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Supporting Information

Size-Specific, Colorimetric Detection of Counter Anions using Helical Poly(phenylacetylene) Conjugated to L-Leucine groups through Urea acceptors

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Synthesis of poly($PA_{0.51}$-*co*-PA-$Leu_{0.49}$). The copolymerization of **PA-Leu** with phenylacetylene was carried out in a dry flask under an argon atmosphere. In a glovebox (under moisture- and oxygen-free argon atmosphere, H_2O, O_2 < 1 ppm), **PA-Leu** (152 mg, 0.50 mmol) and phenylacetylene (65 mg, 0.64 mmol) were weighed into a flask and dissolved in dry DMF (25 mL). To the solution was added a solution of Rh(nbd)BPh_4 (10 mg, 19 μmol) in dry DMF (8.1 mL). After stirring at room tempreture for 24 hours, triphenylphosphine (35 mg, 0.14 μmol) was added to the reaction mixture. The solution was concentrated and then poured into a large amount of acetonitrile. The precipitate was purified by reprecipitation with acetonitrile and then dried under reduced pressure to give **poly($PA_{0.51}$-*co*-PA-$Leu_{0.49}$)** as a yellow powder. The molar fraction of the urea unit in the obtained polymer was estimated to be 0.49 based on the integration ratio between the signal due to the polymer main chain proton (d; 5.74 - 6.07 ppm, see Figure S-2) and those due to the protons of the ethyl ester group (δ; 4.42 - 4.50 ppm, see Figure S-2).

Yield: 149 mg (68.7 %). $M_n = 8.2 \times 10^4$, $M_w/M_n = 2.8$

Determination of Binding Constants (K_s) on the basis of Hill analysis. For calculating the apparent binding constant (K_s), we used Hill equation, $\log(Y/1-Y) = n\log|G| + n\log(K_s)$, where Y, G, *n* are fractional saturation, the Hill coefficient, and the concentration of the guest, respectively.[1, 2]

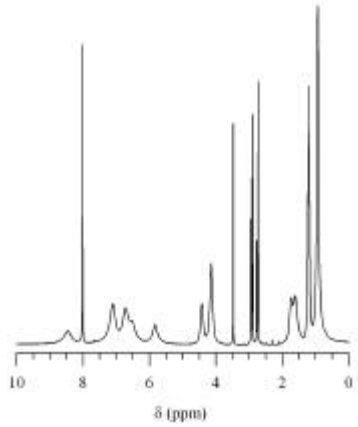

Figure S-1. ^{1}H NMR spectrum of **poly-PA-Leu** in [D_7]DMF.

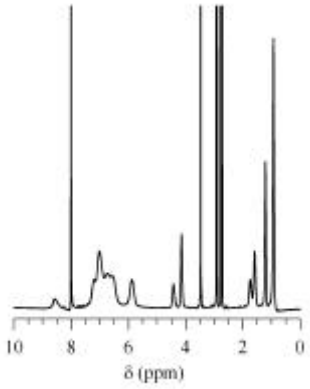

Figure S-2. ^{1}H NMR spectrum of **poly(PA$_{0.51}$-*co*-PA-Leu$_{0.49}$)** in [D_7]DMF.

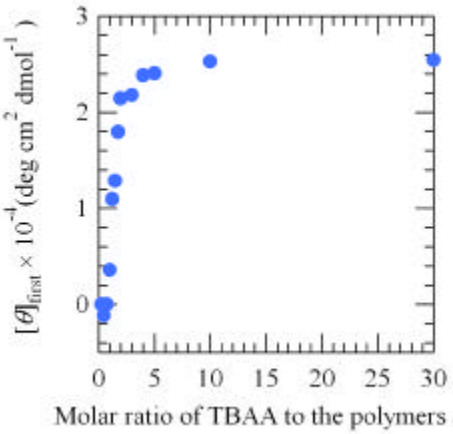

Figure S-3. Titration curve of the $[q]_{first}$ values. CD measurements of **poly-PA-Leu** with TBAA were carried out in THF at r.t. ([monomeric units of **poly-PA-Leu**] = 3.3 mmol·L^{-1} and [TBAA]/[monomeric units of **poly-PA-Leu**] = 0 ~ 30).

