

Supporting Information

Extreme enhancement of secondary chirality through coordination-driven steric changes of terpyridyl ligand in glutamide-based molecular gels

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Figure S1

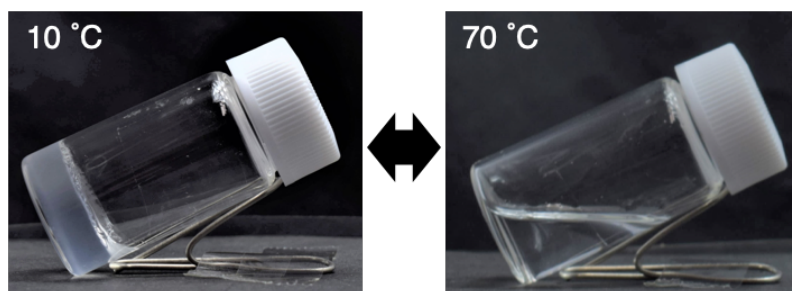


Figure S1 Photographic images of a 9:1 cyclohexane-methanol solution of **G-tpy** (5 mM) at 10 °C (gel phase) and 70 °C (sol phase).

Table S1

Table S1 Gelation property of **G-tpy** in various organic solvent

Solvent	G-tpy	
	70 °C	10 °C
Methanol	S	I
Ethanol	S	I
Ethyl acetate	I	I
Chloroform	S	S
Benzene	I	I
Cyclohexane	I	I
Chloroform-Cyclohexane (9 : 1)	S	I
Chloroform-Cyclohexane (5 : 5)	S	G
Chloroform-Cyclohexane (1 : 9)	I	I
Ethanol-Cyclohexane (9 : 1)	S	I
Ethanol-Cyclohexane (5 : 5)	S	I
Ethanol-Cyclohexane (1 : 9)	S	G

