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Electronic Supplementary Information

Sensing of Linear Alkylammonium Ions by a 5-Pyrenoylamido-Calix[5]arene Solution and Monolayer Using Luminescence Measurements

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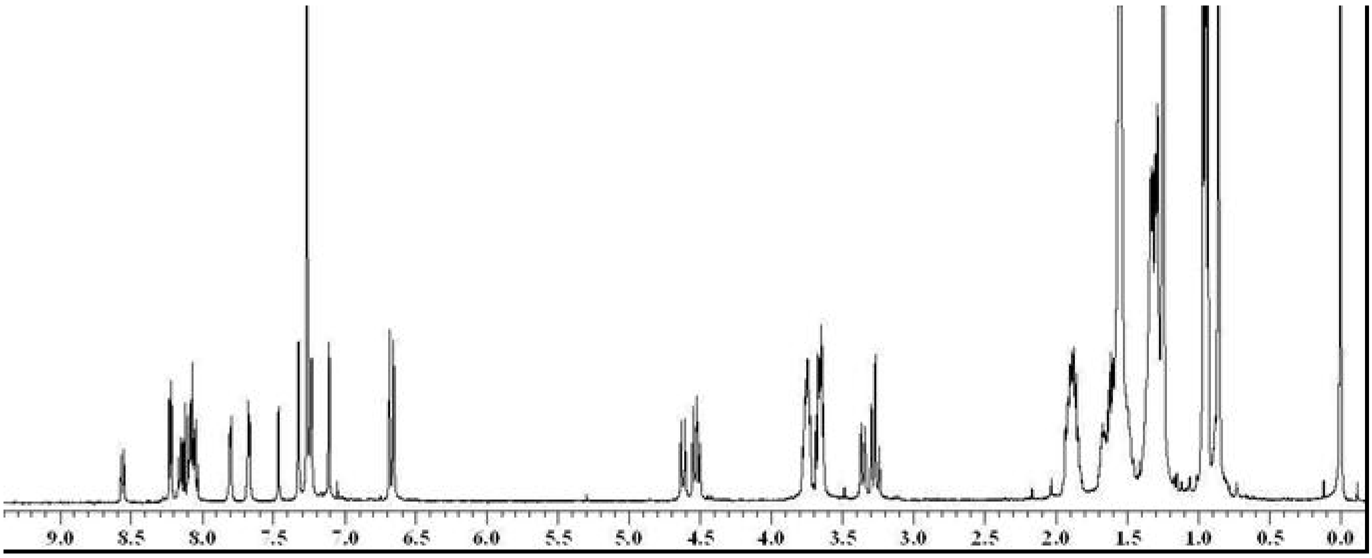

Figure S1. [1]H NMR spectrum of the compound **2** in $CDCl_3$.

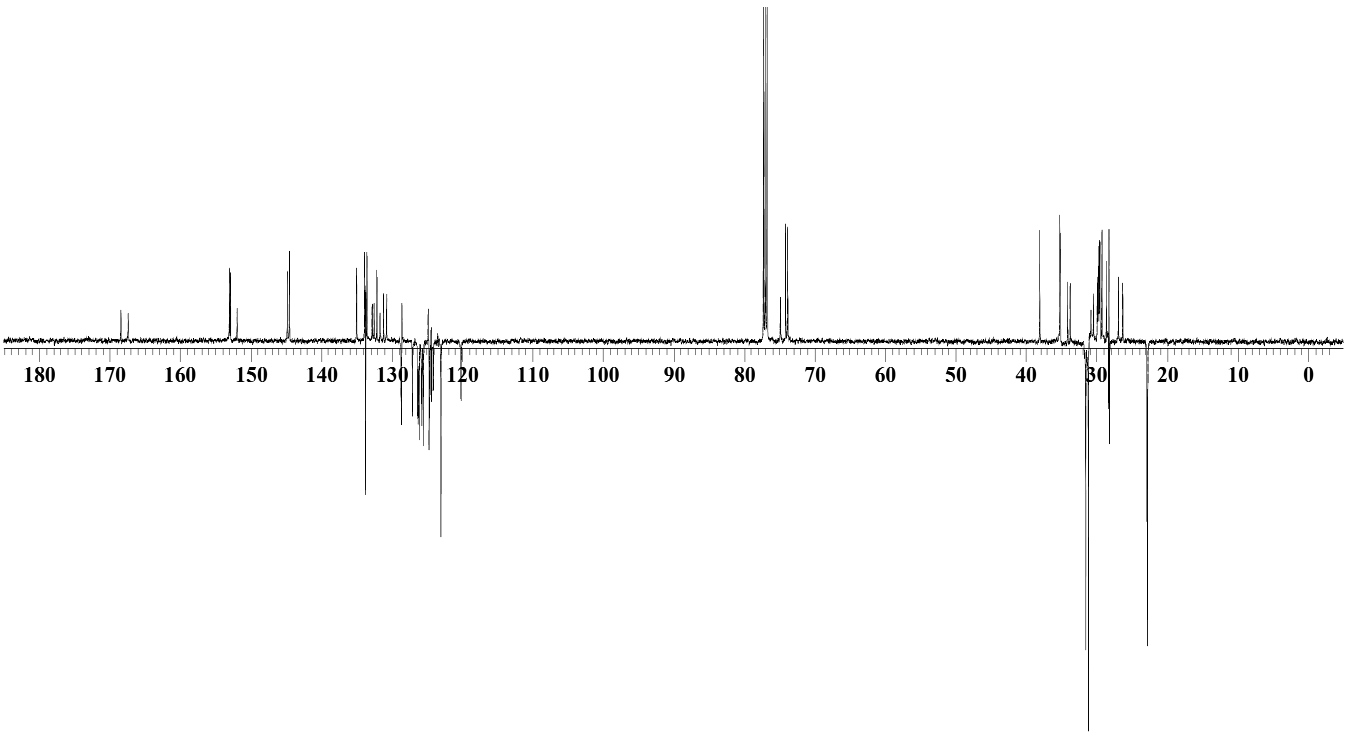

Figure S2. APT spectrum of the compound **2** in $CDCl_3$.

