Supplementary Material (ESI) for Dalton Transactions


# Zinc-cyclen Coordination to UTP, TTP or Pyrophosphate induces Pyrene Excimer Emission

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## Supporting Information

## 1. Emission Spectra and Evaluation of Binding Studies

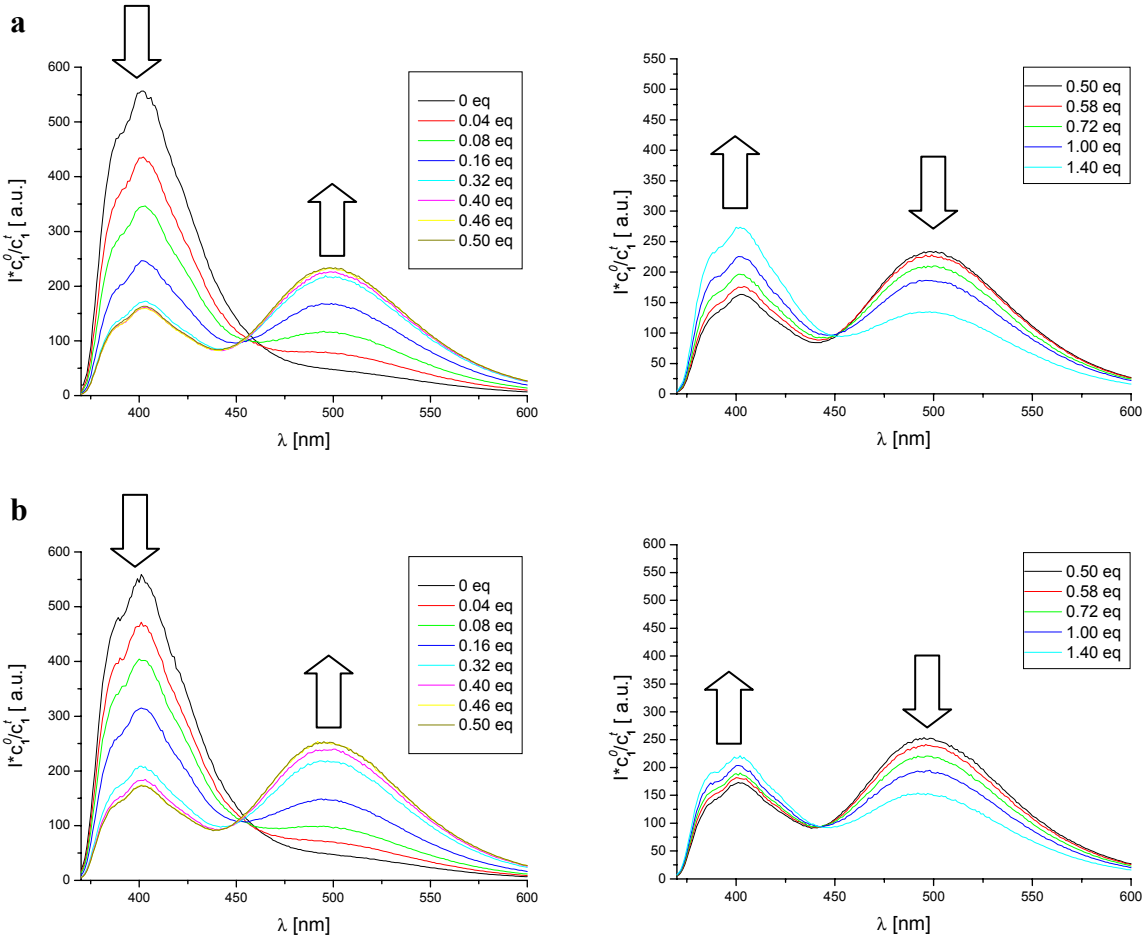



**Figure S1:** Emission spectra of compound **1** titrated with (a) UMP and (b) UDP, respectively. [**1**] = 0.5 mM, [UMP] = [UDP] = 1.0 mM; left side shows successively addition of up to 0.5 equiv. of nucleotide hence, formation of 2:1-aggregates indicated by arising excimer and decreasing monomer emission; right side displays disruption of 2:1 stoichiometry observable as increase in monomer emission, while excimer emission decreases

