Supplementary Information For

Transition from Low Molecular Weight Non-gelating Oligo(amide-triazoles)s to a Restorable, Halide-Responsive Poly(amide-triazole) Supramolecular Gel

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Contents

1. Synthesis ................................................................................................................................. 3
   1.1 General ................................................................................................................................. 3
   1.2 Synthesis of Oligomer 2 ...................................................................................................... 4
   1.3 Synthesis of Oligomer 3 ...................................................................................................... 7
   1.4 Synthesis of Control Compound 4 ..................................................................................... 10
2. Job Plot Analysis – Determination of Binding Stoichiometry ............................................... 11
3. $^1$H NMR Titration Experiment – Determination of Association Constant ....................... 13
   3.1 $^1$H NMR Titration Experiment of 2 vs TBACl ................................................................. 14
   3.2 $^1$H NMR Titration Experiment of 2 vs TBABr ................................................................. 15
   3.3 $^1$H NMR Titration Experiment of 2 vs TBAI .................................................................. 16
   3.4 $^1$H NMR Titration Experiment of 3 vs TBACl ................................................................. 17
   3.5 $^1$H NMR Titration Experiment of Control 4 vs TBACl ..................................................... 18
4. Hill Plot of the Binding between Compound 3 and Cl$^-$ .......................................................... 19
5. Fitting with Non-cooperative Model ....................................................................................... 20
6. FTIR Studies ............................................................................................................................. 21
7. Scanning Electron Microscopy (SEM) Analysis ....................................................................... 22
8. Mass Spectrum of 2•TBACl ................................................................................................... 25
9. List of Spectra ......................................................................................................................... 26
1. Synthesis

1.1 General

All reagents were purchased from commercial suppliers and used without further purification unless otherwise specified. Dichloromethane was freshly distilled from calcium hydride under nitrogen. Tetrahydrofuran (THF) was freshly distilled from sodium/benzophenone ketyl under nitrogen prior to use. N,N-dimethylformamide (DMF) was freshly distilled from magnesium sulphate under vacuum prior to use. For all copper catalyzed azide-alkyne cycloaddition (CuAAC) reactions, the solvents were used directly without any purification prior to use. All reactions were carried out at 298 K under nitrogen unless otherwise specified. The progress of reaction were monitored by thin layer chromatography (TLC) performed on Merck pre-coated silica gel 60F$_{254}$ plates, and the compounds were visualized under UV and/or using a spray solution of 5% (wt/v) dodecamolybdophosphoric acid in ethanol followed by heating. Flash column chromatography was carried out on columns of Merck Kwiselgel 60 (230–400 mesh).

$^1$H NMR (400 MHz) and $^{13}$C NMR (100 MHz) spectra were obtained on a Brüker Avance DPX 400 spectrometer. Unless otherwise specified, all spectra were obtained in CDCl$_3$ at 298 K. The deuterated solvent residual signals were used as the internal standard. The Chemical shift ($\delta$) values were reported as parts per million (ppm) in $\delta$ scale. The coupling constants ($J$) were reported in hertz. Melting points were measured on an Electrothermal® 9100 digital melting point apparatus. High resolution electrospray ionization (ESI) mass spectrometry were performed on a Finnigan MAT 95XL Mass Spectrometer using electrospray ionization (ESI) technique. The reported mass to charge ratio ($m/z$) were mono-isotopic.
1.2 Synthesis of Oligomer 2

Scheme S1. Synthesis of oligomer 2.