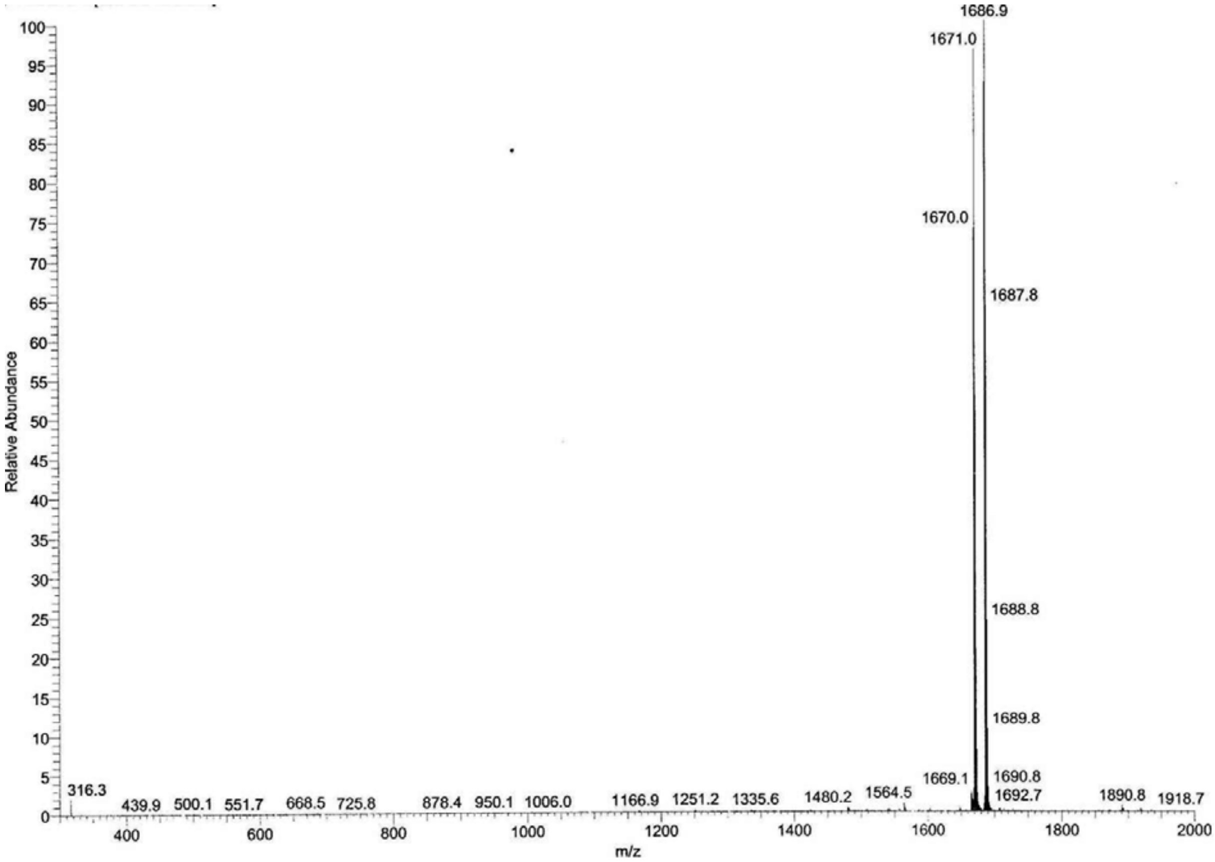

Figure S3. ESI-MS of the compound **2.**

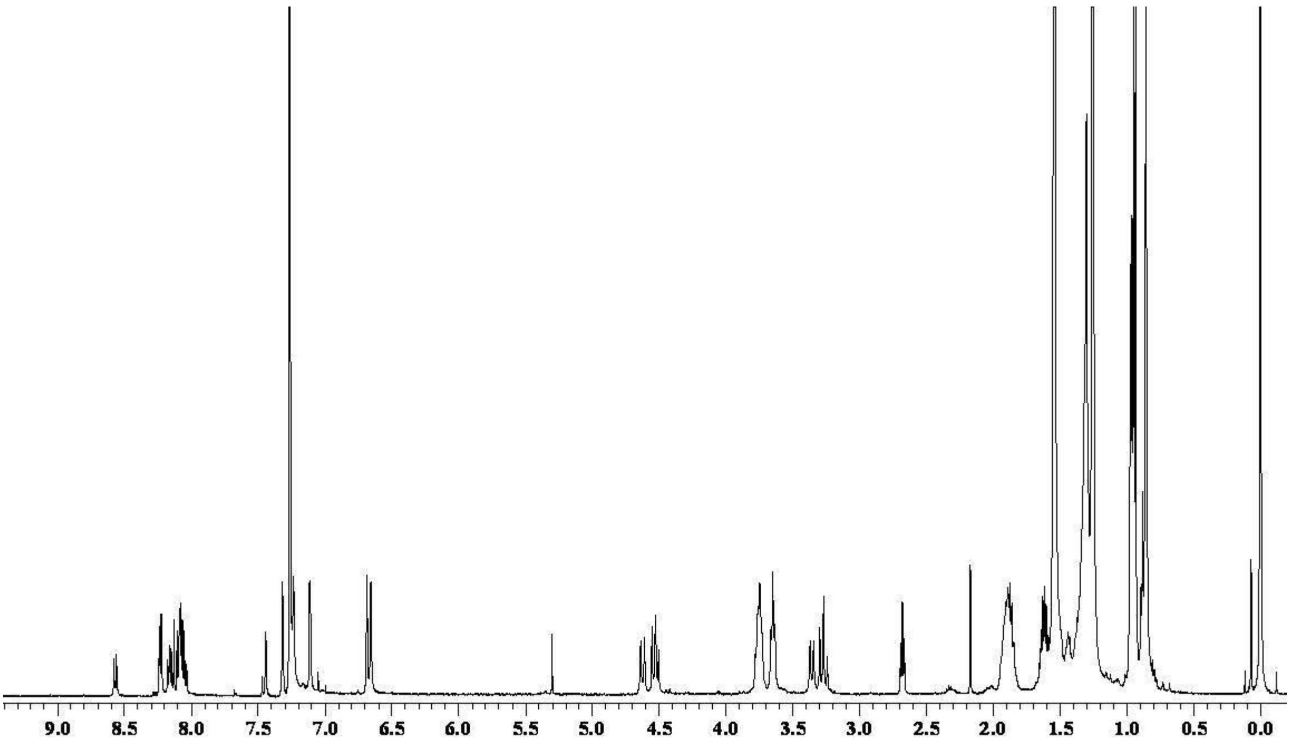

Figure S4. ^{1}H NMR spectrum of **PyC5-NH$_2$** in $CDCl_3$.

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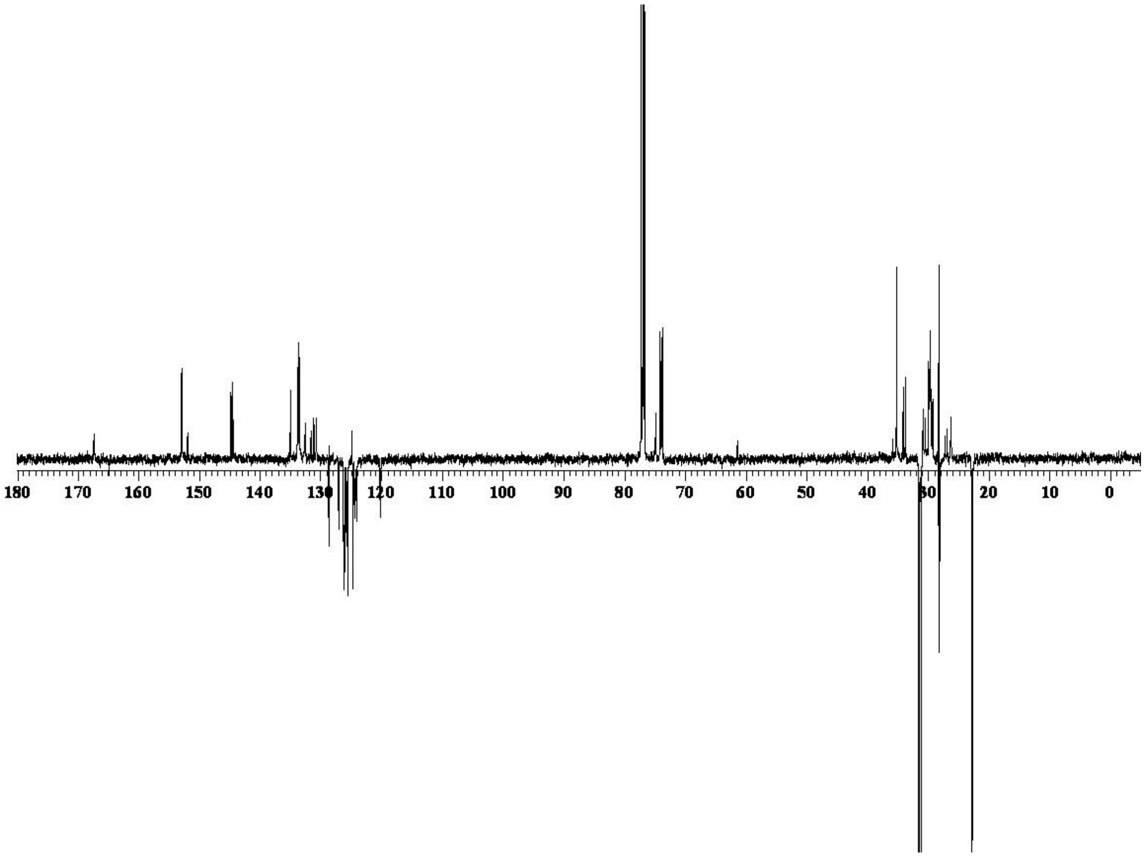

Figure S5. APT spectrum of **PyC5-NH$_2$** in $CDCl_3$.