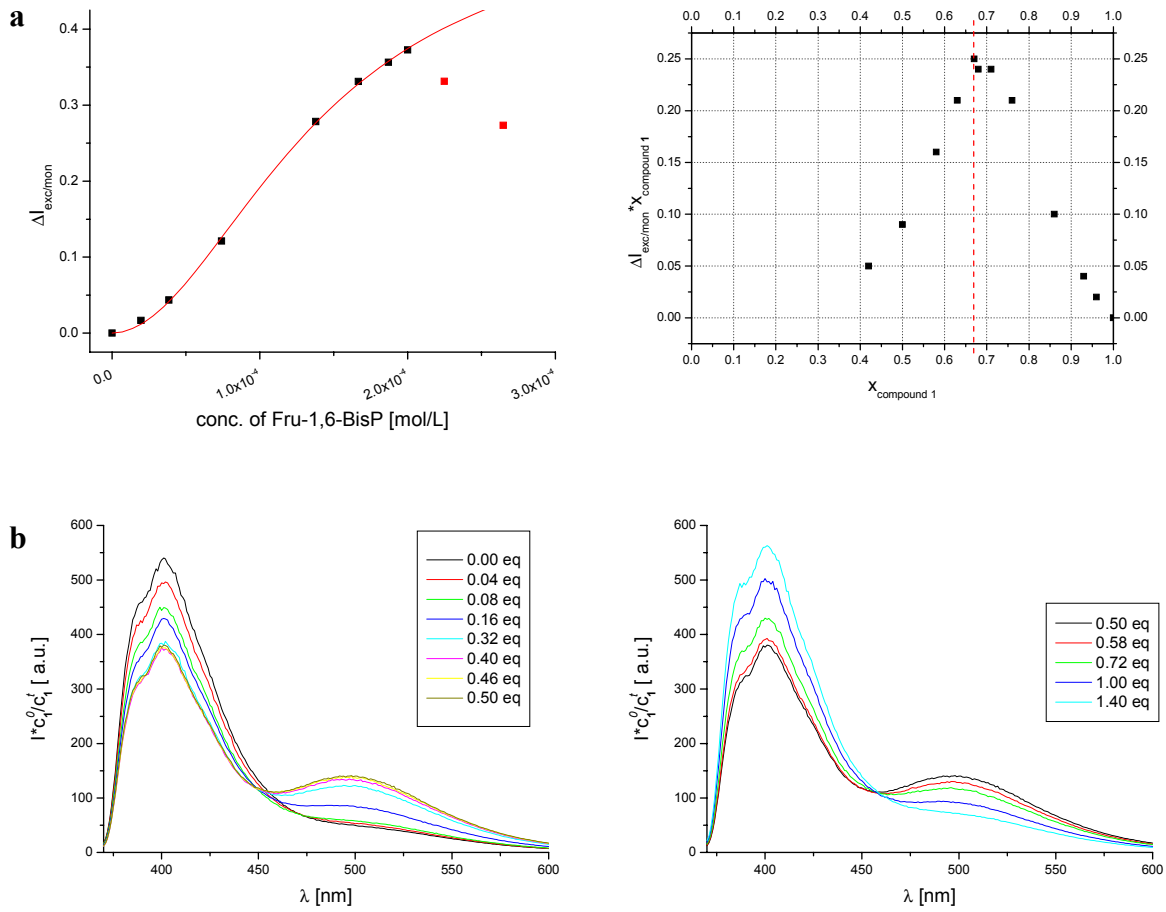



**Figure S2:** Titration of compound **1** with fructose-1,6-bisphosphophosphate. (a) Titration curve (left) and Job's plot analysis (right) for titration of [1] = 0.5 mM with [Fru-1,6-bisP] = 1.0 mM at pH 7.4 in HEPES buffered aqueous solution. (b) Obtained emission spectra show the typical behavior of successive formation (left) and disruption (right) of the corresponding ternary complex