[**G-tpy**] = 5 mM

S: Soluble, I: Insoluble, G: Gelation

Figure S2

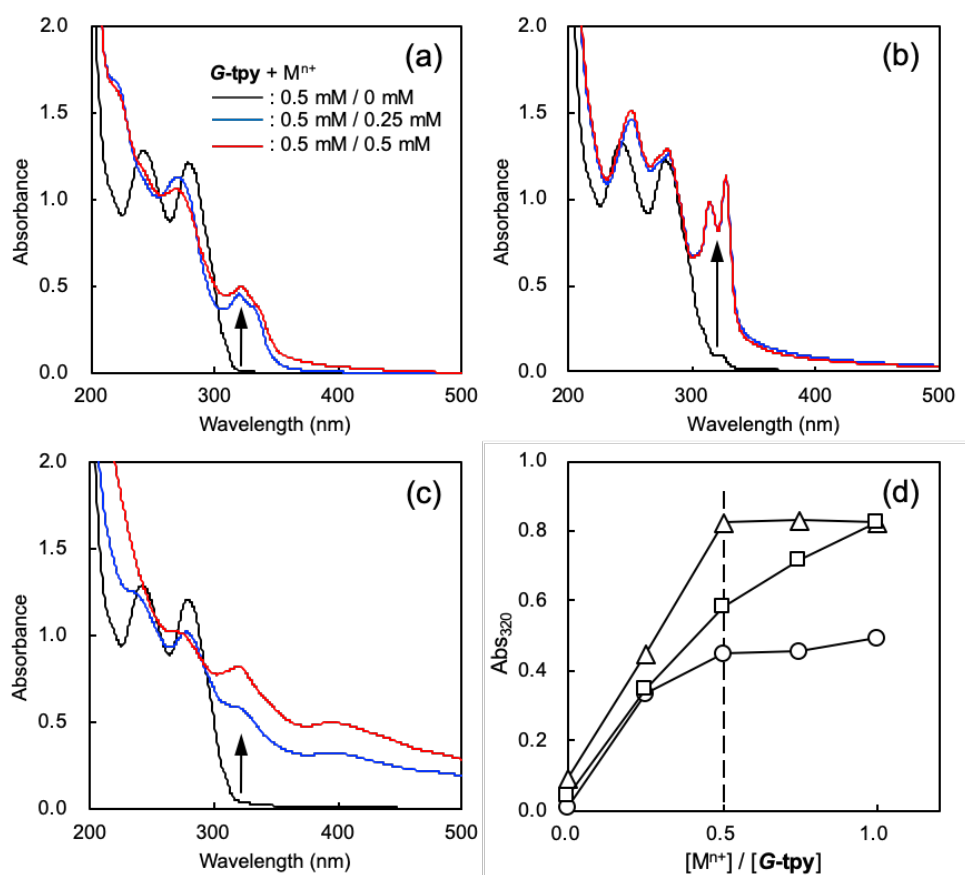


Figure S2. (a–c) UV-vis spectra of **G-tpy** without and with metal ions (a: Cu^{2+} , b: Zn^{2+} , c: Ru^{3+}), and (d) relationships between absorbance at 320 nm and metal-ion concentration (circle: Cu^{2+} , triangle: Zn^{2+} , square: Ru^{3+}).

Figure S3

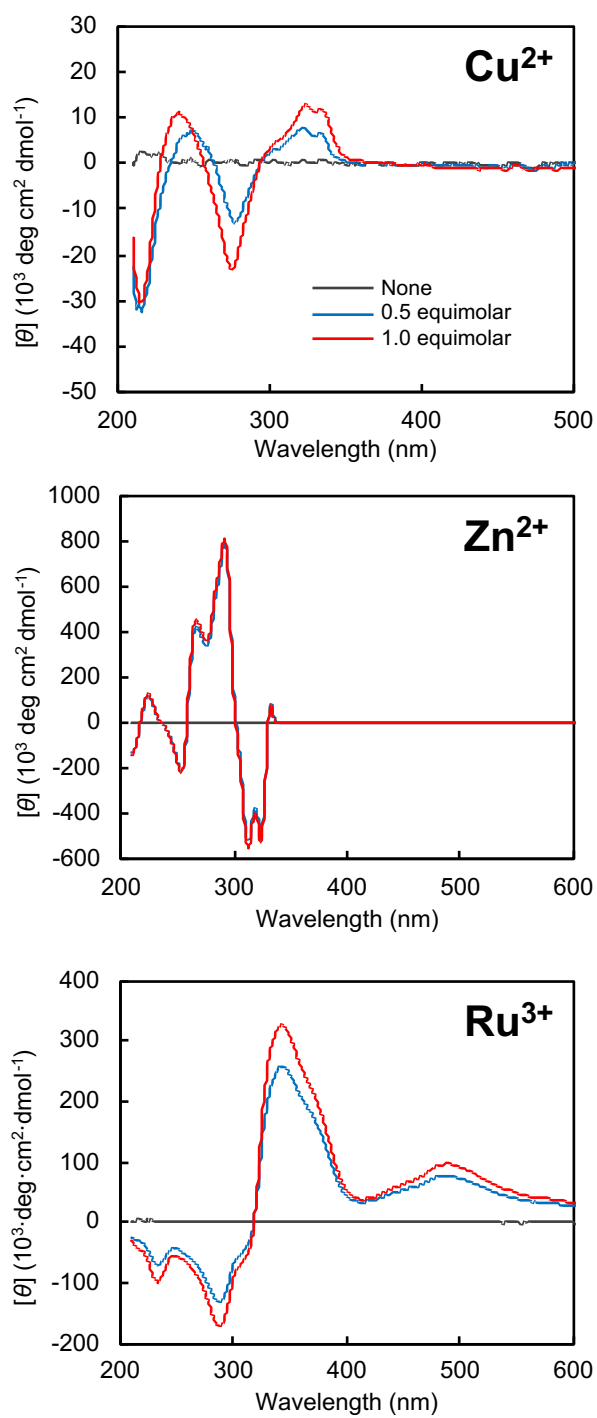
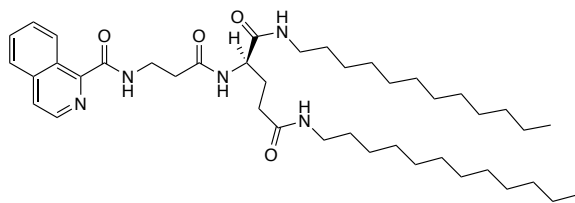
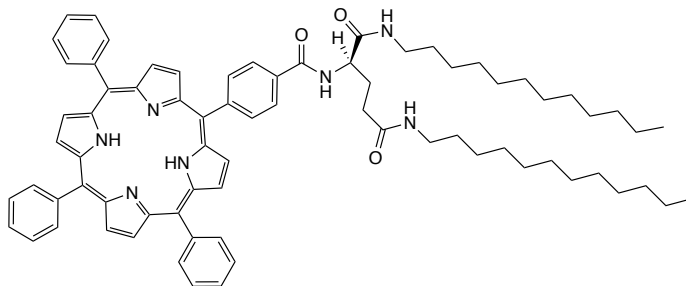


