Electronic Supplementary Information for

Proton Triggered Circularly Polarized Luminescence in Orthogonal- and Co-assemblies of Chiral Gelator with Achiral Perylene Bisimide

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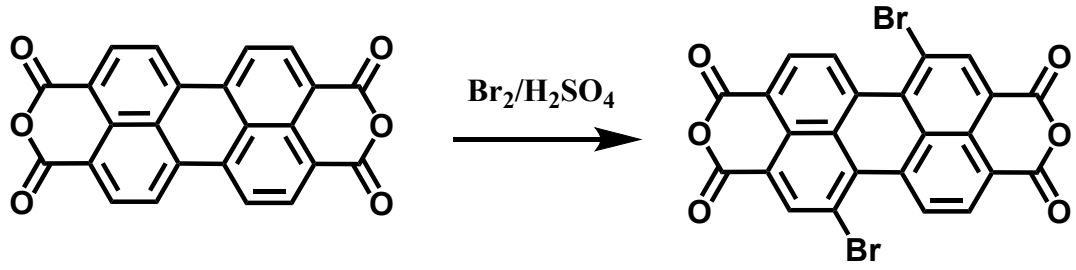
S1. Synthetic procedures and PET process

Materials: All reagents and solvents were used as received otherwise indicated. The PBI and gelator LBG/DBG are synthesized according to literature.

Characterizations: The ^{1}H NMR spectra were recorded on a Bruker Fourier 300 (300 MHz) spectrometer. Infrared spectra were recorded on KBr pellets using JASCO FTIR-660 spectrometer. UV-vis and CD spectra were obtained using Hitachi U-3900 spectrophotometer and JASCO J-850 spectrophotometers, respectively. Fluorescence spectra of both the solution and gels were measured on an F-4500 fluorescence spectrophotometer using a xenon lamp as the excitation source and CPL spectra was measured on JASCO CPL-200. Laser scanning confocal microscopy was recorded on the Olympus FV1000-IX81. Fluorescence microscopy was recorded on the Olympus X83 using high-pressure mercury lamp as excitation source for fluorescent images. The absolute fluorescence quantum yield was measured by using an absolute PL quantum yield spectrometer (Edinburg FLS-980 fluorescence spectrometer) with a calibrated integrating sphere and fluorescence lifetime measurements were recorded on the same spectrometer using time-correlated single photon counting (TCSPC). X-ray diffraction (XRD) was achieved on Rigaku D/Max-2500 X-ray diffractometer (Japan) with Cu/Kα radiation (λ=1.5406Å. Scanning electron microscopy (SEM) was performed on a Hitachi S-4800 FE-SEM with an accelerating voltage of 10 kV.

Synthesis of 1，7-dibromobis(N-(N',N'-diethylaminoethyl))-perylene bisimide(PBI):

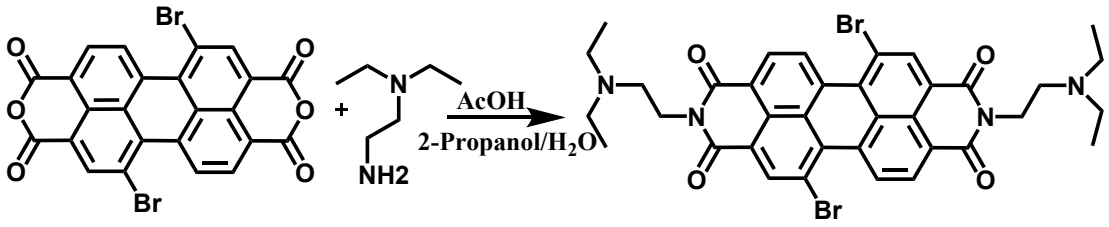


1 2

Scheme S1 Synthesis of dibromo-substituted perylenetetra-carboxylic dianhydride

A mixture of perylenetetracarboxy-3,4,9,10-dianhydride 1 (20 g, 51 mmol) in sulfuric acid (98%, 250 ml) was stirred at room temperature for 2 h. After heating to 85 °C, iodine (600 mg, 2.3 mmol) was added. Then bromine (18 g, 112.6 mmol) was added dropwise. Stirring was

continued for about 16 h at 85 °C. After cooling to room temperature, the excess of bromine was eliminated by bubbling argon in the reaction mixture. The reaction product was precipitated by slow addition of iced water (1000 ml). After filtration the solid was washed with water until the mixture was pH neutral. After drying at 120 °C in vacuo, the crude product 2 could not be purified owing to its insolubility in organic solvents.



