Supporting information

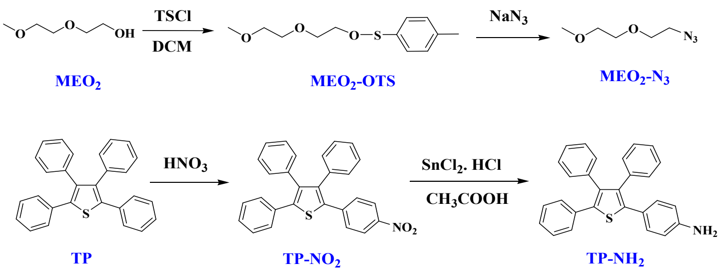
Influence of Secondary Structure on the AIE-Related Emission Behavior of Amphiphilic Polypeptide Containing a Hydrophobic Fluorescent Terminal and Hydrophilic Pendant Groups

Li-Yang Lin, Po-Chiao Huang, Deng-Jie Yang, Jhen-Yan Gao, and Jin-Long Hong*

Department of Materials and Optoelectronic Science, National Sun Yat-Sen
University, Kaohsiung 80424, Taiwan

Materials

Compounds of MEO_2-N_3[1)], TP-NO_2[2)] and TP-NH_2[2)] were prepared according to the Scheme S1 and detailed as follow:



Scheme S1. Syntheses of TP-NO_2, TP-NH_2 and MEO_2-N_3.

Synthesis of 2,5-bis(4-nitrophenyl)-3,4-diphenylthiophene (TP-NO_2): A mixture of TP (10 g, 25.74 mmol) and glacial acetic acid (200 mL) was vigorously stirred at 110 °C to result in a homogeneous suspension, to which mixed liquids of glacial acetic acid (20 mL) and concentrated nitric acid (10 mL) were added quickly. After stirring at 100 °C for another 3 h, the yellow suspension was filtered to obtain the crude product. Continuous washing of the crude product with water was performed until the neutral condition (pH = 7) was reached. Column chromatography with hexane eluent yielded the final product (11.21 g; 90% yield). Mp: 220 °C; ^{1}H NMR (500 MHz, DMSO, Fig. S2).

Synthesis of 2,5-bis(4-aminophenyl)-3,4-diphenylthiophene (TP-NH_2): TPNO_2 (2.51 g, 5.25 mmol) and glacial acetic acid (25 mL) were charged into a 250 mL round-bottom flask equipped with a reflux condenser, nitrogen inlet and outlet. A solution of stannous chloride dihydrate (12.5 g, 55.4 mmol) in conc. HCl (4 mL) was then added quickly and the whole mixture was heated at 100 °C for 5 h. The mixture was cooled in an ice–salt bath. The solid dihydrochloride salt was filtered and re-dissolved in 15–20 mL of hot water, to which another portion of conc. HCl (3 mL) was added. After cooling to room temperature, the hydrochloride salt was collected by filtration and dried before re-dissolution in water. A 40% aq. NaOH solution was slowly added to the product solution in an ice–salt bath to the extent of pH = 12. The solid precipitates were then filtered and washed several times with cold water before being dried in a vacuum oven at 40 °C. The crude solid product was recrystallized twice from toluene to yield the white needle-like crystals as the final product (1.75 g, 80% yield). Mp: 283 °C; ^{1}H-NMR (500 MHz, DMSO, Fig. S3).

Synthesis of 1-(2-methoxyethoxy)-2-azidoethane (MEO_2 -N_3): MEO_2OH (18.3 mL, 0.15 mol), methanesulfonyl chloride (21.2 mL, 0.18 mol), and THF (200 mL) were placed in a 500 mL round-bottom flask in an ice bath. Then triethylamine (25 mL, 0.18 mol) was added dropwise over 20 min. The reaction mixture was gradually warmed to room temperature and stirred overnight. The mixture was diluted by the addition of 200 mL H_2O and the pH was adjusted to neutral by adding $NaHCO_3$. Sodium azide (11.8 g, 0.18 mol) was added, and the reaction mixture was heated to evaporate THF and then refluxed overnight. After cooling to room temperature, the mixture was extracted by ethyl acetate. The combined organic phase was dried over $MgSO_4$, filtered, and evaporated to obtain yellow oil. The crude product was chromatographed on silica gel with a CH_2Cl_2 /MeOH mixed solution ((CH_2Cl_2 : MeOH v/v) = 15 : 1) as the eluent; ^{1}H-NMR (500 MHz, $CDCl_3$, Fig. S1)

References

1) Y. Cheng, C. He, C. Xiao, J. Ding, X. Zhuang and X. Chen, *Polym. Chem.*, **2011**, 2, 2627–2634.