Figure S3 CD spectra of **G-tpy** without and with metal ions.
[**G-tpy**] = 0.5 mM.

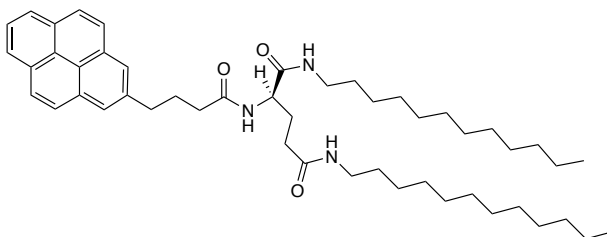
Figure S4



G-iq



G-por



G-pyr

Figure S4 Chemical structures of **G-iq**, **G-por** and **G-pyr**.

Figure S5

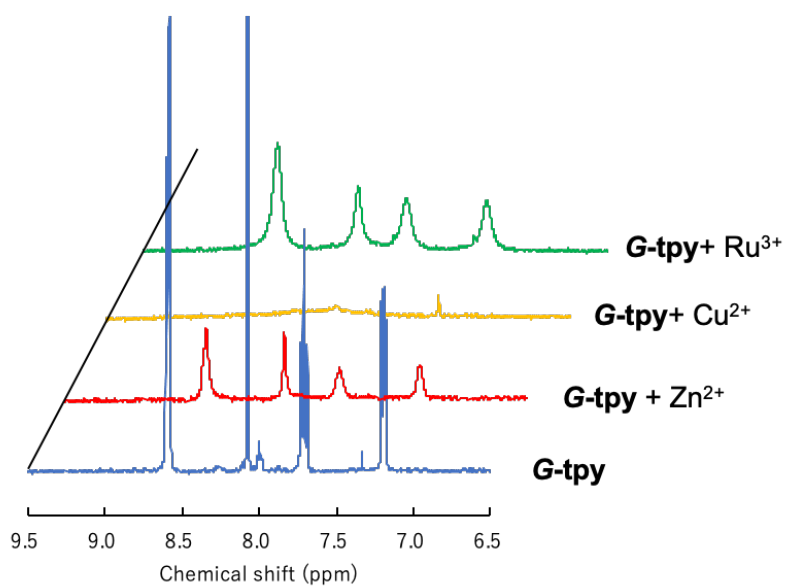


Fig. S5 ¹H NMR spectra of **G-tpy** without and with metal ions.
Solvent: cyclohexane-*d*12 and ethanol-*d*6 (9 : 1). [**G-tpy**] = [metal ion] = 2.5 mM.

