Electronic Supplementary Information for

Optically active quantum dots with induced circularly polarized luminescence in amphiphilic peptide dendron hydrogel

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1. Experimental section

**Materials:** All the starting materials and solvents were obtained from commercial suppliers and used as received. Milli-Q water (18.2 MΩ•cm) was used in all cases. Behenic Acid was purchased from Alfa Aesar. Tert-butoxycarbonyl (Boc)-L/D-Glutamic acid, L-Glutamic acid dibenzyl ester hydrochloride and D-Glutamic acid dimethyl ester hydrochloride were purchased from TCI. Quantum Dots (QDs) was purchased from Suzhou Xingshuo Nanotech Co., Ltd. Amide condensation reaction was carried on using 1-ethyl-3-(3-dimethyllaminopropyl) carbodiimide hydrochloride (EDC•HCl)/1-hydroxybenzotrizole (HOBr) condensation agent. The final compounds were purified by column chromatography and confirmed the molecular structures by $^1$H-NMR, MALDI-TOF-MS. BGAc molecules were synthesized via synthetic route in Supplementary Information (Fig. S1).

**Characterization:** $^1$H NMR spectra were recorded on a Bruker Advance III 400 (400 MHz) spectrometer. Mass spectra were performed on a BIFLEIII matrix-assisted laser desorption/ionization time of flight mass spectrometry (MALDI-TOF-MS) instrument. FT-IR spectra were recorded on a PerkinElmer Frontier spectrophotometer. XRD analysis was performed on a Rigaku D/Max-2500 X-ray diffractometer (Japan) with Cu Kα radiation (λ=1.5406 Å), which was operated at a voltage of 40 kV and a current of 200 mA. Samples were vacuum-dried for XRD measurements. CD measurements were conducted on a JASCO J-1500 CD spectrometer. UV spectra were obtained on Hitachi U-3900 UV/vis spectrophotometer. CPL measurements were performed with a JASCO CPL-200 spectrometer. Fluorescence spectra were recorded on a Hitachi F-4500 fluorescence spectrophotometer. Cuvettes of 0.1 mm were used for measuring the CD spectra of samples, respectively. Cuvettes of 1 mm were used for measuring the CPL, UV-vis, and FL spectra of samples. TEM was performed on Tecnai G2 20 S-TWIN at accelerating voltages of 200 kV. AFM was performed by using Tapping Mode (Nanoscope IIIa, Digital Instruments) with a Fast-scan B tip. The fully aging assemblies were cast on carbon-coated Cu grids (BGAc was stained) or mica slices; the trapped solvent in the assemblies was evaporated under ambient conditions before the TEM or AFM measurements. All operations were performed at room temperature unless otherwise specified.
Synthesis of L/D-BGAc

1. Synthesis of L-BGAc

1.1. Synthesis of L-Boc-GBn

L-Boc-GBn was synthesized according to the reported procedures.\(^1\)

To a 250 mL flask, were charged with L-Glutamic acid dibenzyl ester hydrochloride (4.50 g, 0.0124 mol), dichloromethane (100 mL) and triethylamine (5 mL). The mixture was stirred for 0.5 h at room temperature. After that, L-Boc-glutamic acid (1.54 g, 0.0062 mol) were added and the mixture was stirred at 0 °C for another 0.5 h. Subsequently, 1-Ethyl-3-(3-dimethyllaminopropyl)carbodiimide hydrochloride (EDC·HCl, 2.87 g, 0.015 mol) and 1- hydroxybenzotrizole (HOBt, 2.03 g, 0.015 mol) were added to the mixture. The mixture was stirred and the temperature was kept at 0 °C 3 h, then the ice bath was removed and stirring was continued for another 72 h at room temperature. The resulting mixture was poured into deionized water and washed by water several times. By rotary evaporation, the solvent was removed and after purification by silica column chromatography (CH₂Cl₂/ethyl acetate 2:1, \(R_f=0.20\)), the white solid was obtained via rotary evaporation, then the powder (L-Boc-GBn) was dried under vacuum at 30 °C (3.06 g, yield: 57%).

\(^1\)H-NMR: (400 MHz, CDCl₃, 25 °C, TMS) : δ (ppm) = 1.35 – 1.45 (9 H, s), 1.79 – 2.05 (4 H, m), 2.15 – 2.52 (8 H, m), 3.91 – 4.03 (1 H, s), 4.70 – 4.77 (1 H, m), 4.78 – 4.86 (1 H, m), 5.04 – 5.17 (8 H, m), 7.28 – 7.41 (20 H, m), 7.51 – 7.59 (1 H, d), 7.77 – 7.85 (1 H, d).

