Electronic Supplementary Information


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1. Materials and methods

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All reactions were performed in atmosphere unless noted. All reagents were commercially available and used as supplied without further purification. Solvents were either employed as purchased or dried according to procedures described in the literature. Compound \textit{EtP[5]A} was prepared by published literature procedures.\textsuperscript{51} NMR spectra were collected on either a Bruker Avance DMX 300 MHz spectrometer or a Bruker Avance DMX 400 MHz spectrometer with internal standard tetramethylsilane (TMS) and signals as internal references, and the chemical shifts (\(\delta\)) were expressed in ppm. 2D COSY and NOESY experiments were performed on a Bruker DPX 400 MHz spectrometer. Low-resolution electrospray ionization mass spectra (LR-ESI-MS) were obtained on Finnigan MatTSQ 7000 instruments. High-resolution electrospray ionization mass spectra (HR-ESI-MS) were recorded on an Agilent 6540Q-TOF LCMS equipped with an electrospray ionization (ESI) probe operating in positive-ion mode with direct infusion.

2. \textit{Synthesis of Guest}
Synthesis of $G_1$:

1,4-butanediamine (0.44 g, 5 mmol) and triethylamine (1.02 g, 10 mmol) were added in dichloromethane (50 mL). Then benzyl chloroformate (1.71 g, 10 mmol) was dropped to the mixture in ice-bath in 10 minutes. The mixture was stirred at room temperature for 12 hours. The reaction mixture was filtered and washed with dichloromethane. The filtrate was washed by brine and dried by $\text{Na}_2\text{SO}_4$. The organic layer was evaporated under vacuum, and the residue was further purified by flash column chromatography on silica gel (dichloromethane/methanol = 160/1, v/v) to afford $G_1$ (1.64 g, 92.0 %), m.p. 146−147 °C. 

$^1\text{H} \text{NMR}$ (300 MHz, chloroform-$d$, 298 K) $\delta$ (ppm): 7.35−7.37 (m, 10H, ArH), 5.10 (s, 4H, CH$_2$), 4.79 (s, 2H, NH), 3.20 (s, 4H, CH$_2$), 1.53 (s, 4H, CH$_2$). $^{13}\text{C} \text{NMR}$ (75 MHz, chloroform-$d$, 298 K) $\delta$ (ppm): 156.5, 136.6, 128.5, 128.1, 66.7, 40.6, 27.2. LR-ESI-MS is: $m/z$ calcd for $[\text{M} + \text{H}]^+$, 357.18, found 357.15; calcd for $[\text{M} + \text{Na}]^+$, 379.16, found 379.15. HR-ESI-MS is: $m/z$ calcd for $[\text{M} + \text{Na}]^+$, $C_{20}H_{24}N_2O_4Na^+$, 379.1628, found 379.1631.

![Scheme S1 Synthesis of $G_1$](image)

*Fig. S1 $^1\text{H} \text{NMR}$ spectrum (300 MHz, chloroform-$d$, 298 K) of $G_1$*
Scheme S2 Synthesis of G2

Synthesis of G2: 1,4-butanediamine (0.44 g, 5 mmol) and triethylamine (1.52 g, 15 mmol) were added in dichloromethane (50 mL). Then hydrocinnamoyl chloride (2.53 g, 15 mmol) was dropped to the mixture in ice-bath in 10 minutes. The mixture was stirred at room temperature for 12 hours. The reaction mixture was filtered and washed with dichloromethane. The filtrate was washed by brine and dried by Na$_2$SO$_4$. The organic layer was evaporated under vacuum, and the residue was further purified by flash column chromatography on silica gel (dichloromethane/methanol = 60/1, v/v) to afford G2 (1.28 g, 72.7 %), m.p. 176−178 °C. $^1$H NMR (300 MHz, chloroform-$d$, 298 K) δ (ppm): 7.31−7.19 (m, 10H, ArH), 5.78 (s, 2H, NH), 3.18 (d, J = 5.66 Hz, 4H, CH$_2$), 2.97 (t, J = 7.59 Hz, 4H, CH$_2$), 2.50 (t, J = 7.62 Hz 4H, CH$_2$), 1.35 (t, J = 6.24 Hz, 4H, CH$_2$). $^{13}$C NMR (75 MHz, chloroform-$d$, 298 K) δ (ppm): 172.4, 140.9, 128.5, 128.4, 126.2, 38.9, 38.5, 31.8, 26.6. LR-ESI-MS is: m/z calced for [M + H]$^+$, 353.22, found 353.15; calced
for [M + Na]+, 375.20, found 375.15. HR-ESI-MS is: m/z calcd for [M + Na]+, C22H28N2O2Na+, 375.2043, found 375.2044.