2) S.T. Li, Y. C. Lin, S. W. Kuo, W. T. Chuang and J. L. Hong, *Polym. Chem.*, **2012**, 3, 2393–2402.

Table S1. Variation of secondary structures[a] upon adding NaCl to the aqueous solution of TP-PPLG-*g*-MEO$_2$ (= 1.5 x 10^{-5} M)

[NaCl]	α-Helix (%)	β-Sheet (%)	Turn (%)	Random coil (%)
0.0 M	72.9	3.0	0.0	24.1
0.017 M	39.9	25.1	14.8	20.2
0.051 M	27.3	38.2	15.7	18.8
0.085 M	24.0	33.5	21.7	22.9
0.119 M	23.5	35.5	19.4	21.6
0.154 M	23.3	32.3	21.8	22.6

[a] evaluated by fitting the circular dichroism spectra of Figure 7 by Spectra Manager program.

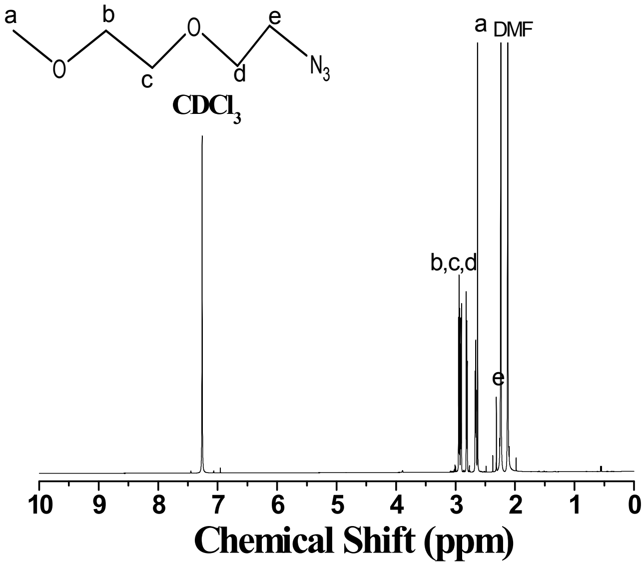


Figure S1 ^{1}H NMR spectra of MEO_2-N_3 ($CDCl_3$)

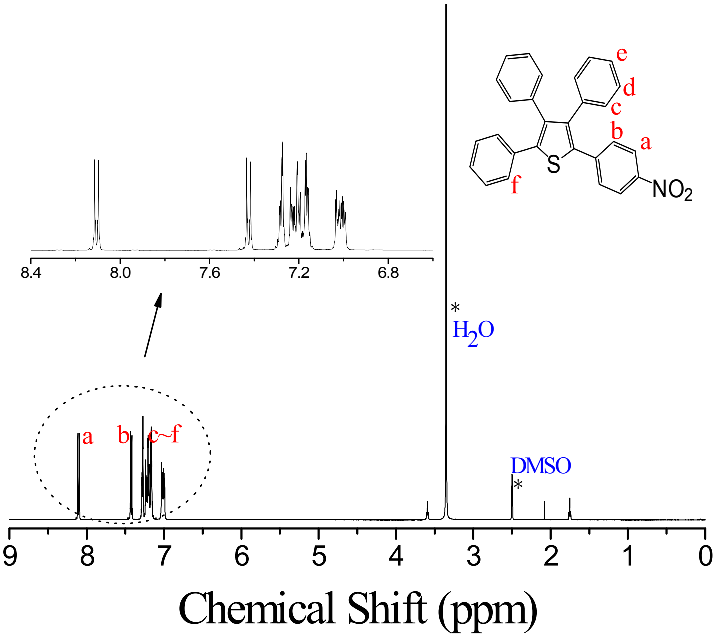


Figure S2 ^{1}H NMR spectra of TP-NO_2 (d_6-DMSO).

