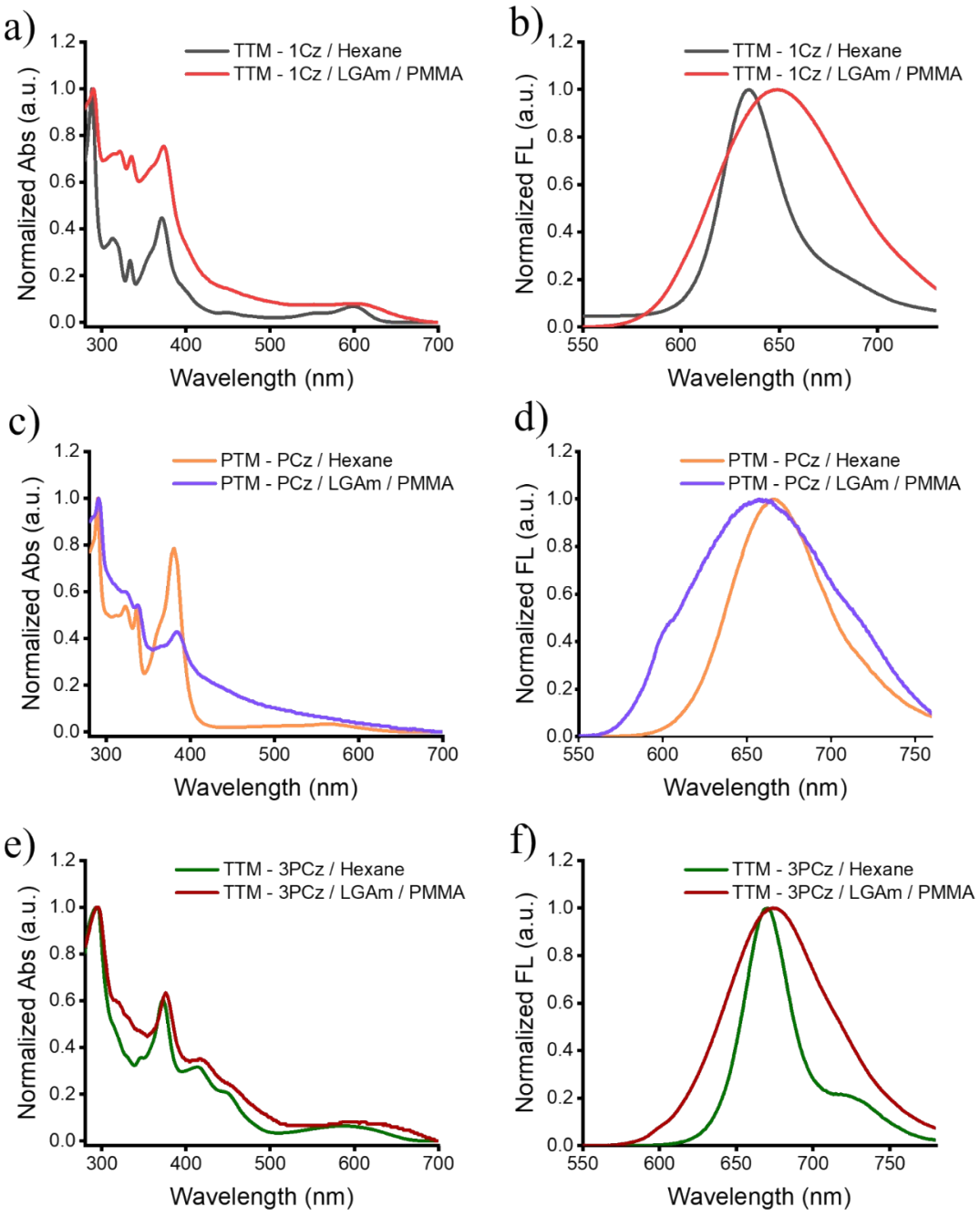

Fig. S3 (a), (c), (e) Normalized absorption spectra of TTM-1Cz, PTM-PCz and TTM-3PCz in hexane and PMMA films, respectively. The solution concentration is 1 mM, and the test optical path is 1 mm. The UV-vis spectra were recorded from 280 nm to 700 nm. (b), (d), (f) Normalized emission spectra of TTM-1Cz, PTM-PCz and TTM-3PCz in hexane and PMMA films, respectively, excited at 380 nm.