6: 1-bromo-3-methylbutane (5.0 mL, 41.7 mmol) and K₂CO₃ (6.80 g, 49.2 mmol) were added to a stirred solution of methyl salicylate 5 (5.00 g, 32.9 mmol) in DMF (40 mL). The reaction mixture was allowed to stir at 25 °C for 24 h. Water (80 mL) and Et₂O (80 mL) was added to quench the reaction. The organic layer was separated and the aqueous layer was extracted with Et₂O (2 × 80 mL). The combined organic extracts were washed with saturated NaCl, dried (MgSO₄) and concentrated to give a pale yellow liquid. It was then purified by flash column chromatography (hexane/EtOAc = 10:1 gradient to 3:1) to afford the target compound 6 (6.73 g, 30.3 mmol, 92 %) as a colorless oil. Rf: 0.23 (hexane/EtOAc = 9:1). ¹H NMR: δ 0.96 (6 H, d, J = 6.8, CH₃), 1.74 (2 H, q, J = 6.4, CH₂CH₂CH), 1.81–1.95 (1 H, m, CHMe₂), 3.87 (3 H, s, COOCH₃), 4.05 (2 H, t, J = 6.4, OCH₂), 6.88–7.00 (2 H, m, ArH), 7.39–7.46 (1 H, m, ArH), 7.74–7.79 (1 H, m, ArH).
$^{13}$C NMR: δ 22.5, 24.9, 37.8, 51.7, 67.2, 113.0, 119.9, 120.4, 131.5, 133.2, 158.5, 166.8. m/z (ESI) 245 (M + Na$^+$, 100 %). HRMS (ESI) Calcd for C$_{13}$H$_{18}$O$_3$ + Na$^+$: 245.1148, found 245.1150.

7: A solution of compound 6 (2.01 g, 9.04 mmol) in THF (10 mL) was added dropwise to a stirring solution of lithium aluminum hydride (LAH) (350 mg, 9.4 mmol) in THF (10 mL) at 0 °C. The reaction temperature was raised to 25 °C after 30 min. Upon stirring for 4 h, the reaction mixture was poured into water (10 mL) carefully. Aqueous HCl (30 mL 1.2 M) was added to neutralize the mixture and the organic layer was separated. The aqueous layer was then extracted with Et$_2$O (2 × 20 mL). The combined organic layers were washed with saturated NaCl, dried (MgSO$_4$), and concentrated to give the alcohol 7 (1.67 g, 8.67 mmol, 96 %) as a colorless oil. The oil was used in the next step without further purification. $R_f$: 0.21 (hexane/EtOAc = 2:1). $^1$H NMR: δ 0.98 (6 H, d, $J = 6.4$, CH$_3$), 1.72 (2 H, q, $J = 6.4$, CH$_2$CH$_2$CH), 1.77–1.90 (2 H, m, CHMe$_2$), 4.06 (2 H, t, $J = 6.8$, OCH$_2$), 4.69 (2 H, s, ArCH$_2$OH), 6.85–6.96 (2 H, m, ArH), 7.20–7.30 (2 H, m, ArH). $^{13}$C NMR: δ 22.6, 25.2, 38.0, 62.0, 66.3, 110.9, 120.5, 128.5, 128.8, 129.3, 156.9. m/z (ESI) 194 (M$^+$, 20 %). HRMS (ESI) Calcd for C$_{12}$H$_{18}$O$_2$+: 194.1301, found 194.1302.

9: A solution of alcohol 7 (1.00 g, 5.15 mmol) in THF (5 mL) was added dropwise to a solution of SOCl$_2$ (5 mL) in THF (10 mL) at 0 °C. The reaction mixture was stirred for 2 h and then quenched by pouring into iced water (20 mL). The mixture was then extracted with Et$_2$O (3 × 10 mL) and the combined organic extracts were washed with saturated Na$_2$CO$_3$, saturated NaCl, dried (MgSO$_4$), and concentrated to give the chloride 8 as a pale yellow oil. $R_f$: 0.68 (hexane/EtOAc = 9:1) 8 was used directly without further purification. Sodium azide (1.40 g, 21.5 mmol) was added to a stirring solution of 8 (0.67 g, 10.0 mmol) in DMF (10 mL). The reaction mixture was stirred at 25 °C for 48 h. Water (20 mL) was added to quench the reaction. The solution mixture was then extracted with Et$_2$O (3 × 15 mL). The combined organic extracts were washed with saturated NaCl, dried (MgSO$_4$) and then concentrated to give a yellow liquid. The liquid was purified by flash column chromatography (hexane/EtOAc = 15:1 gradient to 9:1) to afford the desired compound 9 (2.08 g, 5.77 mmol, 91 %) as a colorless liquid. $R_f$: 0.73 (hexane/EtOAc = 9:1); $^1$H NMR: δ 0.98
(6 H, d, J = 6.4, CH₃), 1.72 (2 H, q, J = 6.4, CH₂CH₂CH), 1.80–1.92 (1 H, m, CHMe₂), 4.03 (2 H, t, J = 6.8, OCH₂), 4.36 (2 H, s, ArCH₂N₃), 6.87–6.97 (2 H, m, ArH), 7.22–7.33 (2 H, m, ArH). ¹³C NMR: δ 22.7, 25.2, 38.0, 50.3, 66.5, 111.3, 120.4, 124.0, 129.8, 130.1, 157.2. m/z (ESI) 219 (M⁺, 35 %). HRMS (ESI) Calcd for C₁₂H₁₇N₃O⁺: 219.1366, found 219.1370.

