Electronic Supplementary Information for

Stoichiometry-controlled inversion of circularly polarized luminescence in co-assembly of chiral gelators with achiral tetraphenylethylene derivative

Pengyu Li,a Baozhong Lü,a Dongxue Han,b Pengfei Duan,b Minghua Liu*b and Meizhen Yin*a

a. State Key Laboratory of Chemical Resource Engineering, Beijing Laboratory of Biomedical Materials, Beijing University of Chemical Technology, Beijing 100029, P. R. China, E-mail: yinmz@mail.buct.edu.cn.
b. CAS Center for Excellence in Nanoscience, CAS Key Laboratory of Nanosystem and Hierarchical Fabrication, Division of Nanophotonics, National Center for Nanoscience and Technology (NCNST), Beijing 100190, P. R. China. E-mail: liumh@iccas.ac.cn.
1. **Experimental Section**

**Materials:** All chemical materials were purchased from commercial sources and used without further purification unless particularly pointed out. PTPE and gelator DGG/LGG are synthesized according to literature.

**Characterizations:** The $^1$H NMR spectra were recorded on a Bruker Fourier 400 (400 MHz) spectrometer at room temperature. Fourier transform infrared (FT-IR) spectra were recorded using a Thermo Nicolet Nexus FT-IR devise with the Smart Golden Gate ATR attachment in the range of 4000-500 cm$^{-1}$ with 2 cm$^{-1}$ resolution. UV-vis and CD spectra were obtained using Hitachi U-3600 spectrophotometer and JASCO J-810 spectrophotometers, respectively. Fluorescence spectra of both the solution and cogels were measured on an FM-400 fluorescence spectrophotometer (Horiba JobinYvon FluoroMax-4 NIR, NJ, USA) using a xenon lamp as the excitation source. CPL spectra were measured on JASCO CPL-200. The percentage contribution of each lifetime component to the total decay curve and the absolute fluorescence quantum yield were 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) patterns of the powder were recorded using a Rigaku 2500VB2+PC diffractometer using the Cu Kα radiation ($\lambda=1.541844$ Å) at 40 kV and 50 mA with the step-scanned mode in 0.04° (2θ) per step and count time of 10s/step in the range from 0.5 to 10° and 3 to 40°. The surface morphology was investigated by field emission scanning electron microscopy (FESEM, JSM-7500F, JEOL, Japan).
Scheme S1. Synthesis routes of 1,1,2,2-tetrakis(4-(pyridin-4-yl)phenyl)ethene (PTPE).

**Synthesis of 4Br-TPE:** A three-necked flask equipped with a magnetic stirrer was added zinc powder (5.5 g, 81.5 mmol) and 100 mL THF under N₂ atmosphere. After the mixture was cooled to -5 - 0 °C, TiCl₄ (14 mL, 130.8 mmol) was dropwise added by a syringe and the temperature was kept under 10 °C. The suspending mixture was warmed to room temperature and stirred for 0.5 h, then refluxed for 2.5 h. The mixture was cooled to -5 - 0 °C again and stirred for 10 min. A solution of 4, 4'-dibromobenzophenone (11.1 g, 32.7 mmol) in THF (50 mL) was added slowly. Then the reaction mixture was refluxed until the reaction finished (monitored by TLC, one main product spot). After quenched with 10% K₂CO₃ aqueous solution, the mixture was extracted with CH₂Cl₂. The combined organic phase was dried over anhydrous Na₂SO₄ and concentrated. The residue was purified by column chromatography to give a white solid 4Br-TPE (11.4 g, 67.0%), which was directly used in the next step. ¹H NMR (400 MHz, CDCl₃) δ = 7.26 (d, J = 8.2 Hz, 8H), 6.84 (d, J = 8.3 Hz, 8H).