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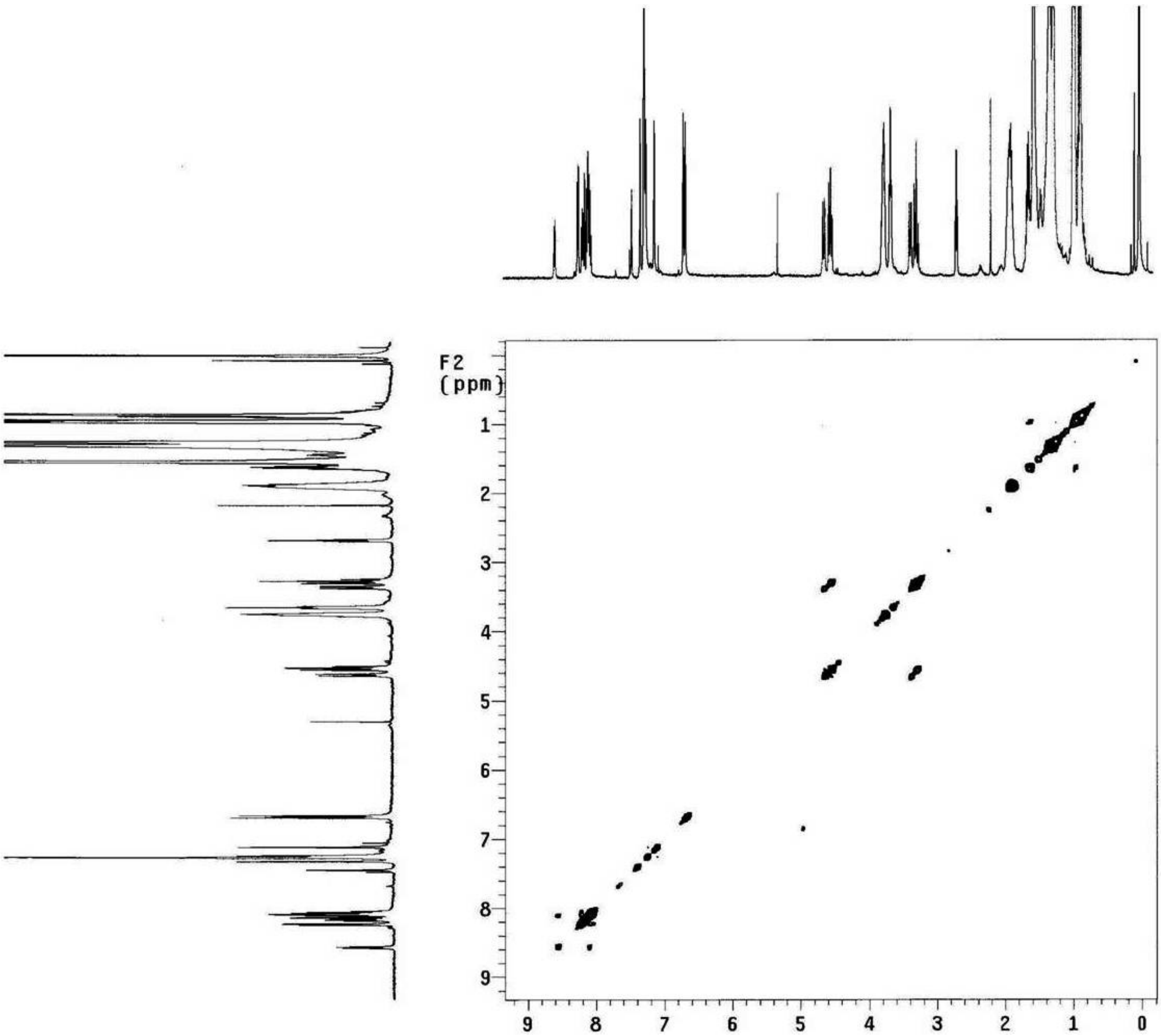

Figure S6. 2D-gCOSY spectrum of **PyC5-NH$_2$** in $CDCl_3$.

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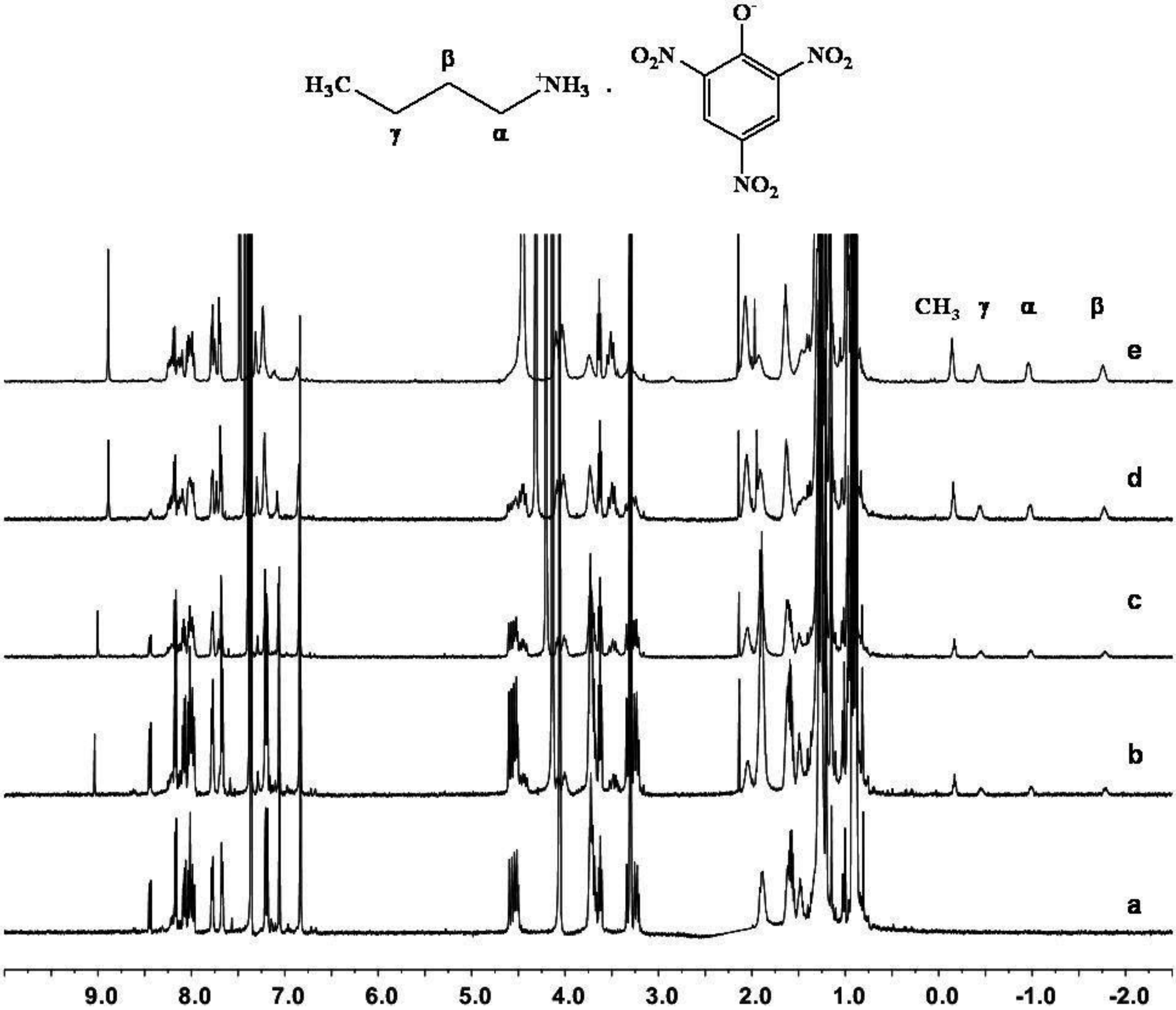