2: An aqueous CuSO₄ (0.20 mL, 0.056 M) solution was added to a stirred solution of 10¹ (120 mg, 0.26 mmol), 9 (125 mg, 0.58 mmol) and sodium ascorbate (10 mg, 0.05 mmol) in DMF (1.8 mL) at 25 °C. After 12 h, warm DMF was added to the solution mixture until a clear solution was obtained, and then the mixture was poured into water (15 mL). The solid was then filtered, washed with a mixture of Et₂O/EtOH and then purified by column chromatography (EtOAc) to afford 2 (224 mg, 0.25 mmol, 95 %) as a white solid. M.p. 42–45 °C; Rf: 0.53 (EtOAc); ¹H NMR: ([D₈]-THF) δ 0.87–0.95 (24 H, m, CCH₃), 1.14–1.90 (21 H, m), 4.01 (4 H, t, J = 6.8, OCH₂), 4.16 (2 H, t, J = 6.8, OCH₂), 4.54 (4 H, d, J = 6.0, NCH₂Triaz), 5.47 (4 H, s, ArCH₂Triaz), 6.83–6.88 (2 H, m, ArH), 6.93–6.97 (2 H, m, ArH), 7.09–7.14 (2 H, m, ArH), 7.22–7.27 (2 H, m, ArH), 7.66 (2 H, s, TriazH), 7.76 (2 H, s, ArH), 9.29 (2 H, t, J = 6.0, NH). ¹³C NMR: ([D₈]-THF) δ 22.7, 22.9, 26.8, 29.2, 30.4, 31.9, 35.5, 36.6, 38.4, 38.6, 49.3, 69.7, 111.0, 112.1, 121.0, 123.2, 124.7, 130.4, 130.6, 145.9, 152.0, 157.5, 163.9, 168.3. m/z (ESI) 915 (M + Na⁺, 100 %). HRMS (ESI) Calcd for C₅₁H₇₃N₉O₅ + Na⁺: 914.5627, found 914.5632.

1.3 Synthesis of Oligomer 3

Scheme S2. Synthesis of oligomer 3.

12: Aqueous CuSO$_4$ (0.40 mL, 0.056 M) was added to a stirred solution of 11$^1$ (273 mg, 0.63 mmol), 12$^1$ (108 mg, 0.30 mmol) and sodium ascorbate (20 mg, 0.1 mmol) in DMF (3.6 mL) at 25 °C. After 12 h, water (10 mL) and ethyl acetate (10 mL) were added to quench the reaction. The organic layer was separated and the aqueous layer was extracted with ethyl acetate (2 × 10 mL). The combined organic extracts were washed with saturated NaCl, dried (Na$_2$SO$_4$) and concentrated to give a yellow solid. The solid was then purified by
flash column chromatography (hexane/EtOAc = 2:1 gradient to 1:2) to obtain 13 (627 mg, 0.51 mmol, 81 %) as a white solid. M.p. 55–50 °C; Rf: 0.50 (Hexane/EtOAc = 1:2); 1H NMR: δ 0.76–0.90 (36 H, m, CCH3), 1.05–1.80 (36 H, m), 3.85 (4 H, t, J = 6.4, OCH2), 3.90 (6 H, s, COOCH3), 4.05 (4 H, t, J = 6.4, OCH2), 4.66 (4 H, d, J = 6.0, NCH2Triaz), 5.41 (4 H, s, ArCH2Triaz), 6.73 (2 H, s, ArH), 7.52 (2 H, s, TriazH), 7.64 (2 H, d, J = 2.4, ArH), 7.77 (2 H, d, J = 2.4, ArH), 8.58 (2 H, t, J = 6, NH). 13C NMR: δ 22.5, 22.7, 25.0, 25.9, 28.4, 29.6, 31.0, 34.9, 35.8, 37.5, 37.9, 48.9, 52.8, 67.2, 69.4, 110.9, 113.9, 114.5, 122.6, 124.2, 144.6, 148.1, 150.4, 151.6, 163.6, 165.0, 167.4. m/z (ESI) 1244 (M + Na+, 100 %). HRMS (ESI) Calcd for C68H104N10O10 + Na+: 1243.7829, found 1243.7825.