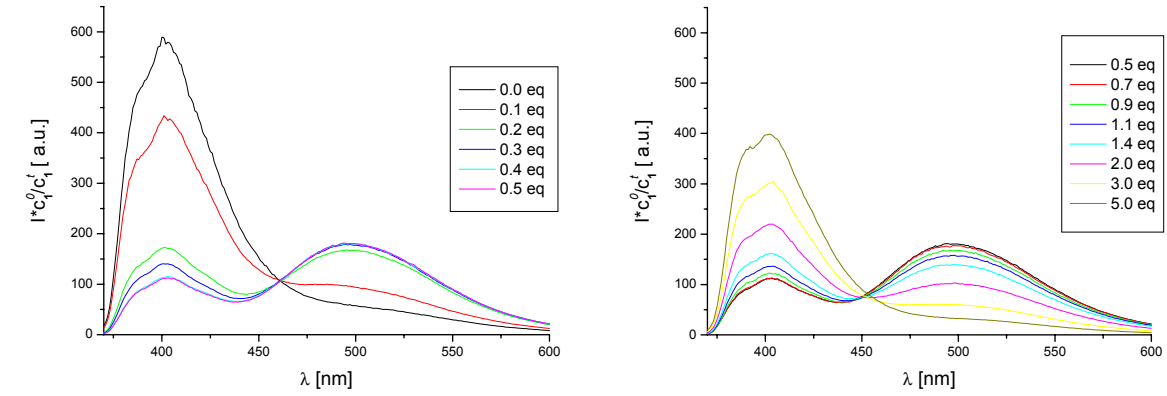



**Figure S3:** Emission spectra obtained for titration of compound **1** with TTP. Obtained emission spectra show the typical behavior of successive formation (left) and disruption (right) of the corresponding ternary complex; [1] = 0.5 mM, [TTP] = 5.0 mM