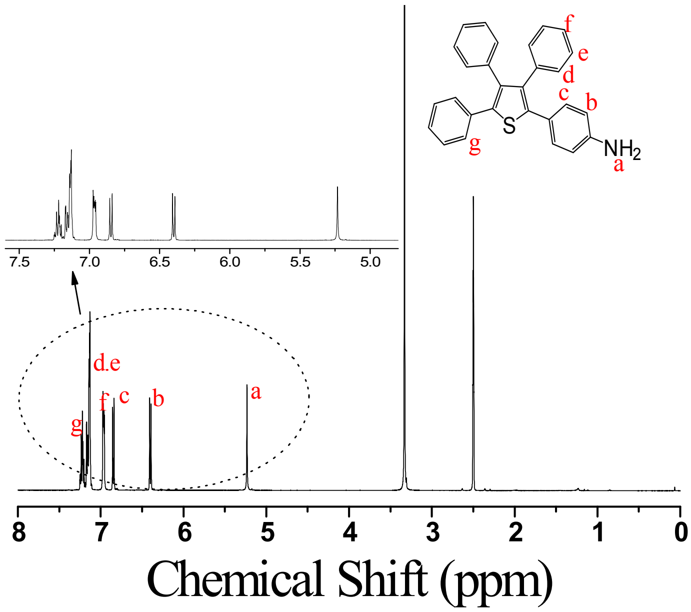


Figure S3 ^{1}H NMR spectra of TP-NH$_2$ (d_6-DMSO).

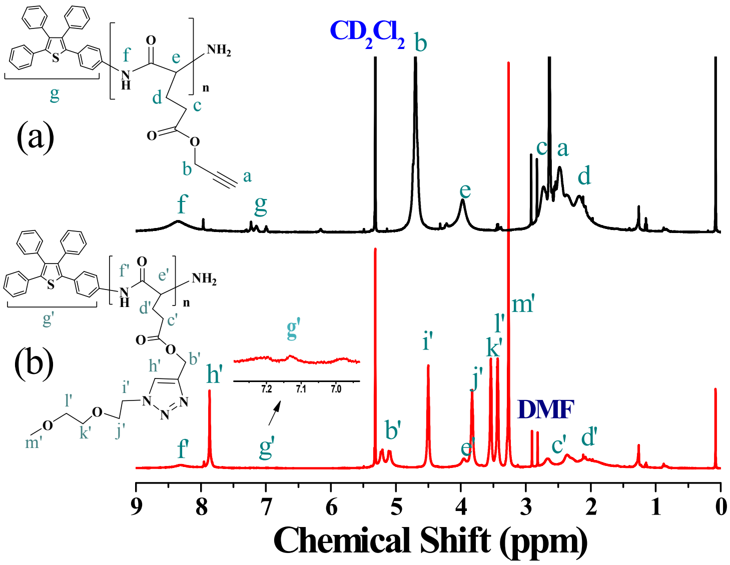


Figure S4 ^{1}H NMR spectra of (a) TP-PPLG and (b) TP-PPLG-*g*-MEO$_2$ (in CD$_2$Cl$_2$).