**Fig. S3** ¹H NMR spectrum (300 MHz, chloroform-d, 298 K) of G2

**Fig. S4** ¹³C NMR spectrum (75 MHz, chloroform-d, 298 K) of G2
Synthesis of \textbf{G3}: 1,4-butanediamine (0.44 g, 5 mmol) and triethylamine (1.01 g, 10 mmol) were added in dichloromethane (50 mL). Then di-tert-butyl dicarbonate (2.18 g, 10 mmol) was dropped to the mixture in ice-bath in 10 minutes. The mixture was stirred at room temperature for 12 hours. The reaction mixture was filtered and washed with dichloromethane. The filtrate was washed by brine and dried by \text{Na}_2\text{SO}_4. The organic layer was evaporated under vacuum, and the residue was further purified by flash column chromatography on silica gel (dichloromethane/methanol = 80/1, \(v/v\)) to afford \textbf{G3} (1.34 g, 92.9 \%), m.p. 139–140 °C. \(^1\text{H}\) NMR (300 MHz, chloroform-\(d\), 298 K) \(\delta\) (ppm): 4.53 (s, 2H, NH), 3.12 (s, 4H, CH\(_2\)), 1.50 (m, 4H, CH\(_2\)), 1.44 (s, 18H, CH\(_3\)). \(^{13}\text{C}\) NMR (75 MHz, chloroform-\(d\), 298 K) \(\delta\) (ppm): 156.0, 79.2, 40.3, 28.4, 28.4. LR-ESI-MS is: \(m/z\) caleld for \([\text{M} + \text{H}]^+\), 289.21, found 289.15; calcd for \([\text{M} + \text{Na}]^+\), 311.19, found 311.15. HR-ESI-MS is: \(m/z\) caleld for \([\text{M} + \text{Na}]^+\), \(C_{14}H_{28}N_2O_4Na^+\), 311.1941, found 311.1943.

![Scheme S3 Synthetic route to G3](image)

\textit{Fig. S5} \(^1\text{H}\) NMR spectrum (300 MHz, chloroform-\(d\), 298 K) of \textbf{G3}
Fig. S6 $^{13}$C NMR spectrum (75 MHz, chloroform-$d$, 298 K) of G3

Scheme S4. Synthetic route to G4

Synthesis of G4: 1,4-butanediamine (0.44 g, 5 mmol) and triethylamine (1.52 g, 15 mmol) were added in dichloromethane (50 mL). Then butyryl chloride (1.60 g, 15 mmol) was dropped to the mixture in ice-bath in 10 minutes. The mixture was stirred at room temperature for 12 hours. The reaction mixture was filtered and washed with dichloromethane. The filtrate was washed by brine and dried by Na$_2$SO$_4$. The organic layer was evaporated under vacuum, and the residue was further purified by flash column chromatography on silica gel (dichloromethane/methanol = 40/1, v/v) to afford G4 (0.46 g, 40.3%), m.p. 164–165 °C. $^1$H NMR (300 MHz, chloroform-$d$, 298 K) $\delta$ (ppm): 5.85 (s, 2H, NH), 3.28 (d, $J = 5.95$ Hz, 4H, CH$_2$), 2.16 (t, $J = 7.48$ Hz, 4H, CH$_2$), 1.73–1.63 (m, 4H, CH$_2$), 1.56–1.52 (m, 4H, CH$_2$), 0.95 (t, 6H, CH$_3$). $^{13}$C NMR (75 MHz, chloroform-$d$, 298 K) $\delta$ (ppm): 173.4, 39.0, 38.6, 26.9, 19.2, 13.8. LR-ESI-MS is: m/z calcd for [M + H]$^+$, 229.19, found 229.15; calcd for [M + Na]$^+$, 251.17, found 251.15. HR-ESI-MS is: m/z calcd for [M + Na]$^+$, C$_{12}$H$_{24}$N$_2$O$_2$Na$^+$, 251.1730, found 251.1729.
Fig. S7 $^1$H NMR spectrum (300 MHz, chloroform-$d$, 298 K) of G4

Fig. S8 $^{13}$C NMR spectrum (75 MHz, chloroform-$d$, 298 K) of G4
Scheme S5. Synthetic route to G5