2 3

Scheme S2 Synthesis of 1，7-dibromobis(N-(N',N'-diethylaminoethyl))-perylene bisimide (PBI)

A suspension of 2 (2.75 g, 5 mmol) obtained from the above reaction, 2-(diethylamino)ethylamine (0.70 mL, 5.0 mmol), and acetic acid (1.5 g) in H_2O/2-propanol (1:1, v/v, 40 mL) were stirred at 80 °C under argon for 24 h. The mixture was cooled to room temperature. After evaporation of the solvent, The product was purified by silica gel column chromatography (200–300 mesh, 30 cm long and 4 cm diameter) with CH_2Cl_2/MeOH (20:1, v/v, Rf = 0.40) as eluent and 3 (1,7-dibromobis(N-(N',N'-diethylaminoethyl))-perylene bisimide) was obtained after evaporation of the solvent as a brownish red powder (2.5 g, 66 %).

^{1}H NMR (400 MHz, Chloroform-*d*) δ 9.39 (d, *J* = 8.1 Hz, 2H), 8.83 (s, 2H), 8.61 (d, J = 8.1 Hz, 2H), 4.57-4.17 (t, *J* = 7.4 Hz, 4H), 2.97 (t, *J* = 7.4 Hz, 4H), 2.84 (q, *J* = 7.1 Hz, 8H), 1.18 (t, *J* = 7.2 Hz, 12H). ^{13}C NMR (400 MHz, Chloroform-*d*): δ (ppm) 175.63, 163.14, 162.77, 162.31, 161.96, 138.01, 137.92, 132.98, 132.79, 132.62, 132.27, 130.02, 129.89, 129.79, 129.56, 128.94, 128.35, 127.97, 127.93, 126.76, 125.94, 123.02, 122.89, 122.45, 122.20, 121.62, 120.77, 48.95, 47.02, 46.98, 37.09, 36.84, 22.01, 11.05, 10.97. HR-MS (MALDI) m/z: calcd: 744.0947, found: 744.0952 $[M]^+$.

Fabrication of the cogels: 10 mg LBG/DBG were added to a capped test tube with PBI (5×10^{-5} mol/L) ethanol mixing solution (500 μl ethanol), the mixture was heated until the solid was dissolved completely. The solution was subsequently cooled down to room temperature under

ambient conditions. After 10 min, the gel formed. The formation of cogels were determined by the absence of flow of the solvent when the tube was inverted.

S2. Supplementary Figures and Tables

Table S1. Optical properties of protonated PBI solution and protonated PBI doped cogel.

Solution			Cogel		
λ_{ex}	Φ_F	τ_{avg}	λ_{ex}	Φ_F (LBG)	τ_{avg} (LBG)
nm		ns	nm		ns
390	0.58	4.88	390	0.24	5.35

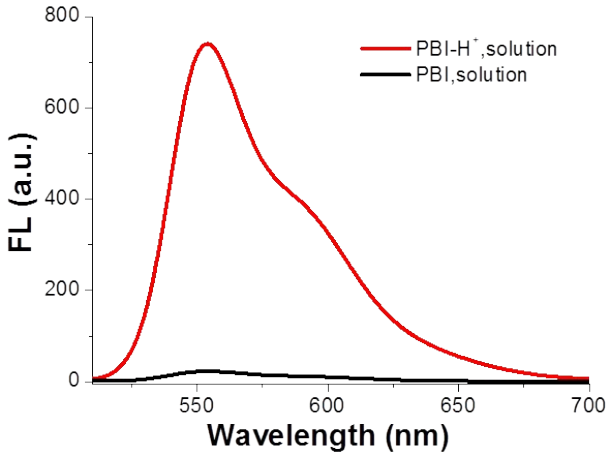


Figure S2 Fluorescence spectra of PBI before and after adding acetic acid excited by 447 nm.