Figure S6

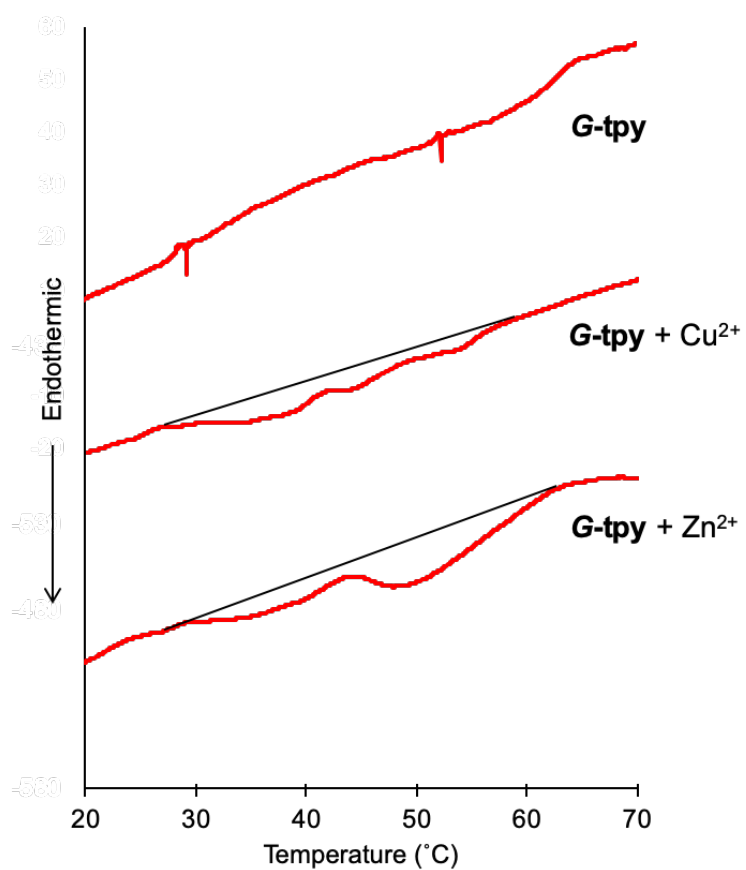


Figure S6 DSC thermograms of **G-tpy** without and with Cu²⁺ and Zn²⁺.
[**G-tpy**] = 10 mM, [metal ion] = 5 mM. Heating rate = 2 °C/min

Figure S7

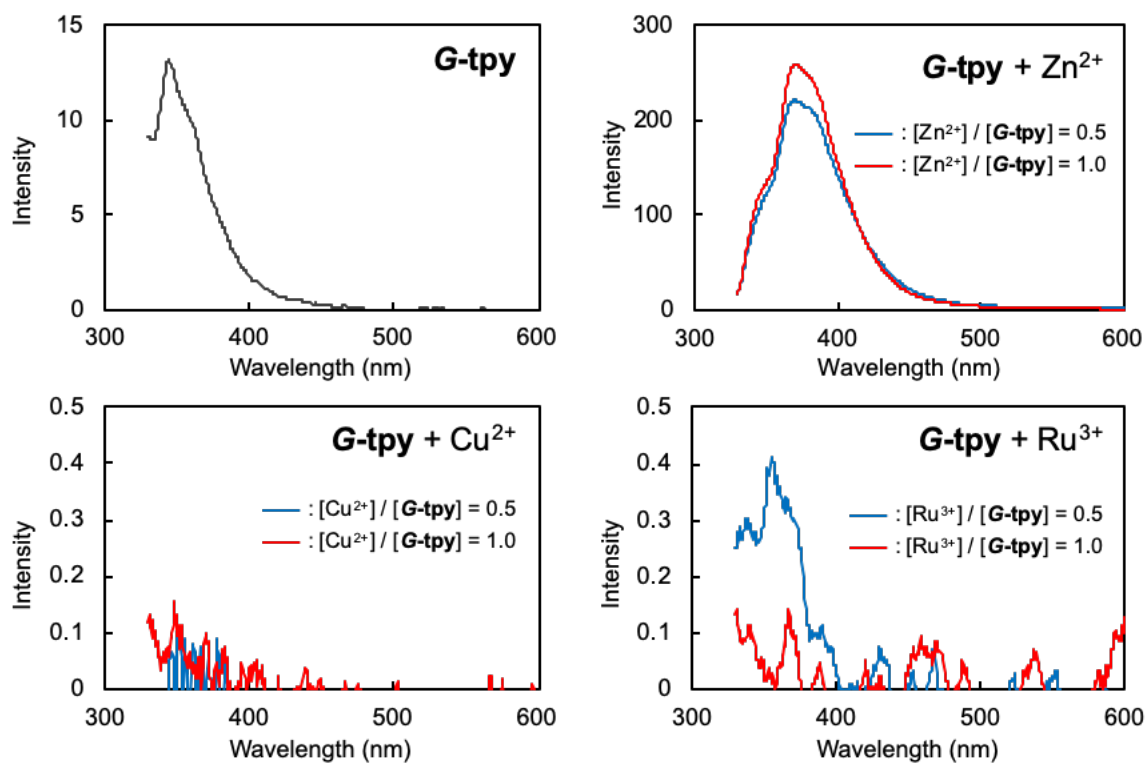


Figure S7 Fluorescence spectra of **G-tpy** without and with various metal ions. [G-tpy] = 0.5 mM, [metal ion] = 0.25 mM and 0.5 mM. Excitation wavelength: 320 nm.