MALDI-TOF-MS calcd. for C₄₈H₅₅N₃O₁₂ m/z = 865.7. found: (M +Na)⁺: m/z = 888.1.

1.2. Synthesis of L-BGBn

This process includes two steps:

I: To a 250 mL flask, were charged with 5 mL COOHCF₃ and L-Boc-GBn (1.74 g, 0.002 mol). The mixture was stirred after adding 100 mL CH₂Cl₂ for 3 h to remove Boc group. After dried via vacuum distillation, viscous oil was obtained to use for
next step without purification.

II: The crude product from step I was dissolved in dichloromethane (100 mL) and TEA (5 mL) was added to the solution. The mixture was stirred at 0 °C for 0.5 h. Subsequently, behenic acid (0.77 g, 0.0024 mol) was added to the above solution and the mixture was stirred at 0 °C for another 30 min. After that, EDC (0.46 g, 2.4 mmol) and HOBt (0.32 g, 2.4 mmol) were added and the mixture was stirred at 0 °C for another 0.5 h, and then the ice bath was removed. Stirring was continued for another 72 h at room temperature. The resulting mixture was poured into deionized water and washed by water several times. By rotary evaporation, the solvent was removed and after purification by silica column chromatography (CH$_2$Cl$_2$/ethyl acetate 2:1, $R_f$ =0.20), the white solid was obtained via rotary evaporation, then the powder (BGBn) was dried under vacuum at 30 °C (1.14 g, yield: 52%).

$^1$H-NMR: (400 MHz, DMSO, 25 °C, TMS) : $\delta$ (ppm) =0.82 – 0.87 (3 H, t), 1.17 – 1.26 (36 H, m), 1.40 – 1.50 (2 H, m), 1.63 – 2.21 (14 H, m), 4.22 – 4.40 (3 H, m), 5.04 – 5.16 (8 H, d), 7.28 – 7.41 (20 H, m), 7.88 – 7.97 (1 H, d), 8.25 – 8.30 (1 H, d), 8.31 – 8.37 (1 H, d).

MALDI-TOF-MS calcd. for C$_{65}$H$_{89}$N$_3$O$_{11}$ m/z =1087.7. found: M$^+$ = 1087.7, (M +Na)$^+$: m/z =1109.7, (M +k)$^+$: m/z = 1125.7.

1.3. Synthesis of L-BGAc

To a 150 mL two-neck flask, equipped with a H$_2$ inlet as catalytically hydrogenated under 1 MPa, were charged with L-BGBn (1.04 g, 1.0 mmol) and 10% Pd/C (0.10 g). After injection of 60 ml of methyl alcohol, the mixture was stirred overnight. Finally, a white powered solid was obtained by filtration to remove residue, evaporation and dried under vacuum at 30 °C (0.43 g, yield: 62%).

$^1$H-NMR: (400 MHz, DMSO, 25 °C, TMS): $\delta$ (ppm) = 0.83 – 0.89 (3 H, t), 1.20 – 1.27 (36 H, s), 1.44 – 1.51 (2 H, s), 1.66 – 2.33 (14 H, m), 4.14 – 4.34 (3 H, m), 7.86 – 7.97 (1 H, m), 8.06 – 8.17 (2 H, m), 12.12 – 13.03 (4 H, br).

MALDI-TOF-MS calcd. for C$_{37}$H$_{65}$N$_3$O$_{11}$ m/z = 727.5. found: (M +Na)$^+$: m/z = 750.

Elemental analysis calcd (%) for: (C$_{37}$H$_{65}$N$_3$O$_{11}$) (%): C, 61.05; H, 9.00; N, 5.77.
found: C, 60.42; H, 9.18; N, 5.71.

2. Synthesis of D-BGAc

2.1. Synthesis of D-Boc-GMe

Briefly, the synthesis scheme of D-Boc-GMe was similar to the synthesis of L-Boc-GBn, except that L-Glutamic acid dibenzyl ester hydrochloride and L-Boc-glutamic acid were replaced by D-Glutamic acid dimethyl ester hydrochloride (2.63 g, 0.0124 mol) and D-Boc-glutamic acid (1.54 g, 0.0062 mol), respectively, then the powder (D-Boc-GMe) was dried under vacuum at 30 °C (2.02 g, yield: 58%).

$^1$H-NMR: (400 MHz, CDCl$_3$, 25 °C, TMS): $\delta$ (ppm) = 1.35 – 1.45 (9 H, s), 1.84 – 2.50 (12 H, m), 3.59 – 3.86 (12 H, m), 3.96 – 4.03 (1 H, s), 4.57 – 4.85 (2 H, m), 5.04 – 5.22 (1 H, m), 7.48 – 8.09 (2 H, m).
MALDI-TOF-MS calcd. for C$_{24}$H$_{39}$N$_3$O$_{12}$ m/z = 561.25. found: (M +Na)$^+$: m/z = 583.5.