**Synthesis of PTPE**
A two-necked round-bottom flask (100 mL) were added tetrakis(4-bromophenyl)ethylene (4Br-TPE, 1.0 g, 1.54 mmol), Pyridine-4-boronic acid (1.14 g, 9.24 mmol) and tetrakis- (triphenylphosphine) palladium (0) (134 mg, 0.11 mmol). The flask was evacuated under vacuum and then flushed with dry nitrogen three times. Anhydrous dioxane (40 mL) and potassium carbonate solution (4 M, 6 mL) were injected into the flask and the mixture was refluxed for 3 days. After slowly cooled to room temperature, the solution was poured into water and extracted with CH₂Cl₂. The collected organic layer was washed with saturated solution of NaCl twice, and then dried over anhydrous Na₂SO₄. After filtration and solvent evaporation, the crude product was purified by silica-gel column chromatography using chloroform/methanol (1:15) as eluent to give a pale yellow solid PTPE (0.3 g, 30.6%). ¹H NMR (400 MHz, CDCl₃) δ=8.63 (d, J = 6.1 Hz, 8H), 7.53 – 7.44 (m, 16H), 7.23 (d, J = 8.3 Hz, 8H). ESI-MS (m/z): calcd: 640.26, found: 641.2702.
Figure S1. $^1$H NMR spectrum of 4Br-TPE in CDCl$_3$.

Figure S2. $^1$H NMR spectrum of PTPE in CDCl$_3$. 
Synthesis of DGG/LGG

DGG/LGG was synthesized from the amidation of dimethyl D-/L-glutamic ester hydrochloride with stearic acid and subsequent hydrolysis in a dilute NaOH methanol solution according to the previous literature.

Figure S3. ESI-MS spectrum of PTPE.

Figure S4. $^1$H NMR spectrum of DGG in $d_6$-DMSO.
Fabrication of the cogels: 20 mg (48 mmol) DGG/LGG were added to a capped test tube with PTPE (3×10^{-3} M for 1:16 and 4.8×10^{-4} M for 1:100) chloroform mixing solution (1.0 mL chloroform), 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.
2. Supplementary Figures and Tables

Table S1. Optical properties of PTPE solution and PTPE doped cogels.

<table>
<thead>
<tr>
<th>Molar ratio</th>
<th>( \lambda_{\text{ex}} ) / nm</th>
<th>( \lambda_{\text{em}} ) / nm</th>
<th>( \Phi_F )</th>
<th>( \tau_{\text{avg}} ) / ns</th>
</tr>
</thead>
<tbody>
<tr>
<td>PTPE Solution</td>
<td>320</td>
<td>525</td>
<td>2.55%</td>
<td>0.40</td>
</tr>
<tr>
<td>PTPE/DGG=1:100</td>
<td>320</td>
<td>525</td>
<td>98.83%</td>
<td>4.07</td>
</tr>
<tr>
<td>PTPE/DGG=1:16</td>
<td>320</td>
<td>525</td>
<td>91.19%</td>
<td>3.65</td>
</tr>
</tbody>
</table>

Figure S6. (a) CPL spectrum and (b) CD spectrum of PTPE/LGG cogel at molar ratios of 1:100 and 1:16. (c) Plot of glum of CPL signal versus PTPE/LGG ratio. (d) Plot of \( g_{\text{CD}} \) versus PTPE/LGG ratio. (The concentration of DGG was fixed at 20 mg/mL.)
Figure S7. Molar-ratio dependent $g_{\text{lum}}$ patterns of cogels: (a) PTPE/DGG; (b) PTPE/LGG.

Figure S8. (a) CPL spectra of PTPE/DGG cogels from molar ratio 1:40 to 1:18; (b) Smoothed CPL patterns from molar ratio 1:28 to 1:20; Plot of glum of CPL signal versus molar ratio in PTPE/DGG cogels (c) and PTPE/LGG cogels (d).

Figure S9. CD spectrum of DGG gel individually.
Figure S10. Normalized absorption spectra of (a) PTPE/DGG cogels and (b) PTPE solution in chloroform.
As shown in Figure S10a, the characteristic peak of PTPE can be detected due to the low content at PTPE/DGG=1:100. However, at PTPE/DGG=1:16, the absorption peak of PTPE arises, which is consistent with the pattern in PTPE solution and the peaks in CD spectrum.

Figure S11. FTIR spectra of DGG gel and PTPE/DGG cogels: (a) full spectra; (b) amplified pattern of circled part of (a).
**Figure S12.** Small-angle XRD (a) and broad-angle XRD (b) of DGG gel and PTPE/DGG cogels.

**Figure S13.** SEM images of PTPE/DGG cogels in chloroform at various molar ratios: (a, a’) DGG gel; (b, b’) PTPE/DGG=1:80; (c, c’) PTPE/DGG=1:64; (d, d’) PTPE/DGG=1:16; (e, e’) PTPE/DGG=1:8.