Figure S8

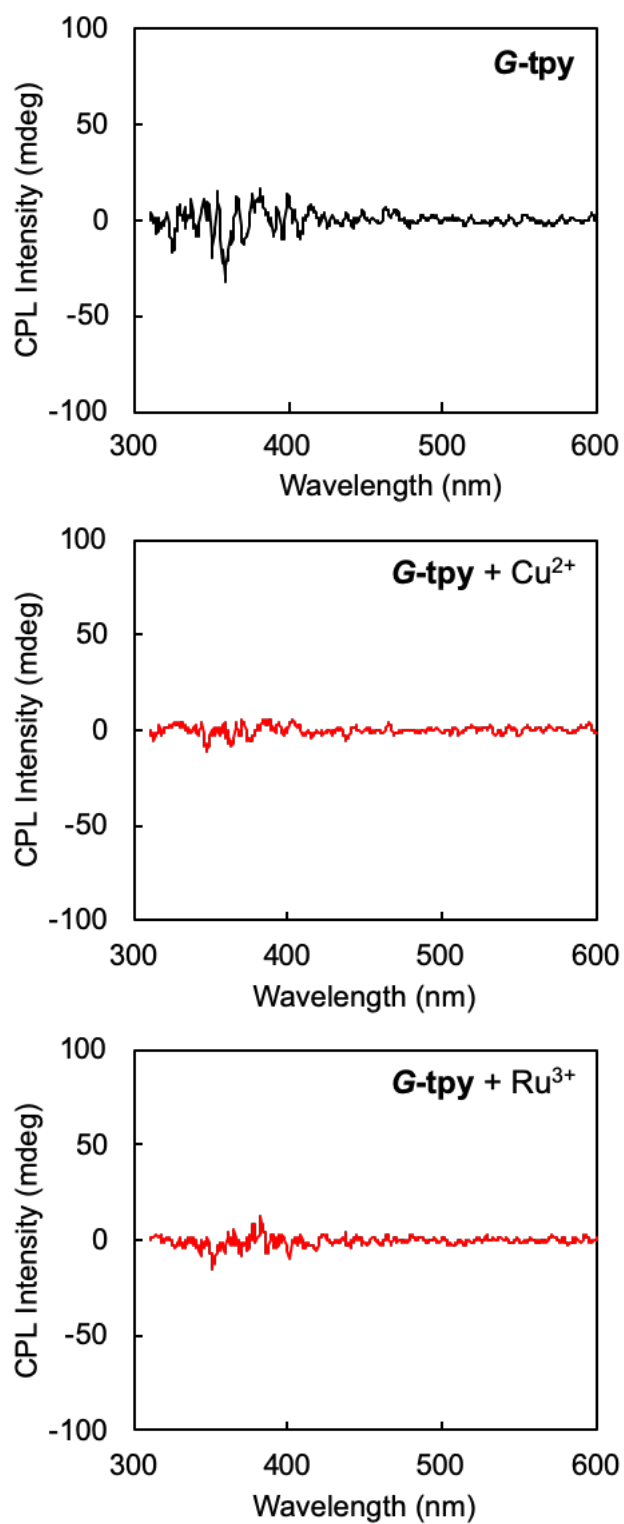


Figure S8 CPL spectra of **G-tpy** without and with Cu²⁺ and Zn²⁺.
[**G-tpy**] = 0.5 mM, [metal ion] = 0.5 mM. Excitation wavelength: 260 nm.