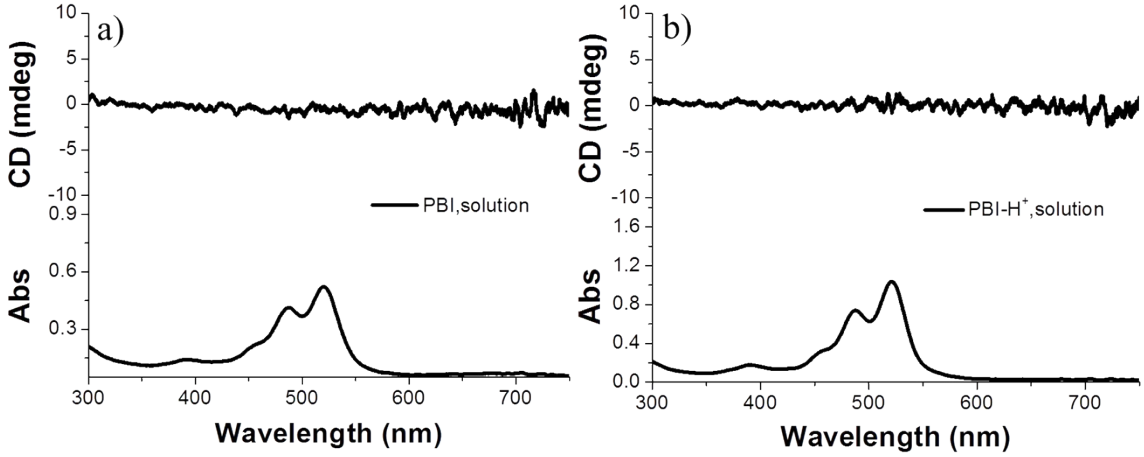


Figure S3 CD spectra of a) PBI in ethanol solution before ([PBI] = 0.05 mM) and b) after ([PBI] = [acetic acid] = 0.05 mM) adding acetic acid.

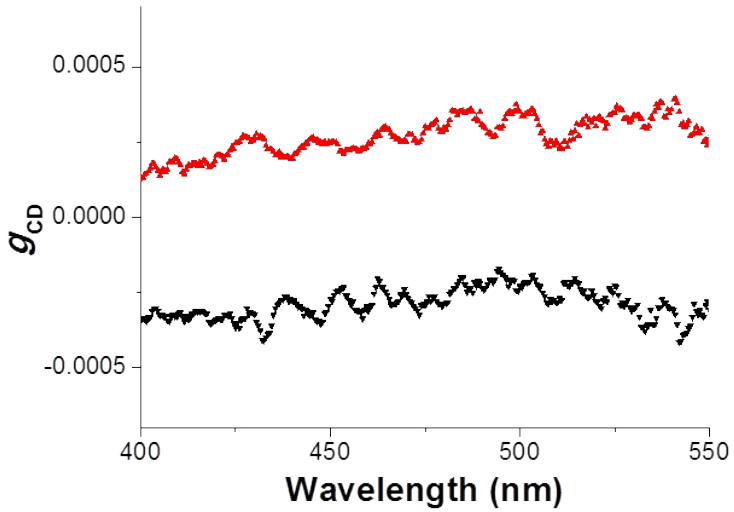


Figure S4 CD spectra (g_{CD}) of the (▼) LBG/PBI and (▲) DBG/PBI cogel in ethanol.

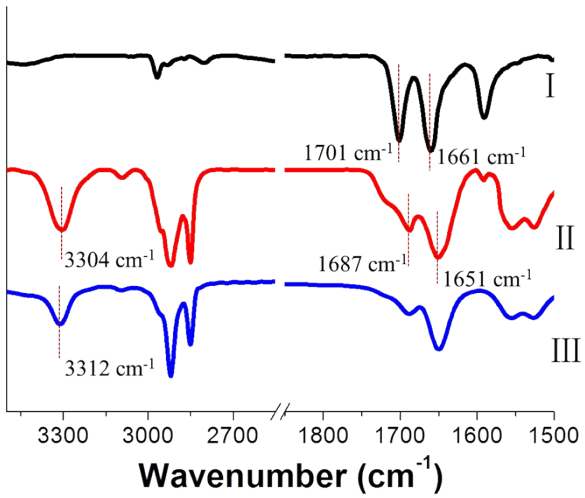


Figure S5 FTIR spectra of PBI powder (I), xerogel from coassembly of gelator LBG and dye PBI, the mixing ratio of LBG/PBI at 60 (II), xerogel of LBG alone (III).