Figure S7. [1]H NMR titration of ***n*-Bu·HPic** with compound **3**. Constant concentration of host **3** (2.00×10^{-3} M) with addition of various concentrations ($0–4.00\times10^{-3}$ M) of guest ***n*-Bu·HPic**. a)compound **3**; b) [H]/[G] 4:1; c) [H]/[G] 2:1; d) [H]/[G] 1:1; e) [H]/[G] 1:2. Signals for the free ***n*-Bu·HPic** guest are absent in the expected 0.8-3 ppm range. In contrast, they appear in the 0– -2 ppm range, thus confirming the endo-complexation of the guest. In addition, an evident intensity increase of these signals parallels the increasing in the guest concentration.

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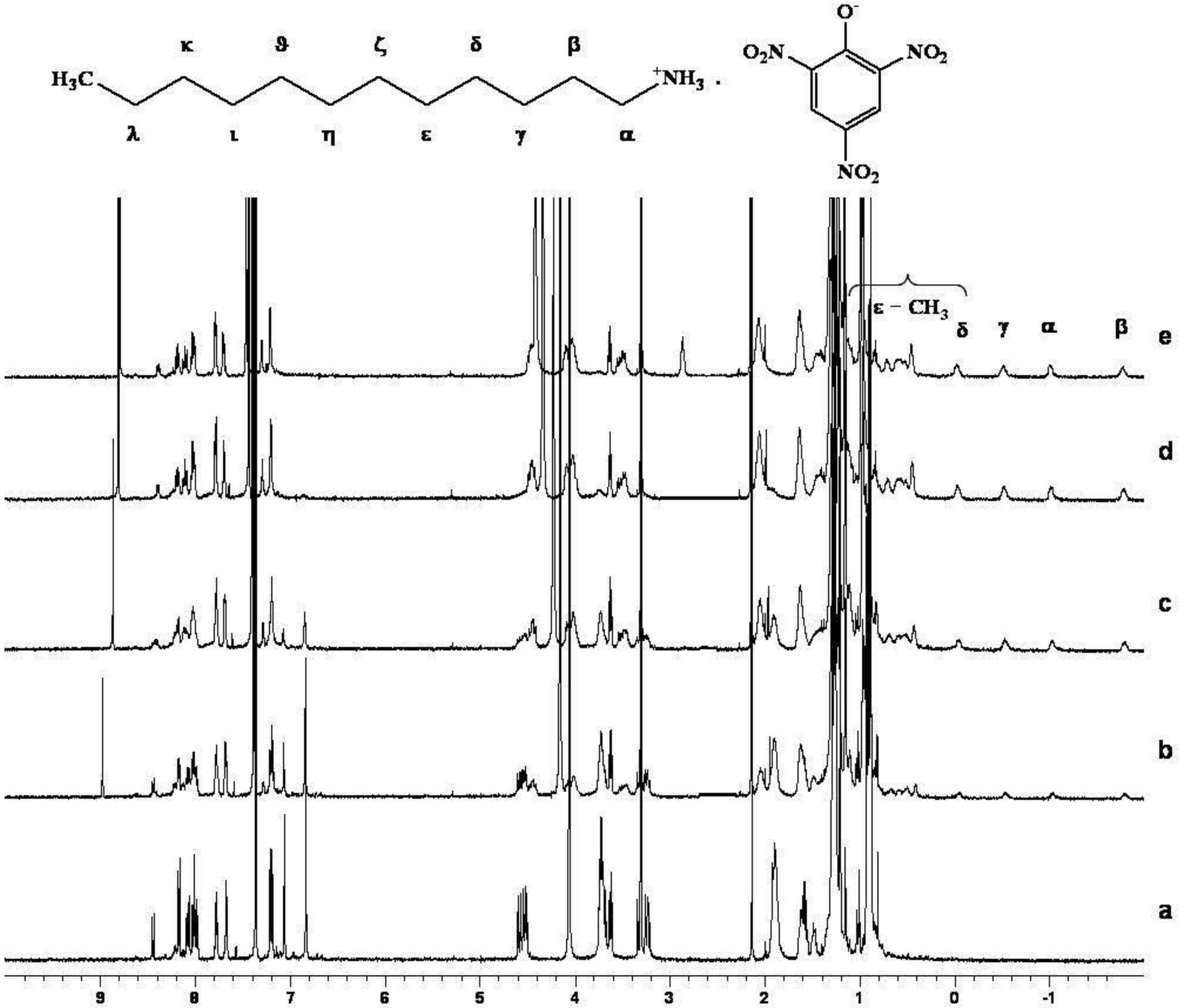

Figure S8. ^{1}H NMR titration of ***n*-$C_{12}NH_2$·HPic** with compound **3**. Constant concentration of host **3** (2.00×10^{-3} M) with addition of various concentrations ($0–4.00\times10^{-3}$ M) of guest ***n*-$C_{12}NH_2$·HPic**. a) compound **3**; b) [H]/[G] 4:1; c) [H]/[G] 2:1; d) [H]/[G] 1:1; e) [H]/[G] 1:2. Signals for the free ***n*-$C_{12}NH_2$·HPic** guest are absent in the expected 0.8-3 ppm range. In contrast, they appear in the 0– -2 ppm range, thus confirming the endo-complexation of the guest. In addition, an evident intensity increase of these signals parallels the increasing in the guest concentration.