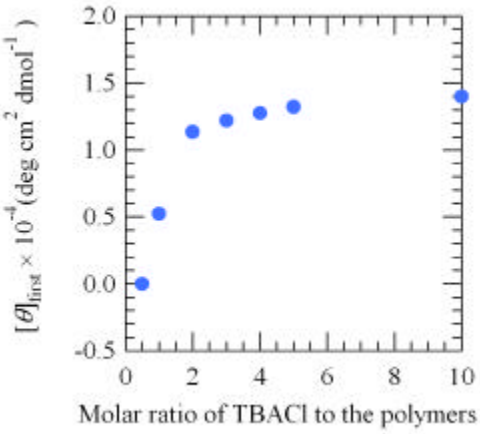

Figure S-4. Titration curve of the $[q]_{first}$ values. CD measurements of **poly-PA-Leu** with TBACl were carried out in THF at r.t. ([monomeric units of **poly-PA-Leu**] = 3.3 mmol·L^{-1} and [TBACl]/[monomeric units of **poly-PA-Leu**] = 0 ~ 10).

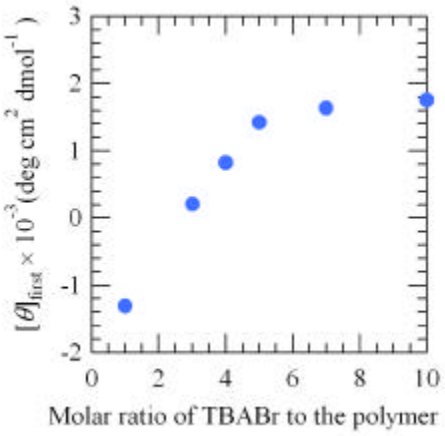

Figure S-5. Titration curve of the $[q]_{first}$ values. CD measurements of **poly-PA-Leu** with TBABr were carried out in THF at r.t. ([monomeric units of **poly-PA-Leu**] = 3.3 mmol·L^{-1} and [TBABr]/[monomeric units of **poly-PA-Leu**] = 0 ~ 10).

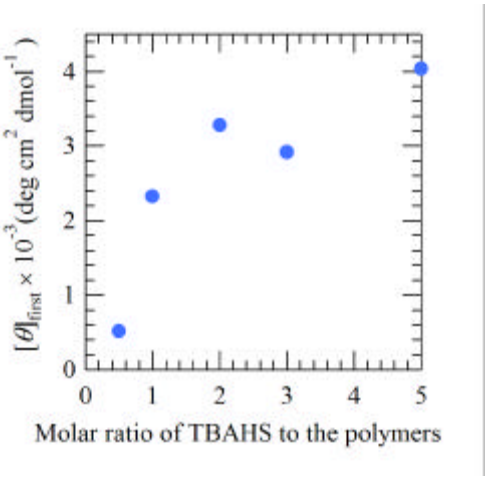

Figure S-6. Titration curve of the $[q]_{first}$ values. CD measurements of **poly-PA-Leu** with TBAHS were carried out in THF at r.t. ([monomeric units of **poly-PA-Leu**] = 3.3 mmol·L^{-1} and [TBAHS]/[monomeric units of **poly-PA-Leu**] = 0 ~ 5).

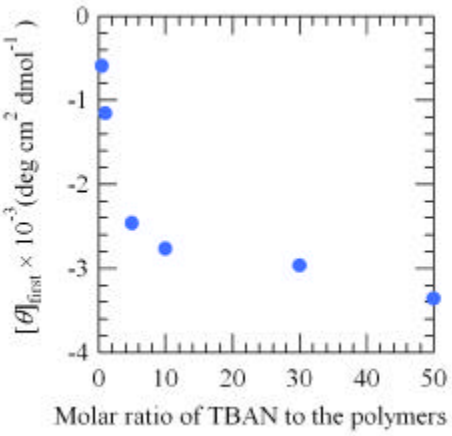

Figure S-7. Titration curve of the $[q]_{first}$ values. CD measurements of **poly-PA-Leu** with TBAN were carried out in THF at r.t. ([monomeric units of **poly-PA-Leu**] = 3.3 mmol·L^{-1} and [TBAN]/[monomeric units of **poly-PA-Leu**] = 0 ~ 50).