Figure S9

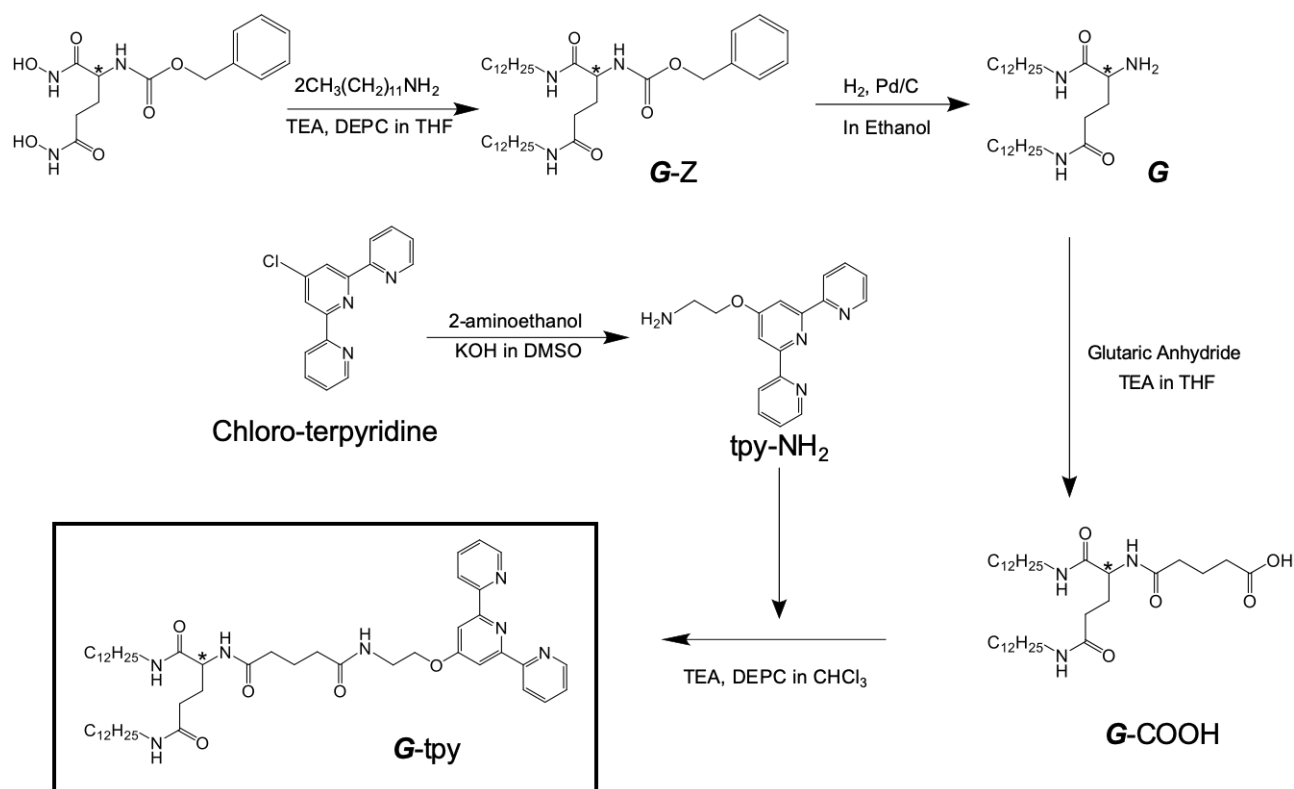


Figure S9 Synthetic procedure of **G-tpy**.