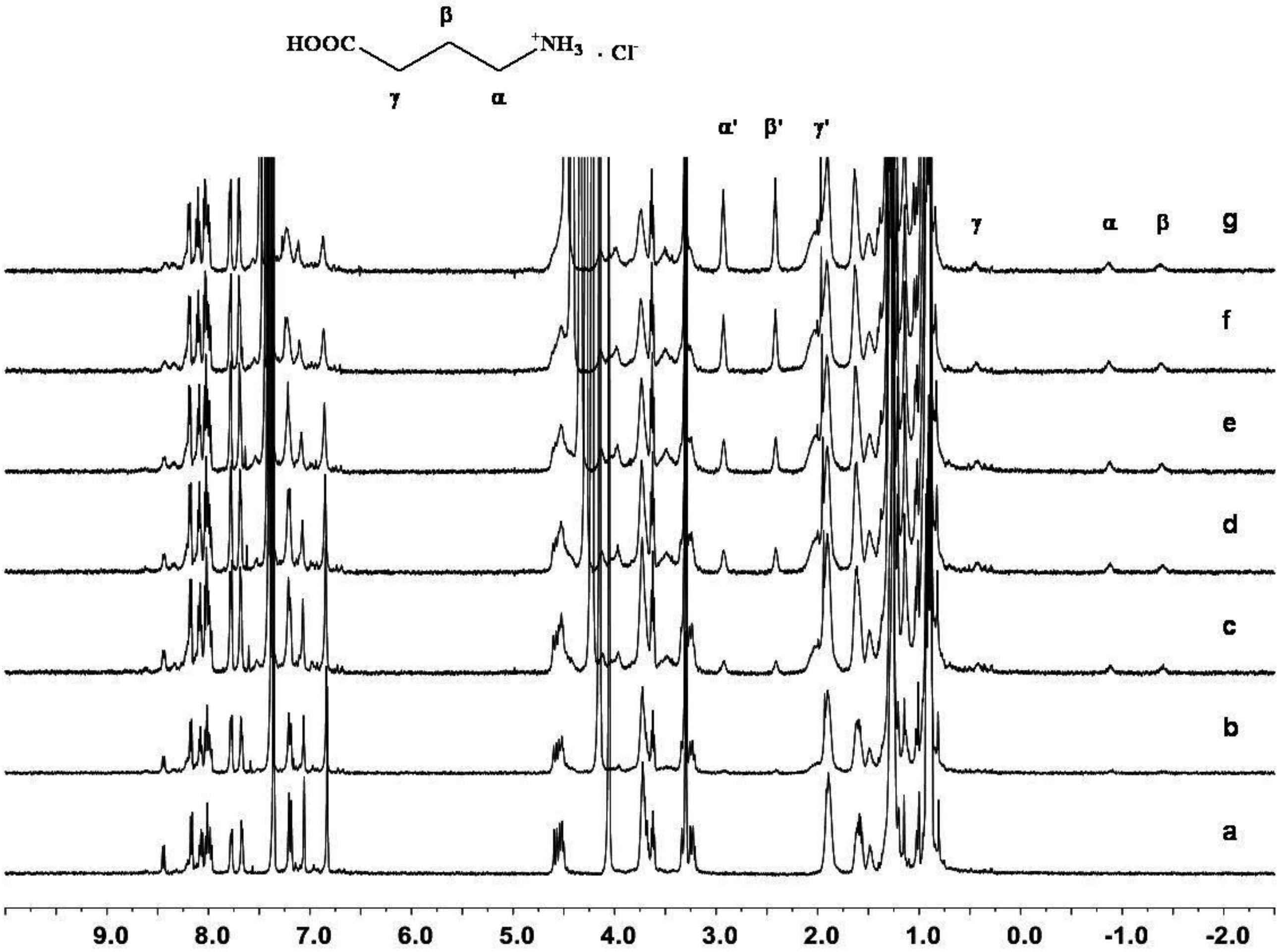

Figure S9. [1]H NMR titration of **GABA·HCl** with compound **3**. Constant concentration of host **3** (2.00×10^{-3} M) with addition of various concentrations (0–4.00×10^{-3} M) of guest **GABA·HCl**. a) compound **3**; b) [H]/[G] 4:1; c) [H]/[G] 2:1; d) [H]/[G] 1:0.75; e) [H]/[G] 1:1; f) [H]/[G] 1:1.5; g) [H]/[G] 1:2. Signals for the free **GABA·HCl** guest are present in the expected 2.0-3.0 ppm range (α' β' γ'). In addition, signals of the complexed gest appear in the 0.5– -1.5 (α, β, γ) ppm range, thus confirming partial endo-complexation of this guest.

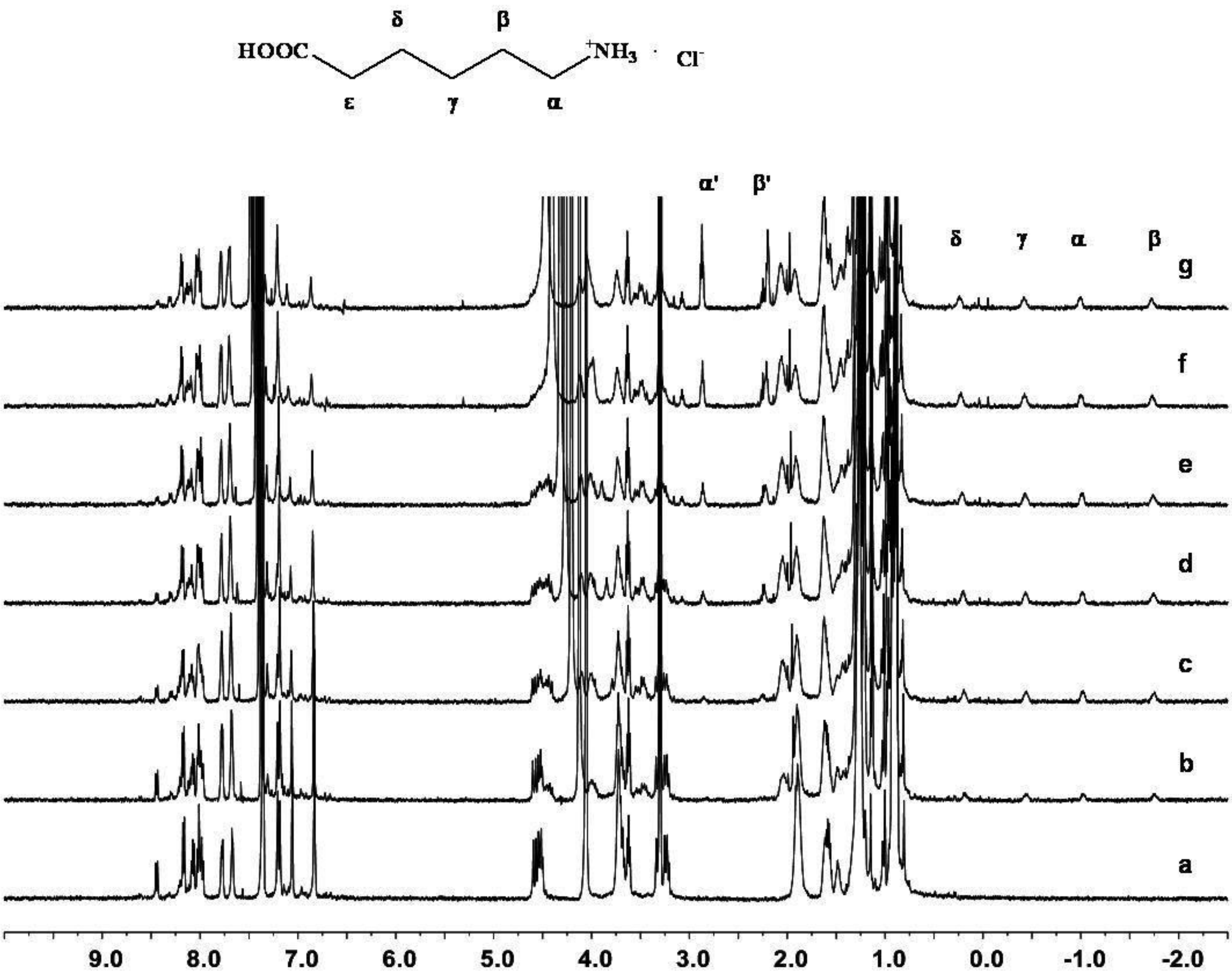

Figure S10. ^{1}H NMR titration of **ε-Ahx·HCl** with compound **3**. Constant concentration of host **3** (2.00×10^{-3} M) with addition of various concentrations ($0–4.00\times10^{-3}$ M) of guest **ε-Ahx·HCl**.

a) compound **3**; b) [H]/[G] 4:1; c) [H]/[G] 2:1; d) [H]/[G] 1:0.75; e) [H]/[G] 1:1; f) [H]/[G] 1:1.5; g) [H]/[G] 1:2. Signals for the free **ε-Ahx·HCl** guest are present in the expected 1.0-3.0 ppm range (α’ β’ γ’ δ’ ε’). In addition, signals of the complexed gest appear in the 1.0 – -2.0 (α, β, γ, δ, ε) ppm range, thus confirming partial endo-complexation of this guest.