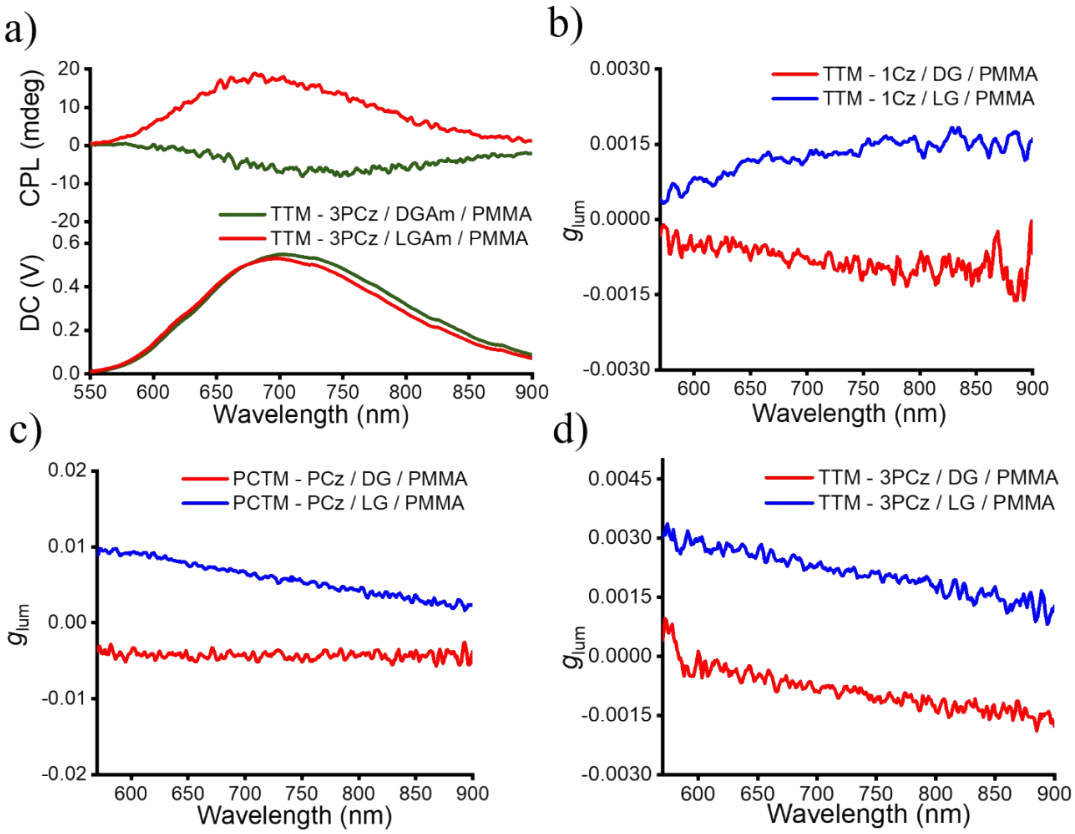

Fig. S4 (a) CPL spectra of the film made from LGAm/DGAm doped in PMMA, excited at 380 nm. The green line indicates the test results of TTM-3PCz/LGAm/PMMA. The red line indicates the test results of TTM-3PCz/ DGAm/PMMA. (b), (c), (d) Evolution of g_{lum} of PMMA films of TTM-1Cz, PTM-PCz and TTM-3PCz, respectively. The red line indicates the test results of TTM-3PCz/PTM-PCz/ TTM-3PCz and DGAm dispersed in PMMA. The blue line indicates the test results of TTM-3PCz/PTM-PCz/TTM-3PCz and LGAm dispersed in PMMA.

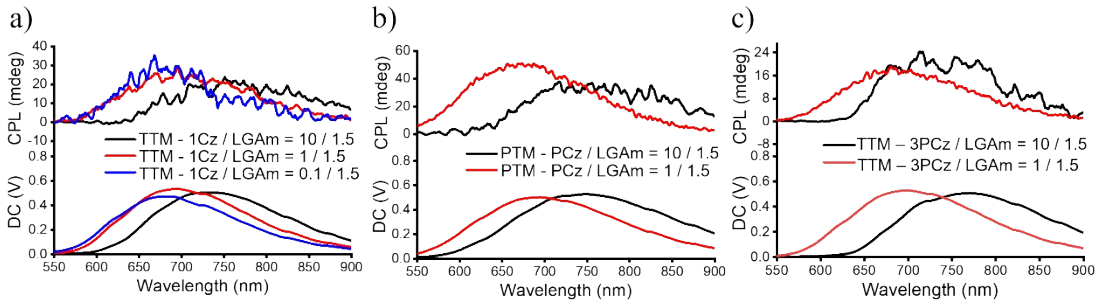

Fig. S5 We have fixed the quantity of PMMA at 10 wt%, the usage of LGAm at 3 × 10^{-3} mmol. By changing the usage of radical from 2 × 10^{-5} to 2 × 10^{-4}, and 2 × 10^{-3} mmol, the corresponding free-standing films were fabricated and tested. (a) CPL spectra of the film made from TTM-1Cz and LGAm doped in PMMA, excited at 380 nm. (b) CPL spectra of the film made from PTM-PCz and LGAm doped in PMMA, excited at 380 nm. When the usage of PTM-PCz was 2 × 10^{-5} mmol, no CPL signal could be detected. (c) CPL spectra of the film made from TTM-3PCz and LGAm doped in PMMA, excited at 380 nm. When the usage of TTM-3PCz was 2 × 10^{-5} mmol, no CPL signal could be detected.