1. Synthesis of **G-Z** [1]

N,N'-Didodecyl-*N*-benzyloxycarbonylglutamide (**G-Z**). *N*-Benzyloxycarbonylglutamic acid (7.0 g, 25 mmol), *n*-dodecylamine (12 mL, 53 mmol), and triethylamine (8.9 g, 63 mmol) were dissolved in THF (400 mL) (23). The solution was cooled to 0 °C, and diethylphosphorocyanidate (DEPC) (10 mL, 64 mmol) was added to the solution and stirred for 1 h at this temperature. After stirring for 1 day at room temperature, the solution was concentrated in vacuo, and the residue was dissolved in 350 mL of chloroform. The solution was washed with 50 mL of 10% NaHCO_3 (3 times), 50 mL of 0.3 N HCl (3 times) and with water until the pH becomes neutral. The solution was dried over Na_2SO_4 , concentrated, and finally recrystallized from ethanol, which gave a white solid powder: yield 10.7 g (68%, 17 mmol); mp 141–143 °C; FT-IR (KBr)/ 3287, 2917, 2850, 1686, 1637, and 1539 cm^{-1} ; ^1H NMR (CDCl_3) δ 0.862-0.896 (t, 6H, CH_3), 1.257 (m, 36H, CH_3 - $(\text{CH}_2)_9$), 1.486 (m, 4H, $\text{CH}_2\text{CH}_2\text{NHC}(=\text{O})$), 1.980 (m, 1H, C^*HCH_2), 2.091 (m, 1H, C^*HCH_2), 2.297 (m, 2H, C^*HCH_2 - $\text{CH}_2\text{C}(=\text{O})$), 3.221 (m, 4H, $\text{CH}_2\text{NHC}(=\text{O})$), 4.144 (m, 1H, C^*H), 5.098 (s, 2H, CH_2Ph), 7.328 (s, 5H, Ph). Anal. Calcd. for $\text{C}_{37}\text{H}_{65}\text{N}_3\text{O}_4$: H, 10.9; C, 72.1; N, 6.82. Found: H, 10.9; C, 71.8; N, 6.75;

2. Synthesis of **G** [1]

*N*₁,*N*₂-didodecyl-L-glutamide (**G**) was synthesized according to our previous report.^[1] mp 117.5–119.5 °C. IR spectrum (KBr): 3326, 2920, 2850, 1634, 1533 cm⁻¹. ¹H NMR (400 MHz, CDCl₃, TMS, 25 °C): δ 0.86–0.90 (t, *J* = 6.0 Hz, 6H, –CH₃), 1.26 (m, 36H, –(CH₂)₉–), 1.49 (m, 4H, –NHCH₂CH₂–), 1.91–1.96 (q, 2H, –C*HCH₂–), 2.30–2.34 (m, 2H, –C*HCH₂CH₂–), 3.20–3.26 (m, 4H, –NHCH₂–), 3.40–3.43 (t, 1H, C*H), 6.08–6.15 (bs, 1H, –NH–), 7.29–7.35 (bs, 1H, –NH–). Anal. Calcd for C₂₉H₅₉N₃O₂: C, 72.3; H, 12.3; N, 8.7. Found: C, 72.1; H, 13.3; N, 8.9.

3. Synthesis of **G-COOH** [2]

*N*¹-4-carboxybutanoyl-*N*²,*N*³-didodecyl-L-glutamide (**G-COOH**): **G-COOH** were synthesized according to our previous report. mp 153.0–155.0 °C. IR spectrum (KBr): 3292, 2920, 2850, 1703, 1637, 1556 cm⁻¹. ¹H NMR (400 MHz, CDCl₃, TMS, 25 °C): δ 0.86–0.90 (t, *J* = 6.0 Hz, 6H, –CH₃), 1.25–1.30 (m, 36H, –(CH₂)₉–), 1.45–1.52 (m, 4H, –NHCH₂CH₂–), 1.90–2.15 (m, 4H, –C*HCH₂CH₂–), 2.30–2.39 (m, 6H, HO(C=O)CH₂CH₂CH₂–), 3.15–3.25 (m, 4H, –NHCH₂–), 4.40–4.50 (m, 1H, C*H), 6.20–6.25 (t, 1H, –NH–), 7.05–7.10 (t, 1H, –NH–), 8.55–8.60 (d, 1H, –NH–). Anal. Calcd for C₃₄H₆₅N₃O₅: C, 68.5; H, 11.0; N, 7.1. Found: C, 67.9; H, 11.7; N, 7.1.

4. Synthesis of **tpy-NH₂** [3]

4'-Chloro-2,2':6',2''-terpyridine (546 mg, 2 mmol) and ethanolamine (360 μl, 3 mmol) were added to a stirred suspension of powdered KOH (560 mg, 10 mmol) in DMSO (10 ml) and stirred at 40 °C for 1 day. The reaction mixture was then added to 80 mL of methylene chloride and wash with 50 mL of water (3 times). The methylene chloride solution was dried over Na₂SO₄ and the solvent was removed. After it was recrystallized by toluene and hexane mixture to give a light yellow powder: yield 345 mg (59%). mp 130.0–132.0 °C. IR spectrum (KBr): 3362, 2920, 2850, 1559, 1412, 1204 cm⁻¹. ¹H NMR (400 MHz, CDCl₃, TMS, 25 °C): δ 3.15–3.17 (t, 2H, *H*_α), 4.25–4.28 (t, 2H, *H*_β), 7.32–7.35 (t, 2H, *H*_{5;5''}), 7.83–7.88 (t, 2H, *H*_{4;4''}), 8.03–8.05 (s, 2H, *H*_{3';5'}), 8.61–8.63 (d, 2H, *H*_{3;3''}), 8.68–8.70 (d, 2H, *H*_{6;6''}).