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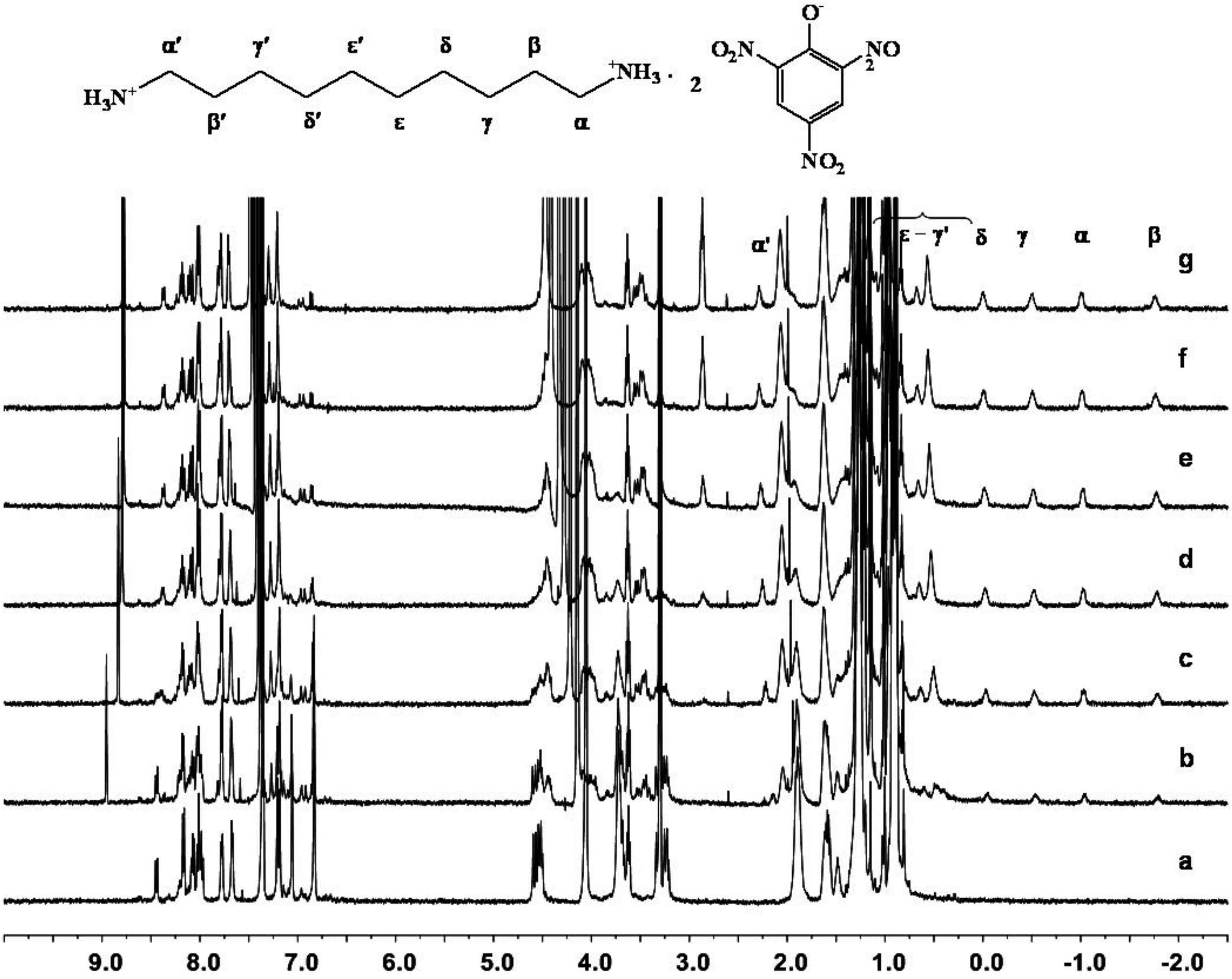

Figure S11. ^{1}H NMR titration of **C_{10}·2NH$_2$·HPic** with compound **3**. Constant concentration of host **3** (2.00×10^{-3} M) with addition of various concentrations ($0–4.00\times10^{-3}$ M) of guest **C_{10}·2NH$_2$·HPic**. a) compound **3**; b) [H]/[G] 4:1; c) [H]/[G] 2:1; d) [H]/[G] 1:0.75; e) [H]/[G] 1:1; f) [H]/[G] 1:1.5; g) [H]/[G] 1:2. Titration experiments of **2** with **C_{10}·2NH$_2$,** give rise to changes in the ^{1}H NMR spectra that are consistent with the formation of a single complexed species, corresponding to the 1:1 host–guest complex, at any [H]/[G] ratios. This conclusion is validated by the appearing in the spectra of a triplet centered at δ=2.25 ppm for **C_{10}·2NH$_2$,** since the addition of the first aliquot of the guest salt. This triplet is assigned to the α'-CH$_2$ protons of the guest and judged of diagnostic value for the formation of the 1:1 host–guest complex.