14: An aqueous KOH (0.5 mL, 2.5 M) solution was added to a stirred solution of compound 13 (281 mg, 0.23 mmol) in ethanol and THF (~1:1, 4 mL) at 25 °C. After 12 h, the mixture was acidified with aqueous HCl (10 mL, 0.3 M). The organic layer was obtained, and the aqueous layer was further extracted with EtOAc (2 × 10 mL). The combined organic extracts were washed with saturated NaCl, dried (Na2SO4), and concentrated to obtain 14 (262 mg, 0.22 mmol, 96 %) as a white solid. M.p. 106–112 °C; Rf: 0.31 (CH2Cl2/MeOH = 9:1); 1H NMR: ([D6]-DMSO, COOH not observed) δ 0.79 (12 H, d, J = 6.8, CCH3), 0.83 (24 H, d, J = 6.4, CCH3), 1.07–1.77 (36 H, m), 3.84 (4 H, t, J = 6.4, OCH2), 4.20 (4 H, t, J = 6.4, OCH2), 4.55 (4 H, d, J = 6.0, NCH2Triaz), 5.44 (4 H, s, ArCH2Triaz), 6.93 (2 H, s, ArH), 7.62–7.70 (4 H, m, ArH), 7.81 (2 H, s, TriazH), 9.55–9.63 (2 H, m, NH). m/z (ESI) 1216 (M + Na+, 100 %). The solubility of the compound was too poor to obtain the 13C NMR spectrum even in [D6]-DMSO. HRMS (ESI) Calcd for C66H100N10O10 + Na+: 1215.7516, found 1215.7514.

15: Benzotriazol-1-yl-oxytrypyrrolidinophosphonium hexafluorophosphate (PyBOP) (180 mg, 0.37 mmol) was added to a stirred solution of 14 (200 mg, 0.17 mmol) and propargylamine (0.1 mL, 1.56 mmol) in DMSO (5 mL). Triethylamine (0.1 mL) was then added to the solution mixture. The reaction was allowed to stir for 24 h at 25°C. EtOAc (15 mL) and H2O (15 mL) was then added to quench the reaction. The organic layer was separated and the aqueous layer was extracted with EtOAc (2 × 15 mL). The combined organic
extracts were washed with saturated NaCl, dried (Na₂SO₄), concentrated and purified by flash column chromatography (hexane/EtOAc = 1:2 gradient to 1:4) to afford the dialkyne 15 (189 mg, 0.15 mmol, 88 %) as a white solid. M.p. 88–93 °C; Rf. 0.38 (hexane/EtOAc = 1:2). ¹H NMR: δ 0.82–0.94 (36 H, m, CH₃), 1.09–1.84 (36 H, m), 2.21–2.26 (2 H, m, C≡CH), 3.90 (4 H, t, J = 6.4, OCH₂), 4.09 (4 H, t, J = 6.4, OCH₂), 4.12–4.22 (4 H, m, CH₂C≡C), 4.65 (4 H, d, J = 6, NCH₂Triaz), 5.46 (4 H, s, NCH₂Triaz), 6.81 (2 H, s, ArH), 7.62 (2 H, s, TriazH), 7.72–7.86 (4 H, m, ArH), 8.11–8.20 (2 H, m, NH), 8.60–8.70 (2 H, m, NH). ¹³C NMR: δ 22.6, 22.8, 25.1, 26.1, 28.4, 28.9, 29.7, 31.1, 34.8, 35.9, 37.6, 37.9, 49.2, 67.4, 69.5, 71.2, 77.5, 79.6, 111.2, 111.4, 114.2, 123.1, 124.2, 145.3, 150.4, 150.51, 150.54, 163.4, 163.9, 167.9. m/z (ESI) 1290 (M + Na⁺, 100 %). HRMS (ESI) Calcd for C₇₂H₁₀₆N₁₂O₈ + Na⁺: 1289.8149, found 1289.8148.