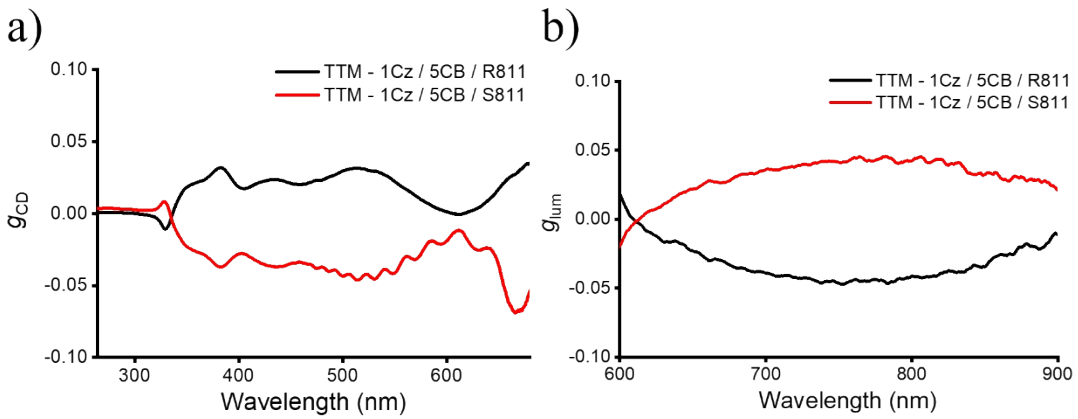

Fig. S6 The chiral liquid crystal sample doped with TTM-1Cz. (a)Evolution of g_{CD} of the mixture; (b) Evolution of glum of the mixture.

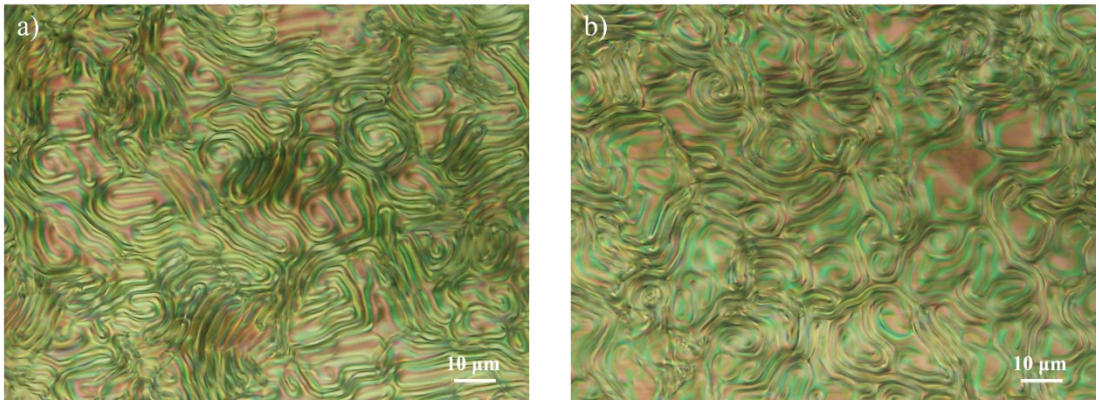

Fig. S7 Polarized optical micrograph (POM) images of TTM-1Cz dispersed into chiral liquid crystal films including (a) TTM-1Cz dispersed into R81/5CB (1 wt%), (b) TTM-1Cz dispersed

into S811/5CB(1 wt%).

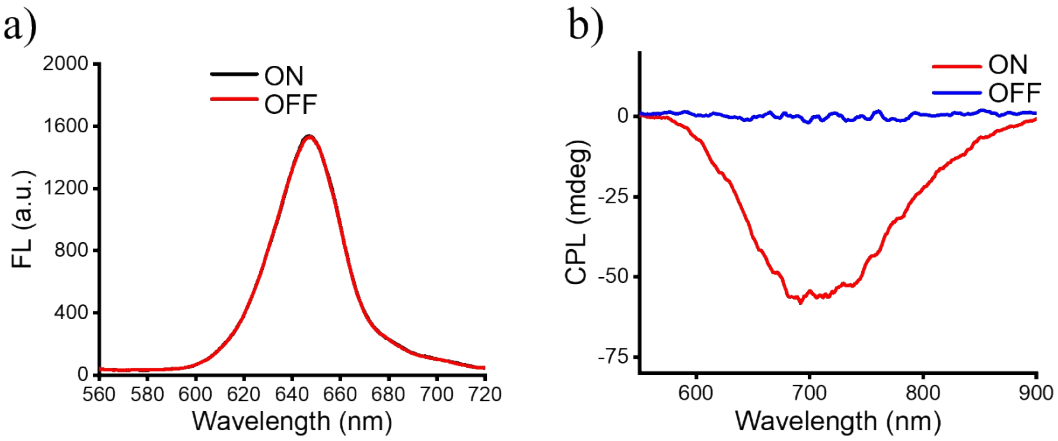

Fig. S8 (a) The fluorescence emission spectra of TTM-1Cz dispersed into R811/5CB (1 wt%) under the direct current electric field, the black line indicates the test results without DC electric field. The red line indicates the test results under the electric field (10 V), respectively. (b) The CPL spectra of TTM-1Cz dispersed into R811/5CB (1 wt%) under the direct current electric field. The red line indicates the test results without DC electric field. The blue line indicates the test results under the electric field (10 V).