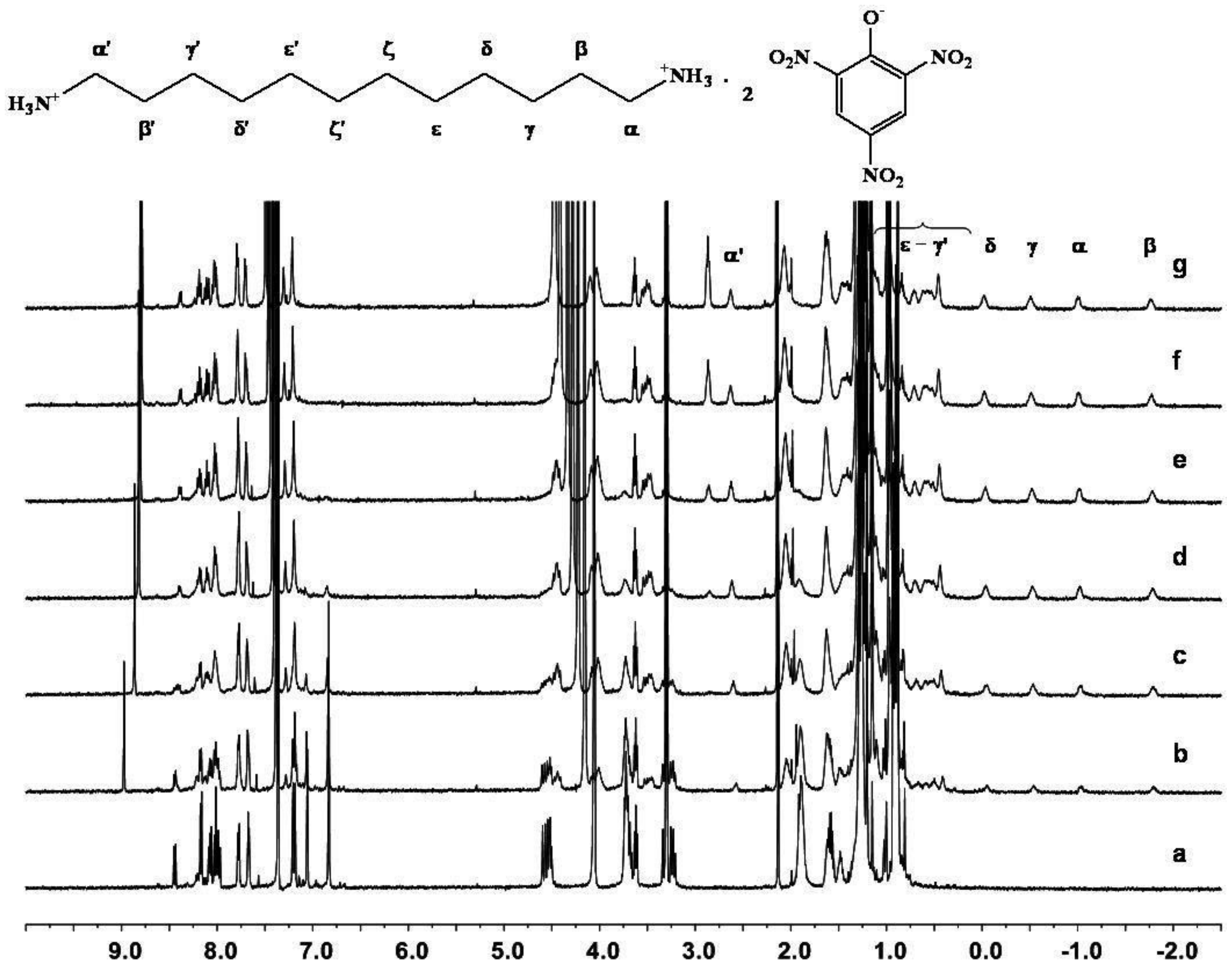

Figure S12. [1]H NMR titration of **C_{12}·2NH_2·HPic** with compound **3**. Constant concentration of host **3** (2.00×10^{-3} M) with addition of various concentrations ($0–4.00\times10^{-3}$ M) of guest **C_{12}·2NH_2·HPic**. a) compound **3**; b) [H]/[G] 4:1; c) [H]/[G] 2:1; d) [H]/[G] 1:0.75; e) [H]/[G] 1:1; f) [H]/[G] 1:1.5; g) [H]/[G] 1:2. Titration experiments of **2** with **C_{12}·2NH_2,** give rise to changes in the [1]H NMR spectra that are consistent with the formation of a single complexed species, corresponding to the 1:1 host–guest complex, at any [H]/[G] ratios. This conclusion is validated by the appearing in the spectra of a triplet centered at δ=2.63 ppm for **C_{12}·2NH_2,** since the addition of the first aliquot of the guest salt. This triplet is assigned to the α'-CH_2 protons of the guest and judged of diagnostic value for the formation of the 1:1 host–guest complex.

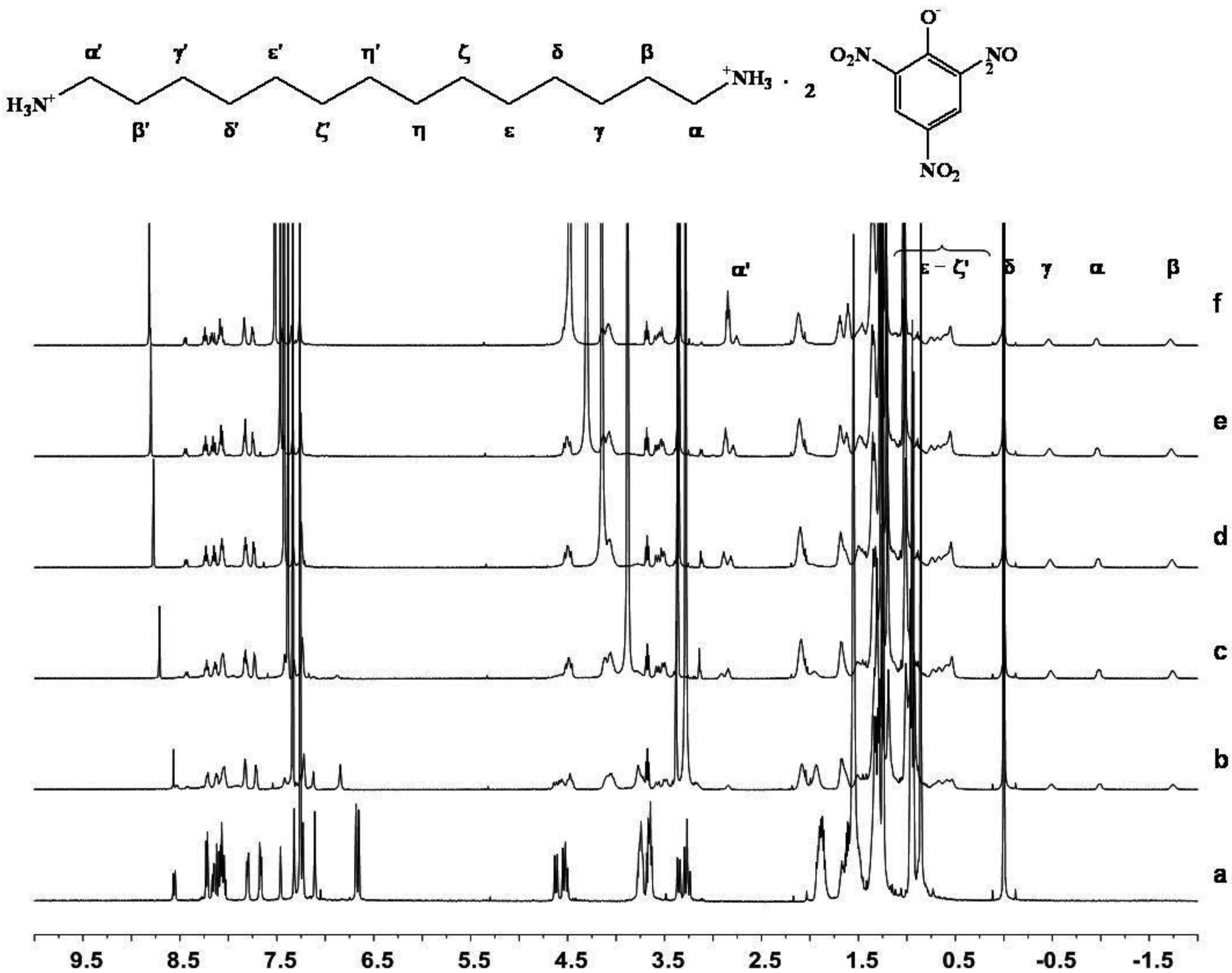

Figure S13. ^{1}H NMR titration of **C_{14}·2NH_2·HPic** with compound **3**. Constant concentration of host **3** (2.00×10^{-3} M) with addition of various concentrations (0–4.00×10^{-3} M) of guest **C_{14}·2NH_2·HPic**.

a) compound **3**; b) [H]/[G] 4:1; c) [H]/[G] 2:1; d) [H]/[G] 1:0.75; e) [H]/[G] 1:1; f) [H]/[G] 1:2. Titration experiments of **2** with **C_{14}·2NH_2,** give rise to changes in the ^{1}H NMR spectra that are consistent with the formation of a single complexed species, corresponding to the 1:1 host–guest complex, at any [H]/[G] ratios. This conclusion is validated by the appearing in the spectra of a triplet centered at δ=2.75 ppm for **C_{14}·2NH_2,** since the addition of the first aliquot of the guest salt. This triplet is assigned to the α'-CH_2 protons of the guest and judged of diagnostic value for the formation of the 1:1 host–guest complex.