3: Aqueous CuSO₄ (0.20 mL, 0.03 M) was added to a stirred solution of 15 (180 mg, 0.14 mmol), 6 (80 mg, 0.36 mmol) and sodium ascorbate (10 mg, 0.05 mmol) in DMF (1.8 mL) at 25 °C. After 12 h, water (10 mL) and ethyl acetate (10 mL) were added to quench the reaction. The organic layer was separated and the aqueous layer was extracted with ethyl acetate (2 × 10 mL). The combined organic extracts were washed with saturated NaCl, dried (Na₂SO₄) and concentrated to give a colorless liquid. It was then purified by flash column chromatography (CH₂Cl₂/EtOAc = 2:1 gradient to 1:3) to obtain 3 (213 mg, 0.12 mmol, 86 %) as a white solid. M.p. 108–115 °C; Rf: 0.10 (CH₂Cl₂/EtOAc = 2:1); ¹H NMR: ([D₈]-THF) δ 0.68–1.10 (48 H, m, CCH₃), 1.15–1.90 (42 H, m), 3.89 (4 H, t, J = 6.4, OCH₂), 4.01 (4 H, t, J = 6.4, OCH₂), 4.15 (4 H, t, J = 6.4, OCH₂), 4.48–4.58 (8 H, m, NCH₂Triaz), 5.39–5.50 (8 H, m, ArCH₂Triaz), 6.80–6.91 (4 H, m, ArH), 6.92–7.00 (2 H, m, ArH), 7.10–7.18 (2 H, m, ArH), 7.20–7.28 (2 H, m, ArH), 7.68 (2 H, s, TriazH), 7.71 (2 H, s, TriazH), 7.72–7.80 (4 H, m, ArH), 9.28–9.40 (4 H, m, NH). ¹³C NMR: ([D₈]-THF) δ 22.7, 22.9, 25.65, 25.74, 25.8, 26.8, 29.2, 30.4, 31.9, 35.5, 36.6, 38.5, 38.63, 38.67, 48.8, 49.1, 49.3, 69.8, 111.0, 112.1, 113.7, 114.7, 121.0, 123.3, 124.7, 125.7, 126.7, 130.0, 130.4, 130.6, 145.9, 146.0, 151.3, 152.0, 156.3, 157.5, 163.9, 168.4. m/z (ESI) 1729 (M + Na⁺, 55 %). HRMS (ESI) Calcd for C₉₆H₁₄₀N₁₈O₁₀ + Na⁺: 1729.0922, found 1729.0952.
1.4 Synthesis of Compound 4


4: Oxalyl chloride (0.75 mL, 8.64 mmol) in CH₂Cl₂ (3 mL) was added dropwise to a stirring solution of the diacid 16 (1.09 g, 2.87 mmol) in CH₂Cl₂ (10 mL) at 0 °C. One drop of DMF in CH₂Cl₂ (1 mL) was then added into the solution mixture. The reaction mixture was allowed to stir for 4 h from 0 °C to 25 °C, and then concentrated under reduced pressure to give the diacyl chloride 17 as a yellow solid, which was used directly without purification by mixing with triethylamine (5 mL) in CH₂Cl₂ (10 mL) at 0 °C. After stirring for about 10 min, a solution of propargylamine (0.50 mL, 7.81 mmol) in CH₂Cl₂ (3 mL) was added dropwise at 0 °C. The reaction mixture was allowed to stir for 10 h at 25 °C, and then quenched by the addition of aqueous HCl (30 mL, 1.2 M). The two layers were separated and the aqueous layer was extracted with CH₂Cl₂ (2 × 30 mL). The combined organic extracts were washed with saturated NaCl solution, dried (Na₂SO₄), filtered and concentrated to give a brown oil. The oil was purified by flash column chromatography (hexane/EtOAc = 3:1 gradient to 1:1) to generate 4 (1.52 g, 2.73 mmol, 95 %) as a colorless oil. Rᶠ: 0.64 (hexane/EtOAc = 2:1); ¹H NMR: δ 0.88 (12 H, d, J = 6.8, CH₃), 1.10–1.55 (13 H, m, CH₂ and CH₂CH₂), 1.75–1.85 (2 H, m, CHMe₂), 4.12 (2 H, t, J = 6.4, OCH₂), 4.60–4.70 (4 H, d, J ≈ 7, ArCH₂), 7.26–7.37 (10 H, m, ArH), 7.87 (2 H, s, ArH), 7.98–8.10 (2 H, t, J ≈ 7, NH). ¹³C NMR: δ 22.8, 26.1, 28.5, 29.7, 31.1, 35.9, 37.6, 43.4, 69.4, 111.4, 127.4, 127.6, 128.6, 138.2, 150.6, 163.9, 167.9. m/z (ESI) 581 (M + Na⁺, 100 %). HRMS (ESI) Calcd for C₃₅H₄₇N₃O₃ + Na⁺: 580.3510, found 580.3516.
2. **Job Plot Analysis – Determination of Binding Stoichiometry**