Synthesis of G4: 1,4-butanediamine (0.44 g, 5 mmol) were added in dichloromethane (50 mL). Then p-tolyl isocyanate (1.33 g, 10 mmol) was dropped to the mixture in ice-bath in 10 minutes. The mixture was stirred at room temperature for 2 hours. The reaction mixture was filtrated. The filter cake was washed by dichloromethane and water. Dry the cake to afford G5 (1.56 g, 88.0 %), m.p. 277–279 °C. $^1$H NMR (300 MHz, DMSO-$d_6$, 298 K) $\delta$ (ppm): 8.26 (s, 2H, NH), 7.25 (d, $J$ =8.47 Hz, 4H, ArH), 7.00 (d, $J$ =8.45 Hz, 4H, ArH), 6.07 (t, $J$ =5.62 Hz, 2H, NH), 3.07 (d, $J$ =5.61 Hz, 4H, CH$_2$), 1.30–1.23 (m, 4H, CH$_2$), 0.87 (t, $J$ =7.29 Hz, 6H, CH$_3$). The clear $^{13}$C NMR spectrum of G5 could not be obtained, because it is not well soluble in DMSO-$d_6$. LR-ESI-MS is: m/z calcd for [M + H]$^+$, 355.21, found 355.15; calcd for [M + Na]$^+$, 377.19, found 377.15. HR-ESI-MS is: m/z calcd for [M + Na]$^+$, C$_{20}$H$_{26}$N$_4$O$_2$Na$^+$, 377.1948, found 377.1951.

Fig. S9 $^1$H NMR spectrum (300 MHz, DMSO-$d_6$, 298 K) of G5
Synthesis of $G_7 p$: 1,4-butanediamine (0.88 g, 10 mmol) and triethylamine (1.21 g, 12 mmol) were added in dichloromethane (170 mL). Then benzyl chloroformate (1.70 g, 10 mmol) was dropped to the mixture in ice-bath in 10 minutes. The mixture was stirred at room temperature for 12 hours. Some precipitates were observed from the reaction solution, and the resulting reaction mixture was extracted by water (20 mL), ethyl acetate (40 mL), and methanol (1 mL). The organic layer was evaporated under vacuum, and the residue was further purified by flash column chromatography on silica gel (dichloromethane/methanol = 40/1, v/v) to afford $G_7 p$ (0.54 g, 24.3\%)

$^1H$ NMR (400 MHz, DMSO-$d_6$, 298 K) $\delta$ (ppm): 7.77 (s, 2H, NH), 7.37–7.31 (m, 5H, ArH), 5.01 (s, 2H, CH$_2$), 3.03–2.98 (m, 2H, CH$_2$), 2.79–2.74 (m, 2H, CH$_2$), 1.55–1.42 (m, 4H, CH$_2$).

Fig. S10 $^1H$ NMR spectrum (400 MHz, DMSO-$d_6$, 298 K) of $G_7 p$. 
Synthesis of Gs: 2-Nitrobenzyl alcohol (0.766 g, 5 mmol) and 1,1-Carbonyldiimidazole (1.62 g, 10 mmol) were added in dichloromethane (100 mL). The mixture was stirred at room temperature for 5 hours. The reaction mixture was washed by brine and dried by Na$_2$SO$_4$. The organic layer was evaporated under vacuum to afford Gs (1.13 g, 91.8 %). $^1$H NMR (300 MHz, DMSO-$d_6$, 298 K) $\delta$ (ppm): 8.36 (s, 1H, CH), 8.19 (d, $J = 8.12$ Hz, 1H, ArH), 7.91–7.83 (m, 2H, CH), 7.71–7.68 (m, 2H, ArH), 7.12 (s, 1H, ArH), 5.79 (s, 2H, CH$_2$).

![Fig. S11 $^1$H NMR spectrum (400 MHz, DMSO-$d_6$, 298 K) of Gs](image)