5. Synthesis of **G-tpy**

G-COOH (0.40 g, 0.67 mmol), **tpy-NH₂** (0.23 g 0.79 mmol), triethylamine (TEA, 2.53 g 3.48 mmol) and diethyl cyanophosphonate (DEPC, 0.45 ml 2.88 mmol) were dissolved in chloroform (200 mL) and the mixture was stirred for 1 hour in the ice water. Then the reaction mixture was stirred for 1 day in the room temperature. The reaction mixture was washed with 50 mL of 0.3 N HCl (3 times), 50 mL of 1 N NaOH (3 times) with water until the pH becomes neutral. The chloroform solution was

dried over Na_2SO_4 and the solvent was removed. After it was recrystallized by methanol to give a white powder: yield 464 mg (80%). mp 192.0–196.0 °C. IR spectrum (KBr): 3292, 2920, 2850, 1637, 1556, 1204 cm^{-1} . ^1H NMR (400 MHz, CDCl_3 , TMS, 25 °C): δ 0.86–0.90 (t, $J = 6.0$ Hz, 6H, $-\text{CH}_3$), 1.25–1.30 (m, 36H, $-(\text{CH}_2)_9-$), 1.45–1.52 (m, 4H, $-\text{NHCH}_2\text{CH}_2-$), 1.90–2.01 (m, 2H, $-\text{C}^*\text{HCH}_2-$) 1.97–2.01 (t, 2H, $-\text{C}^*\text{HNHC}(=\text{O})\text{CH}_2\text{CH}_2-$), 2.30–2.39 (m, 6H, $-\text{CH}_2\text{CH}_2\text{CH}_2\text{C}(=\text{O})-$) 3.15–3.25 (dt, 4H, $-\text{CH}_2-$) 3.66–3.86 (m, 2H, $-\text{C}^*\text{H NHC}(=\text{O})\text{CH}_2\text{CH}_2\text{CH}_2\text{C}(=\text{O})\text{NHCH}_2-$) 4.32–4.50 (m, 3H, $-\text{C}^*\text{HNHC}(=\text{O})\text{CH}_2\text{CH}_2\text{CH}_2\text{C}(=\text{O})\text{NH CH}_2\text{CH}_2-$) 6.10–6.15 (t, 1H, $-\text{NH}-$) 6.63–6.72 (t, 1H, $-\text{NH}-$) 6.89–6.97 (d, 2H, $-\text{NH}-$) 7.32–7.35 (t, 2H, $H_5, 5''$) 7.83–7.88 (t, 2H, $H_4, 4''$) 8.03–8.05 (s, 2H, $H_3, 3''$) 8.61–8.63 (d, 2H, $H_3, 3''$) 8.68–8.70 (d, 2H, $H_6, 6''$). Anal. Calcd for $\text{C}_{34}\text{H}_{65}\text{N}_3\text{O}_5$: C, 70.4; H, 9.2; N, 11.3. Found: C, 70.0; H, 9.7; N, 11.3.

- [1] H. Ihara, M. Takafuji, C. Hirayama, D. F. O'Brien, *Langmuir* 1992, **8**, 1548–1553; H. Hachisako, Y. Murata, H. Ihara, *J. Chem. Soc. Perkin Trans.*, 1999, **2**, 2569–2577.
- [2] M. Takafuji, H. Ihara, C. Hirayama, H. Hachisako, K. Yamada, *Liq. Cryst.*, 1995, **18**, 97–99.
- [3] G. Maayan, B. Yoo and K. Kirshenbaum, *Tetrahedron Lett.*, 2008, **49**, 335–338.