Job plot analyses were performed to determine the binding stoichiometry between the oligomers (2 and 3) and various halide anions (Cl\(^-\), Br\(^-\) and I\(^-\)). The data point for Job plot analyses were obtained from the \(^1\)H NMR (400 MHz) spectra recorded on a \(\text{Br} \text{ü} \text{ker Avance DPX 400 spectrometer at 298 K. For each set of binding experiment, [D}_8\)-THF solutions of the host compound and TBAX were separately prepared with the same concentration. Then they were mixed in ten different NMR tubes with 10:0 (v/v), 9:1, 8:2, 7:3, 6:4, 5:5, 4:6, 3:7, 2:8 and 1:9, respectively.

(a) **Compound 2 + TBACl**

(b) **Compound 2 + TBABr**

(c) **Compound 2 + TBAI**

**Figure S1.** Job Plot analyses of the binding between 2 and (a) TBACl, (b) TBABr and (c) TBAI. Data points were obtained from amide NHs (blue) and triazole CHs (red) resonance signals in \(^1\)H NMR spectra.
The Job plot results (Figure S1) indicated 1:1 binding between 2 and halides (Cl, Br and I), 1:2 binding between 3 and chloride (Figure S2), and 1:1 binding between compound 4 and chloride (Figure S3).
3. **1H NMR Titration Experiment – Determination of Association Constant**

For the titration experiment, 1H NMR spectral data (700 MHz) were measured on a Bruker Avance III 700 spectrometer equipped with UltraShield Plus 700 MHz Magnets at 295 K in [D₈]-THF. Tetrabutylammonium halide (TBAX) were purchased from Sigma-Aldrich and pre-dried under vacuum for 1 day prior to use. To exclude the dilution effect on the host concentration, the added halide solution contained the host with the same concentration. Generally, a mixture of TABX (~50–80 mM) and the host (~2.5 mM) in [D₈]-THF was added successively to host (~2.5 mM), and the chemical shift values of amide NHs, triazole CHs and aromatic protons were recorded.

Curve fittings were performed using the commercial program OriginPro 8.1. As the concentration dependent change of chemical shift value is more pronounced on the amide NH and hence the chemical shift data from this proton are more accurate, the curve fitted binding constants were those derived from amide NH data. Nonetheless, the binding constants derived from the triazole CH data were also shown alongside. Generally the two binding constants agreed well with each other for the same host-guest pair.
3.1 $^1$H NMR Titration Experiment of 2 vs TBACl

Figure S4. (a) Stacked $^1$H NMR spectra ([D$_8$]-THF, 700 MHz, aromatic region) of 2 upon the addition of TBACl; (b) Non-linear curve fitting which use (i) NH and (ii) triazole CH to obtain the association constant.

**Experimental Parameters:**
(1) Concentration of 2 in [D$_8$]-THF: 2.62 mM; (2) Concentration of stock TBACl in [D$_8$]-THF: 67.11 mM.
3.2 $^1$H NMR Titration Experiment of 2 vs TBABr

Figure S5. (a) Stacked $^1$H NMR spectra ([D$_8$]-THF, 700 MHz, aromatic region) of 2 upon the addition of TBABr; (b) Non-linear curve fitting which use (i) amide NHs and (ii) triazole CHs to obtain the association constant.