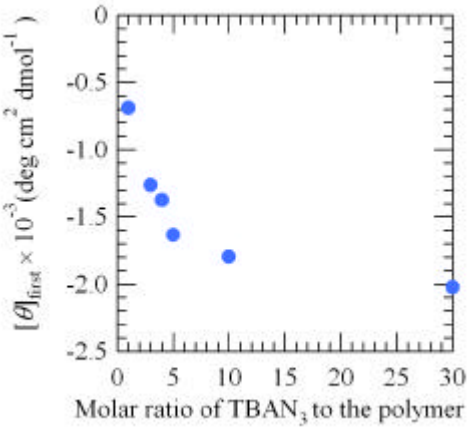

Figure S-8. Titration curve of the $[q]_{first}$ values. CD measurements of **poly-PA-Leu** with $TBAN_3$ were carried out in THF at r.t. ([monomeric units of **poly-PA-Leu**] = 3.3 mmol·L^{-1} and [$TBAN_3$]/[monomeric units of **poly-PA-Leu**] = 0 ~ 30).

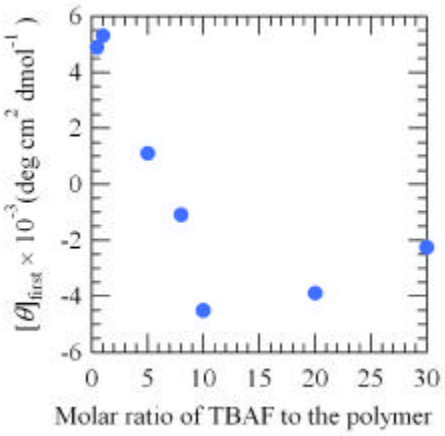

Figure S-9. Titration curve of the $[q]_{first}$ values. CD measurements of **poly-PA-Leu** with TBAF were carried out in THF at r.t. ([monomeric units of **poly-PA-Leu**] = 3.3 mmol·L^{-1} and [TBAF]/[monomeric units of **poly-PA-Leu**] = 0 ~ 30).

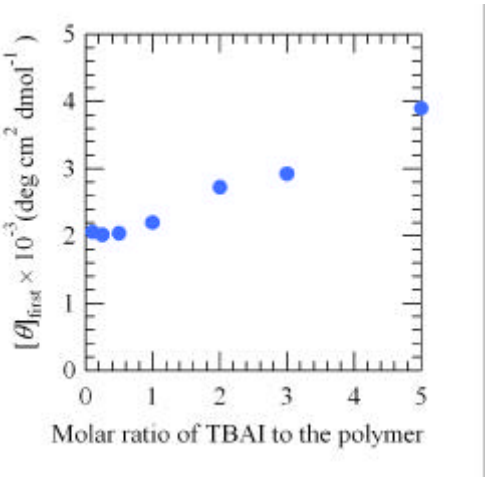

Figure S-10. Titration curve of the $[q]_{first}$ values. CD measurements of **poly-PA-Leu** with TBAI were carried out in THF at r.t. ([monomeric units of **poly-PA-Leu**] = 3.3 mmol·L^{-1} and [TBAI]/[monomeric units of **poly-PA-Leu**] = 0 ~ 5).

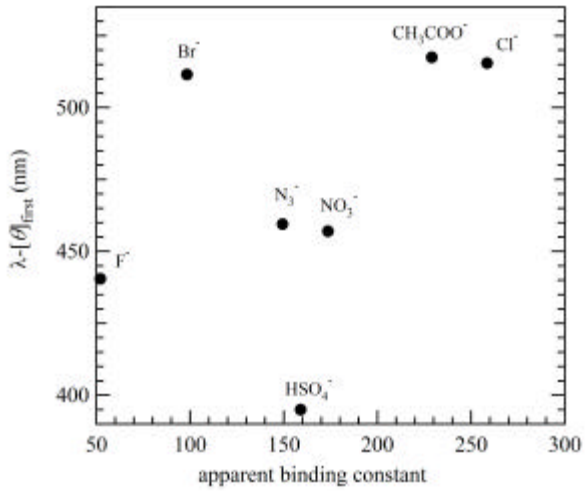

Figure S-11. Relationship between apparent binding constants of anion and λ-$[q]_{first}$.

References

[1] E. Yashima, K. Maeda and O. Sato, *J. Am. Chem. Soc.* **2001**, *123*, 8159-8160.

[2] K. Maeda, H. Mochizuki, M. Watanabe, E. Yashima, *J. Am. Chem. Soc.* **2006**, *128*, 7639-7650.