Synthesis of G6: 1,4-butanediamine (0.088 g, 1 mmol) was added in dichloromethane (30 mL). Then Gs (0.49 g, 2 mmol) was dropped to the mixture. The mixture was stirred at room temperature for 5 hours. The reaction mixture was washed by brine and dried by Na$_2$SO$_4$. The organic layer was evaporated under vacuum to afford G6 (0.72 g, 76.9 %). $^1$H NMR (300 MHz, DMSO-$d_6$, 298 K) $\delta$ (ppm): 8.28 (s, 1H, CH), 8.19 (d, $J = 8.12$ Hz, 1H, ArH), 7.91–7.83 (m, 2H, CH), 7.71–7.68 (m, 2H, ArH), 7.61 (s, 1H, ArH), 5.79 (s, 2H, CH$_2$).
temperature for 12 hours. The reaction mixture was washed by brine and dried by Na$_2$SO$_4$. The organic layer was evaporated under vacuum, and the residue was further purified by flash column chromatography on silica gel (dichloromethane/methanol = 60/1, v/v) to afford G6 (0.21 g, 47.0%), m.p. 174–175 °C. $^1$H NMR (300 MHz, chloroform-$d$, 298 K) δ (ppm): 8.08 (d, $J$=8.10 Hz, 2H, ArH), 7.65–7.60 (m, 4H, ArH), 7.48 (t, $J$=7.54 Hz, 2H, ArH), 5.51 (s, 4H, CH$_2$), 4.94 (s, 2H, NH), 3.23(s, 4H, CH$_2$), 1.58 (s, 4H, CH$_2$, overlapped with the solvent peak of water). $^{13}$C NMR (75 MHz, DMSO-$d_6$, 298 K) δ (ppm): 156.1, 134.5, 129.4, 125.2, 62.3, 27.1. LR-ESI-MS is: $m/z$ calcd for [M + H]$^+$, 447.15, found 447.05; calcd for [M + Na]$^+$, 469.13, found 469.05. HR-ESI-MS is: $m/z$ calcd for [M + Na]$^+$, C$_{20}$H$_{22}$N$_4$O$_8$Na$^+$, 469.1330, found 469.1332.

Fig. S12 $^1$H NMR spectrum (300 MHz, chloroform-$d$, 298 K) of G6
Synthesis of $G_7$: $G_7_p$ (0.20 g, 0.89 mmol) and $G_s$ (0.22 g, 0.89 mmol) were added in DMSO (20 mL). The mixture was stirred at room temperature for 12 hours. The reaction mixture was washed by brine and extracted by ethyl acetate. The organic layer was dried by $Na_2SO_4$ and evaporated under vacuum, and the residue was further purified by flash column chromatography on silica gel (dichloromethane/methanol = 40/1, v/v) to afford $G_7$ (0.20 g, 55.9%). m.p. 117−119 °C. $^1H$ NMR (300 MHz, chloroform-$d$, 298 K) δ (ppm): 8.09 (d, $J$ = 8.06 Hz, 1H, ArH), 7.67−7.57 (m, 2H, ArH), 7.47 (t, $J$ = 7.56 Hz, 1H, ArH), 7.36−7.31 (m, 5H, ArH), 5.51 (s, 2H, CH$_2$), 5.10 (s, 2H, CH$_2$), 3.22 (s, 4H, CH$_2$), 1.56 (s, 4H, CH$_2$, overlapped with the solvent peak of water). $^{13}C$ NMR (75 MHz, chloroform-$d$, 298 K) δ (ppm): 156.5, 155.9, 133.7, 128.5, 128.1, 125.0, 667, 63.2, 40.7, 40.6, 27.2. LR-ESI-MS is: m/z calcd for [M + H]$^+$, 402.16, found 402.10; calcd for [M + Na]$^+$,
424.14, found 424.05. HR-ESI-MS is: $m/z$ calcd for [M + Na]$^+$, C$_{20}$H$_{22}$N$_3$O$_6$Na$^+$, 424.1479, found 424.1479.

![Fig. S14](image1.png)  
**Fig. S14** $^1$H NMR spectrum (300 MHz, chloroform-$d$, 298 K) of G7

![Fig. S15](image2.png)  
**Fig. S15** $^{13}$C NMR spectrum (75 MHz, chloroform-$d$, 298 K) of G7
3. Investigation of the interactions between EtP[5]A and Guest by $^1$H NMR