2.2. Synthesis of D-BGMe

Similar way to obtain L-BGBn was given and D-Boc-GMe (1.12 g, 0.002 mol) was used. instead of L-Boc-GBn, then the powder (D-BGMe) was dried under vacuum at 30 °C (0.95 g, yield: 61%).

$^1$H-NMR: (400 MHz, DMSO, 25 °C, TMS): $\delta$ (ppm) = 0.82 – 0.90 (3 H, t), 1.11 – 1.46 (38 H, m), 1.61 – 2.20 (14 H, m), 2.33 – 2.40 (3 H, t), 3.55 – 3.64 (9 H, s), 4.20 – 4.31 (3 H, m), 7.89 – 7.95 (1 H, d), 8.20 – 8.31 (2 H, m).
MALDI-TOF-MS calcd. for C$_{41}$H$_{73}$N$_3$O$_{11}$ m/z =783.5. found: (M +Na)$^+$: m/z = 806.0.

2.3 Synthesis of D-BGAc

D-BGMe (0.78 g, 1.0 mmol) was added to 10 mL of 3N NaOH aqueous solution, and stirred at 60°C for 5 h. The mixture was treated with 6 N HCl to get pH=1 solution, and white solid was obtained, which was recrystallized in water to get the
product after washed by water several times (0.63 g, yield: 87%).

\(^1\)H-NMR: (400 MHz, DMSO, 25 °C, TMS): \(\delta \) (ppm) = 0.83 – 0.89 (3 H, t), 1.20 – 1.27 (36 H, s), 1.44 – 1.51 (2 H, s), 1.66 – 2.33 (14 H, m), 4.14 – 4.34 (3 H, m), 7.86 – 7.97 (1 H, m), 8.06 – 8.17 (2 H, m), 12.12 – 13.03 (4 H, br).

MALDI-TOF-MS calcd. for \(\text{C}_{37}\text{H}_{65}\text{N}_3\text{O}_{11}\) m/z = 727.5. found: (M +Na): m/z = 750.0, (M +K): m/z = 766.0.

Elemental analysis calcd (%) for: \(\text{C}_{37}\text{H}_{65}\text{N}_3\text{O}_{11}\) (%): C, 61.05; H, 9.00; N, 5.77.
found: C, 60.69; H, 9.19; N, 5.58.

3. Formation of hydrogels:

BGAc (6 mg) was added to a capped tube with 1 mL of aqueous solution and the mixture was heated until the solids were completely dissolved. If it was to obtain a co-gel formed by BGAc and QDs, an aqueous solution of 0.2 mg/mL QDs was used. The solution was then cooled to room temperature under ambient conditions. After a while, the formation of the gel can be confirmed by inverting the test tube. If there was no fluid in the inverted tube, a hydrogel was formed.
3. Supplementary Figures

Fig. S1. Synthetic routes of L-BGAc. (a) triethylamine (TEA), EDC, HOBt, CH$_2$Cl$_2$; (b) I, trifluoroacetic acid (TFA); II, behenic acid, EDC, HOBt, CH$_2$Cl$_2$; (c) Pt/C, H$_2$, methanol.
Fig. S2. Normalized fluorescence spectra of the various CdSe/ZnS Quantum Dots solution in H₂O. [QDs] = 0.2 mg mL⁻¹, λ<sub>ex</sub> = 360 nm.

Fig. S3. Normalized absorption spectra of the L-BGAc hydrogel ([L-BGAc] = 6 mg/mL) and cyan-color QDs/L-BGAc and QDs/D-BGAc cogel ([QDs] = 0.2 mg mL⁻¹, [L-/D-BGAc] = 6 mg mL⁻¹).
Fig. S4. CPL spectra of the cyan QDs/BGAc co-gel excited at 360 nm. The solvent is 
H$_2$O. [BGAc] = 6 mg mL$^{-1}$; [QDs] = 0.2 mg mL$^{-1}$.

Fig. S5. TEM images made from stanined (a-c) and unstained (d-f) BGAc hydrogel: 
fibrous network and bilayers structures at large and small scales, respectively; [BGAc] 
= 6 mg mL$^{-1}$. 
Fig. S6. The enlarged FTIR spectra of co-assemblies and each component.

4. **Supplementary Table**

Table S1. The maximum CPL dissymmetry factor $g_{\text{lum}}$ of QDs/L-BGAc and QDs/D-BGAc hydrogels excited at 360 nm.

<table>
<thead>
<tr>
<th>QDs Color</th>
<th>$g_{\text{lum}}$</th>
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<tr>
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4. **References**