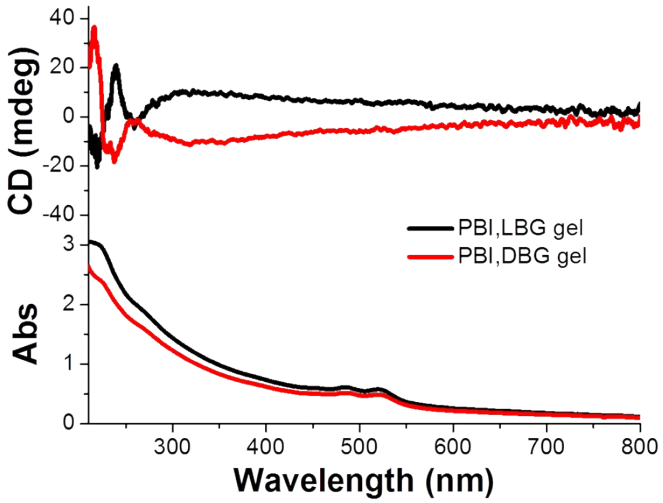


Figure S6 CD spectra of non-protonated cogel ([LBG] = 2.67 mM, [PBI] = 0.05 mM), casting the cogel on quartz to make gel film.

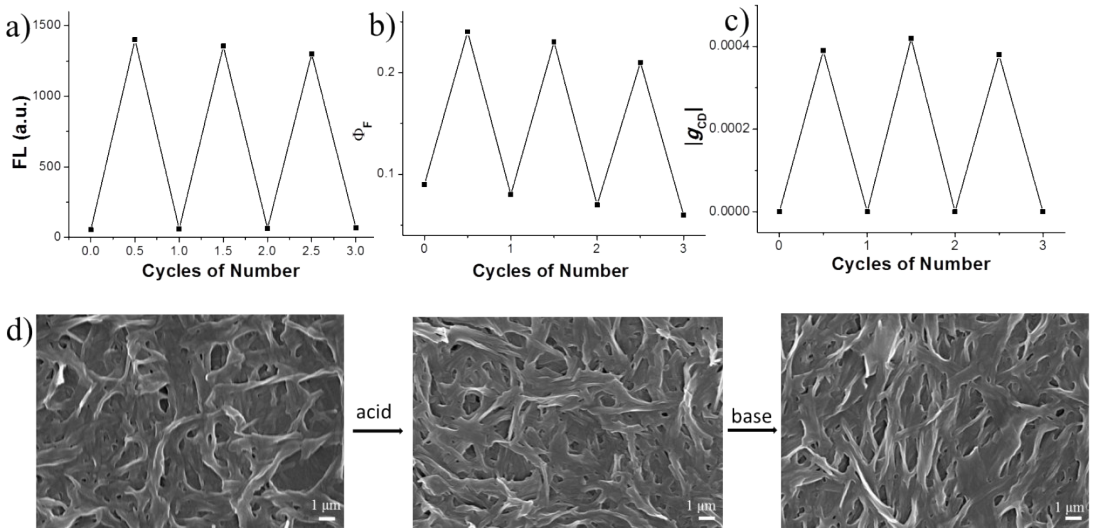


Figure S7 Intensity of a) FL、b) the values of quantum yield (Φ_F)、c) $|g_{CD}|$ value and d) SEM images of the LBG/PBI cogel against the repeated acid-base fumigation cycles.

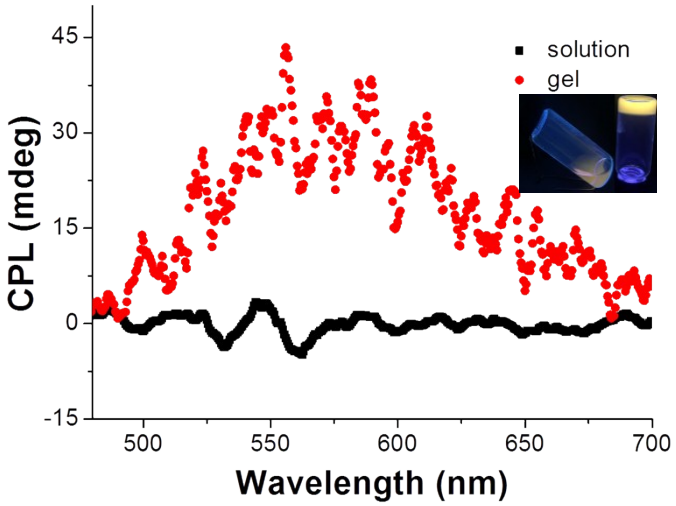


Figure S8 CPL spectra of protonated heating solution and cooling cogel in ethanol ([LBG] = 2.67 mM, [PBI] = [acetic acid] = 0.05 mM) excited at 447 nm.