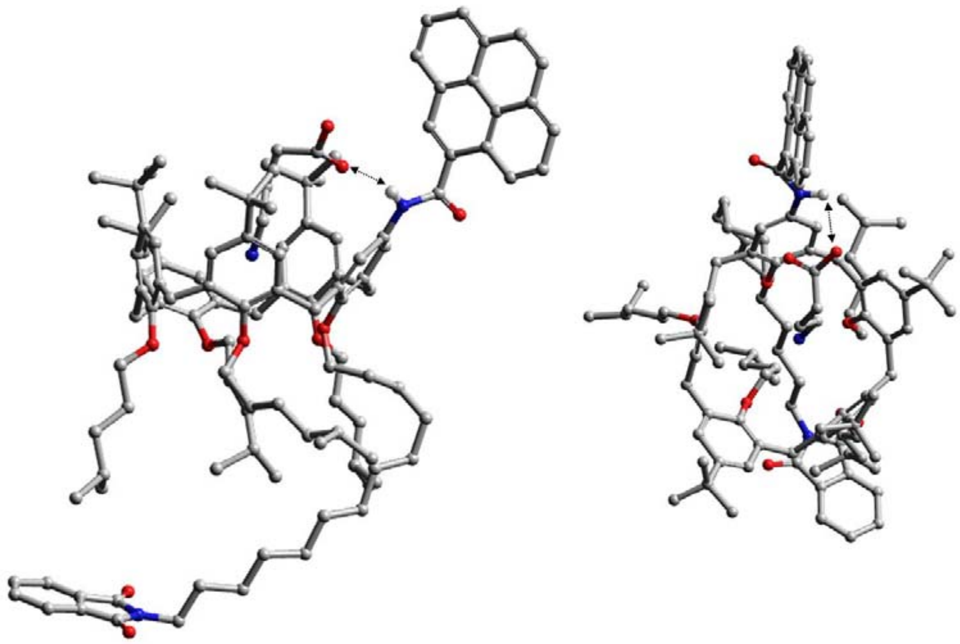

Figure S14. Optimized structures of the 1:1 complexes of **3** with **GABA**. Side view (left) and top view (right). (Hydrogens omitted for clarity).

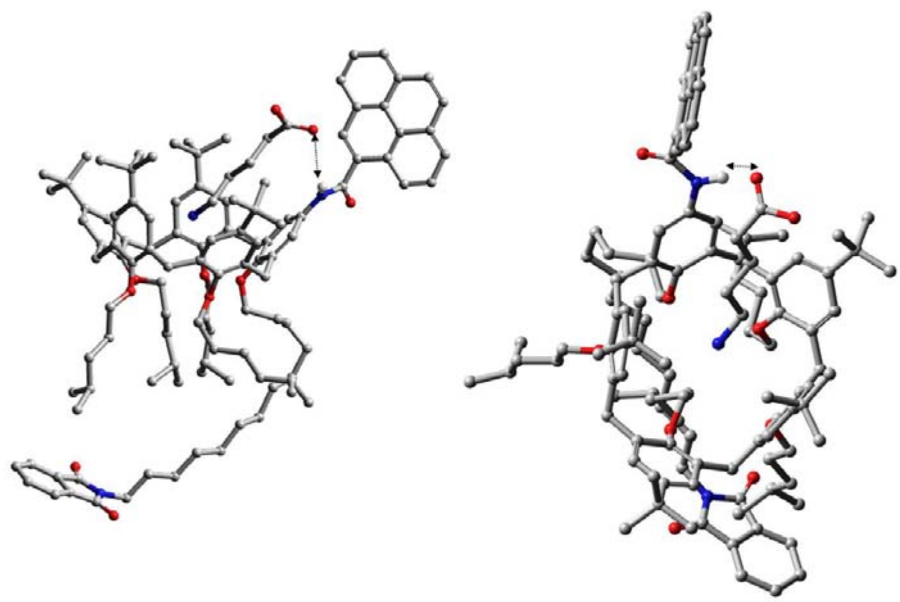

Figure S15. Optimized structures of the 1:1 complexes of **3** with **ε-Ahx**. Side view (left) and top view (right). (Hydrogens omitted for clarity).

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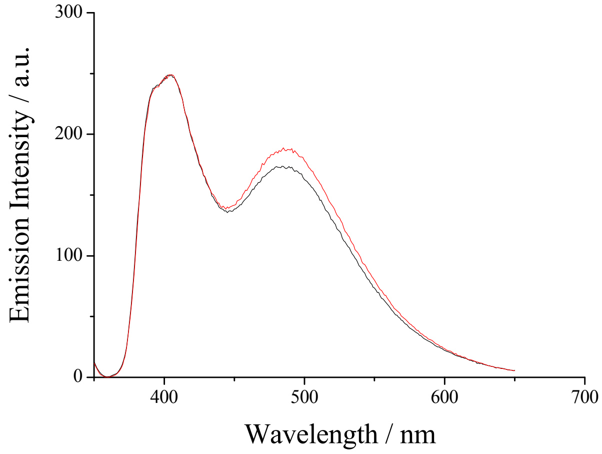

Figure S16. Fluorescence spectra of the **PyC5-NH$_2$** 1.0 x 10^{-5} M $CHCl_3/CH_3OH$ (50:50 v:v) solution (lower intensity) and upon addition of a stoichiometric amount of HCl (higher intensity).

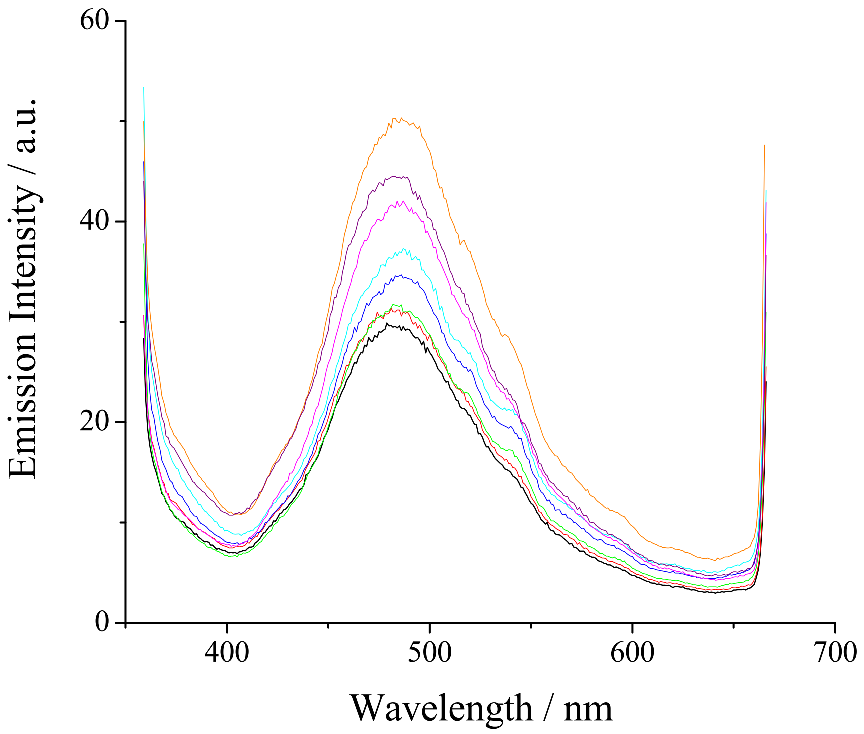

Figure S17. Fluorescence spectra of a representative **PyC5-NH$_2$-SAM** and upon 10 min immersion in $CHCl_3/CH_3OH$ (50:50 v:v) **$C_{12}NH_2$·HCl** solutions. Increasing emission intensities refer to the following increasing **$C_{12}NH_2$·HCl** concentrations: 0, 10, 20, 50, 70, 100, 150 and 200 ppm; λ_{exc} = 343 nm.