Fig. S16 $^1$H NMR spectra (300 MHz, CDCl$_3$, 298 K): (a) EtP[5]A (2.5 mM); (b) equimolar mixture of G1 (2.5 mM) and EtP[5]A (2.5 mM); (c) G1 (2.5 mM); (d) 0.2 mL methanol-$d_4$ was added into the NMR tube with the mixture of G1 (2.5 mM) and EtP[5]A (2.5 mM) in 0.5 mL chloroform-$d$. The association constant $K_{a,G1\cdot EtP[5]A}$ value calculated from integrations of complexed and uncomplexed peaks of H$_{1}$ of EtP[5]A is $\frac{(2.09/3.63) \times 1.00 \times 10^{-3}}{(1 – 2.09/3.63) \times 1.00 \times 10^{-3}} = 1279$ M$^{-1}$. The association constant $K_{a,G1\cdot EtP[5]A}$ value calculated from integrations of complexed and uncomplexed peaks of H$_{b}$ of G1 is $\frac{(1.35/2.35) \times 2.50 \times 10^{-3}}{(1 – 1.35/2.35) \times 2.50 \times 10^{-3}} = 1269$ M$^{-1}$. Therefore, $K_{a,G1\cdot EtP[5]A} = (1279 + 1269)/2 = (1274 \pm 5)$ M$^{-1}$.
**Fig. S17** $^1$H NMR spectra (300 MHz, CDCl$_3$, 298 K): (a) EtP[5]A (2.5 mM); (b) equimolar mixture of G2 (2.5 mM) and EtP[5]A (2.5 mM); (c) G2 (2.5 mM) The association constant $K_{a,G2 \cdot EtP[5]A}$ value calculated from integrations of complexed and uncomplexed peaks of H$_1$ of EtP[5]A is $[(0.16/1.16) \times 2.50 \times 10^{-3}] / [(1 - 0.16/1.16) \times 2.50 \times 10^{-3}]^2 = 74$ M$^{-1}$. The association constant $K_{a,G2 \cdot EtP[5]A}$ value calculated from integrations of complexed and uncomplexed peaks of H$_c$ of G2 is $[(0.08/0.61) \times 2.50 \times 10^{-3}] / [(1 - 0.08/0.61) \times 2.50 \times 10^{-3}]^2 = 69$ M$^{-1}$. Therefore, $K_{a,G2 \cdot EtP[5]A} = (74 + 69)/2 = (71.5 \pm 2.5)$ M$^{-1}$

**Fig. S18** $^1$H NMR spectra (300 MHz, CDCl$_3$, 298 K): (a) EtP[5]A (2.5 mM); (b) equimolar mixture of G3 (2.5 mM) and EtP[5]A (2.5 mM); (c) G3 (2.5 mM)
**Fig. S19** $^1$H NMR spectra (300 MHz, CDCl$_3$, 298 K): (a) EtP[5]A (2.5 mM); (b) equimolar mixture of G4 (2.5 mM) and EtP[5]A (2.5 mM); (c) G4 (2.5 mM)

**Fig. S20** $^1$H NMR spectra (300 MHz, CDCl$_3$, 298 K): (a) EtP[5]A (2.5 mM); (b) equimolar mixture of G6 (2.5 mM) and EtP[5]A (2.5 mM); (c) G6 (2.5 mM)
Fig. S21 ¹H NMR spectra (300 MHz, CDCl₃, 298 K) of (a) EtP[5]A (2.5 mM); (b) equimolar mixture of G7 (2.5 mM) and EtP[5]A (2.5 mM); (c) G7 (2.5 mM). The association constant $K_{a, \text{G7} \cdot \text{EtP}[5]A}$ value calculated from integrations of complexed and uncomplexed peaks of $H_1$ of EtP[5]A is $\frac{[(1.05/2.05) \times 2.50 \times 10^{-3}]^2}{[1 – 1.05/2.05] \times 2.50 \times 10^{-3}} = 861 \text{ M}^{-1}$. The association constant $K_{a, \text{G7} \cdot \text{EtP}[5]A}$ value calculated from integrations of complexed and uncomplexed peaks of $H_b$ of G7 is $\frac{[(0.49/0.96) \times 2.50 \times 10^{-3}]^2}{[1 – 0.49/0.96] \times 2.50 \times 10^{-3}} = 851 \text{ M}^{-1}$. Therefore, $K_{a, \text{G7} \cdot \text{EtP}[5]A} = (861 + 851)/2 = (856 \pm 5) \text{ M}^{-1}$.


Fig. S22 2D NOSEY analysis of equimolar mixture G1<EtP[5]A in CDCl₃ (20 mM, 400 MHz, 298 K)

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5. Study of the photocleavage $G_7\subset EtP[5]A$ via UV 365nm by $^1H$ NMR

*Fig. S23* $^1H$ NMR spectra (300 MHz, CDCl$_3$, 298 K) of (a) $G_7\subset EtP[5]A$ (1 : 1, 2.5mM) in the absence (b) $G_7\subset EtP[5]A$ (1 : 1, 2.5mM) after UV 365 nm.

6. Reference