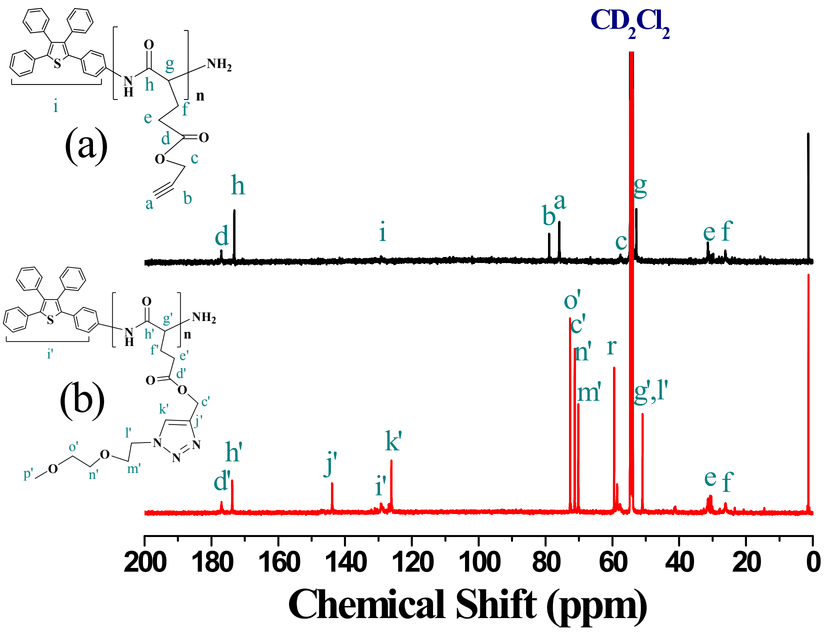


Figure S5. ^{13}C NMR spectra of (a) TP-PPLG and (b) TP-PPLG-*g*-MEO$_2$ (in CD_2Cl_2).

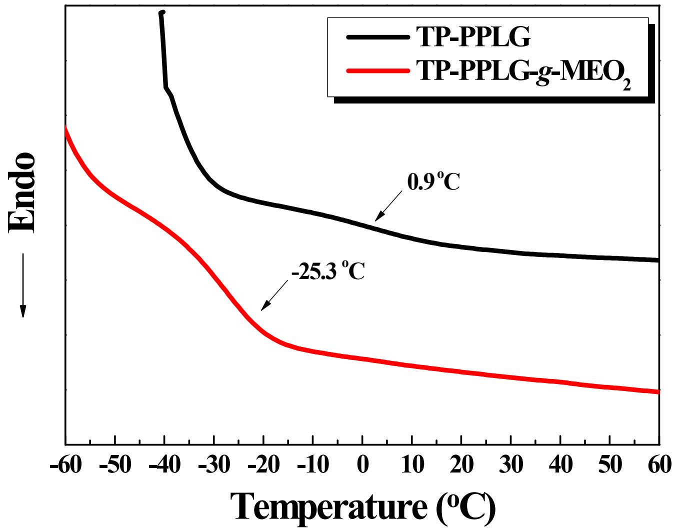


Figure S6. DSC thermograms of TP-PPLG and TP-PPLG-*g*-MEO$_2$ (heating rate = 10 °C/min).

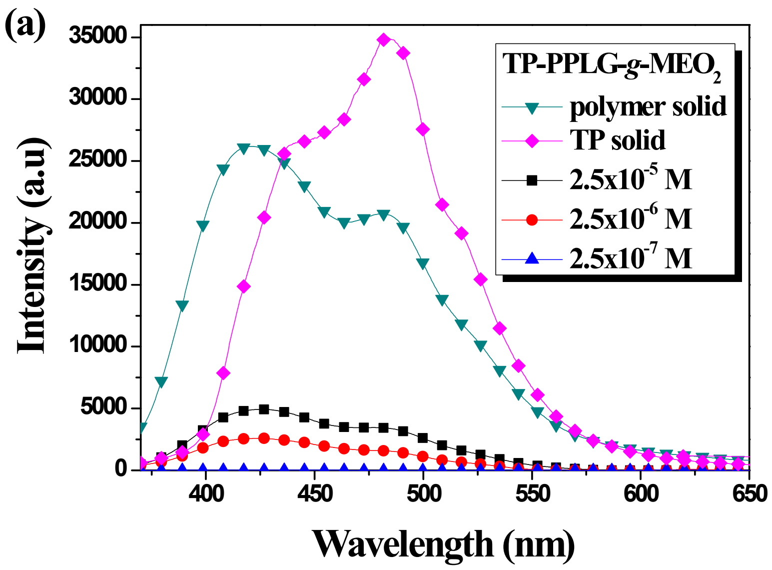


Figure S7. Emission spectra of (a) TP-PPLG-*g*-MEO$_2$ solid and solutions in DCM of different concentration