Experimental Parameters:
(1). Concentration of 2 in [D$_8$]-THF : 2.50 mM; (2). Concentration of stock TBABr in [D$_8$]-THF : 78.48 mM.
3.3 $^1$H NMR Titration Experiment of 2 vs TBAI

Figure S6. (a) Stacked $^1$H NMR spectra (aromatic region) of 2 upon the addition of TBAI; (b) Non-linear curve fitting which use (i) amide NHs and (ii) triazole CHs to obtain the association constant.

Experimental Parameters:
(1) Concentration of 2 in [D$_8$]-THF: 2.43 mM; (2) Concentration of stock TBAI in [D$_8$]-THF: 49.68 mM.
3.4 $^1$H NMR Titration Experiment of 3 vs TBACl

(a)

![Stacked $^1$H NMR spectra ([D$_8$]-THF, 700 MHz, aromatic region) of 3 upon addition of TBACl](image)

(b)

![Non-linear curve fitting which use NH to obtain the association constant](image)

**Figure S7.** (a) Stacked $^1$H NMR spectra ([D$_8$]-THF, 700 MHz, aromatic region) of 3 upon addition of TBACl; (b) Non-linear curve fitting which use NH to obtain the association constant.

**Experimental Parameters:**

(1) Concentration of 3 in [D$_8$]-THF: 2.87 mM; (2) Concentration of stock TBACl in [D$_8$]-THF: 132.8 mM.
3.5 $^1$H NMR Titration Experiment of Control 4 vs TBACl

(a) Stacked $^1$H NMR spectra (aromatic region) of compound 4 upon the addition of TBACl; (b) Non-linear curve fitting which use amide NHs to obtain the association constant.

**Experimental Parameters:**
(1). Concentration of 4 in [D$_8$]-THF: 2.47 mM; (2) Concentration of stock TBAI in [D$_8$]-THF: 77.90 mM.
4. Hill Plot of the Binding between Compound 3 and Cl⁻

**Figure S9.** Hill plot of compound 3 with Cl⁻. A slope of 2.0 was found, which indicated a positive cooperativity.
5. Fitting with Non-cooperative Model

Figure S10. Non-linear curve fitting of 3 vs Cl⁻ base on a non-cooperative model, with $K_1$ fixed as $4 \times K_2$. As can be seen, fitting result was not satisfactory [$r^2 = 0.9855$ (non-cooperative model) vs $r^2 = 0.9986$ (independent model; Figure S7)].

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6. FTIR Studies

Infra-red spectroscopic studies were performed on a Brüker Vertex 70 Fourier-transform spectrometer fitted with a globar source, a CaF$_2$ beam splitter, and a liquid nitrogen cooled HgCdTe detector. All the experiments were conducted using spectrophotometric grade THF at 298 K. All spectra were recorded at 2 cm$^{-1}$ resolution. The sample cell was made of a 0.5 mm Teflon spacer sandwiched by two 4-mm thick CaF$_2$ disks, with 0.1 mm optical path. Build-in ‘atmospheric compensation’ routine from the spectrometer was used in order to minimize the background absorption.

![Figure S11. Stacked IR spectra of (from top to bottom) 2, 2 + TBACl (1 equiv.), 1 and 1 + TBACl (1 equiv.) in THF.](image-url)
7. Scanning Electron Microscopy (SEM) Analysis

Scanning electron microscopy (SEM) was performed on a Quanta 400F field emission scanning electron microscope. The samples analyzed were sputter-deposited with minute amount of gold to prevent charging. 1-Cl was prepared by an air-dried solution mixture of 1:1 1 and TBACl in toluene (binding site : TBACl = 1 : 1)

![SEM image](image)

**Figure S12.** SEM images of freeze dried sample of 1 at 12 K magnification.
Figure S13. SEM images of 1-Cl complex at 10 K magnification.
Figure S14. SEM images of 1-Cl complex at 200 K magnification.
8. Mass Spectrum of 2-TBACl

Mass spectral measurement was conducted on an API QSTAR Pulsar I LC/MS/TOF mass spectrometer in ESI-MS negative ion mode using taurochloric acid as calibration standard.

Theoretical mass peak value for $2^{-35}\text{Cl}^-$ ($C_{51}H_{73}N_9O_5Cl^-$): 926.5428; Found: 926.5471.

**Figure S15.** Mass spectrum of compound 2-Cl$^-$. 
9. List of Spectra