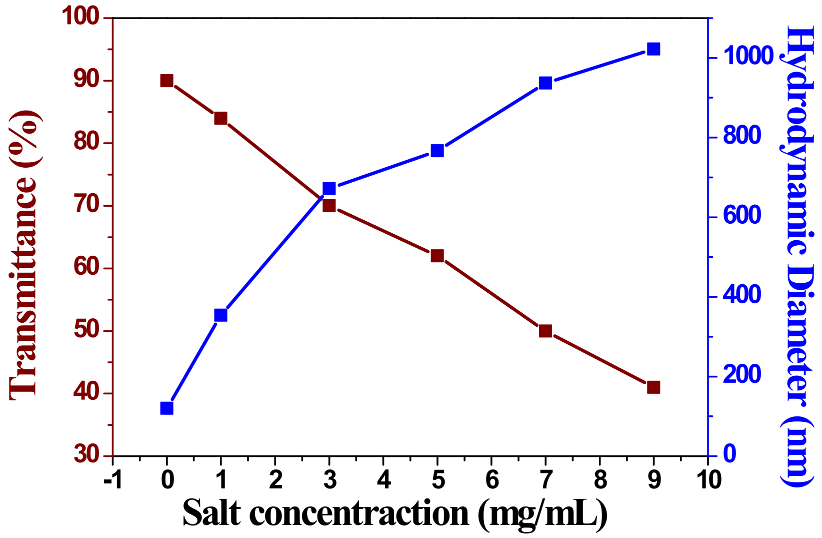


Figure S8. Transmittance (monitored at 600 nm) and hydrodynamic diameter of the aqueous TP-PPLG-*g*-MEO_2 (= $1.5x10^{-5}$ M) solutions containing different amounts of NaCl salt.

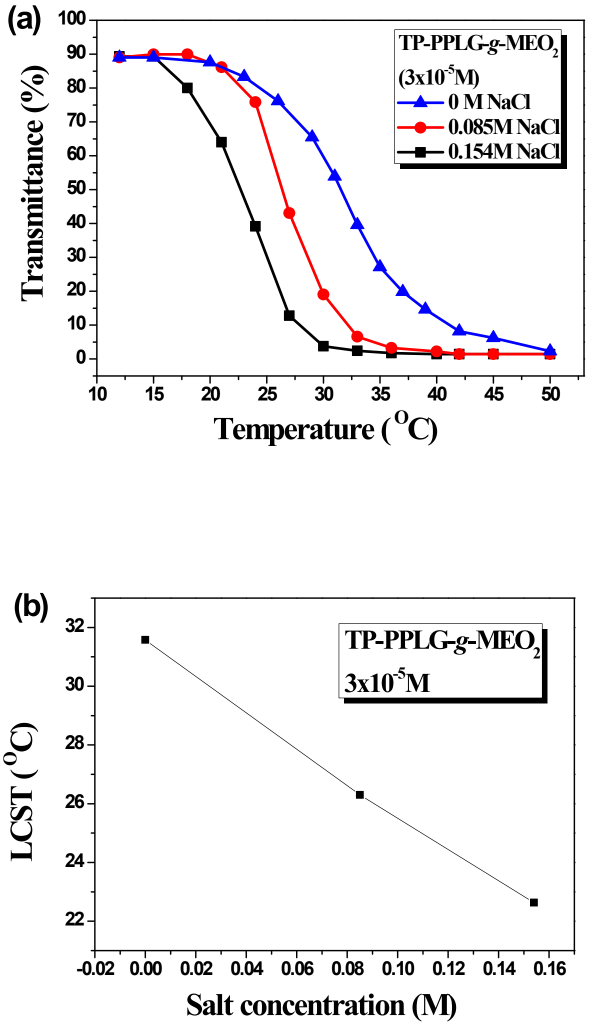


Figure S9. (a) Influence of temperature on the light transmittance of the aqueous TP-PPLG-*g*-MEO$_2$ solutions containing different amounts of NaCl; (b) the lowering of LCST (“salting-out”) with increasing NaCl concentration in the aqueous TP-PPLG-*g*-MEO$_2$ solutions.