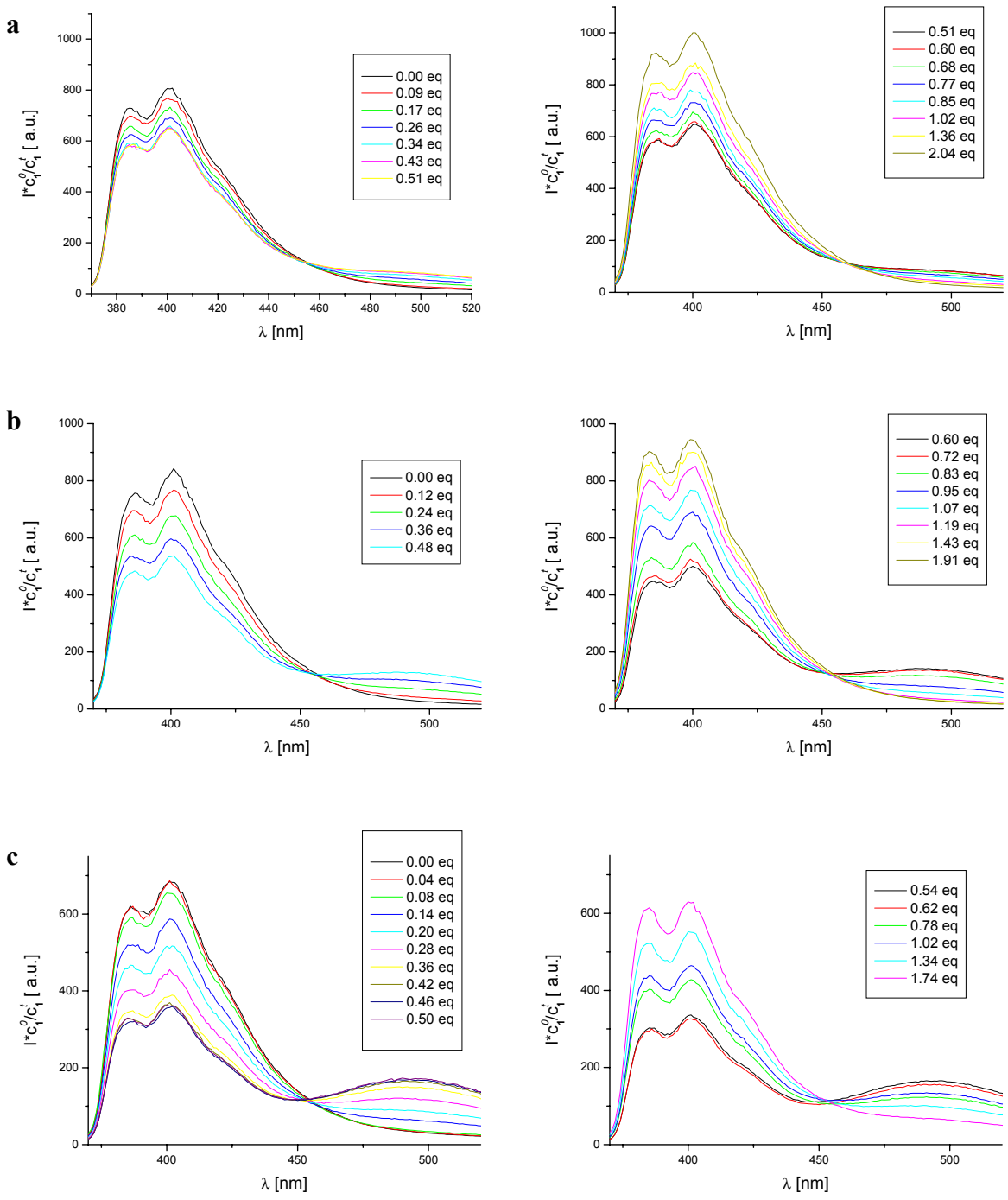



**Figure S4:** Emission spectra obtained for titration of compound **2** with IDP, ITP, UDP and UTP**.** Obtained emission spectra show the typical behavior of successive formation (left) and disruption (right) of the corresponding ternary complex; compound **2** (0.5 mM) was titrated with (a) IDP, (b) ITP, (c) UDP and (d) UTP (1.0 mM) in aqueous HEPES buffer at pH 7.4

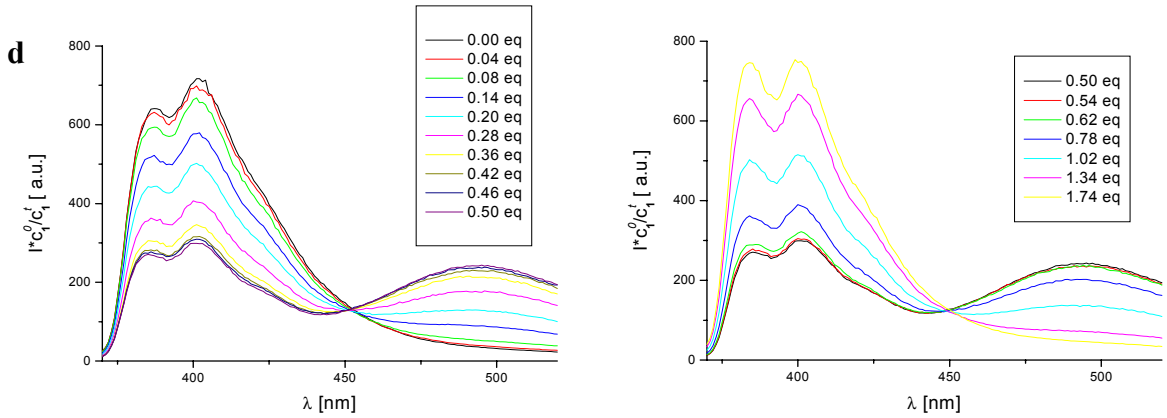



**Figure S4 (cont.):** Emission spectra obtained for titration of compound **2** with IDP, ITP, UDP and UTP**.** Obtained emission spectra show the typical behavior of successive formation (left) and disruption (right) of the corresponding ternary complex; compound **2** (0.5 mM) was titrated with (a) IDP, (b) ITP, (c) UDP and (d) UTP (1.0 mM) in aqueous HEPES buffer at pH 7.4

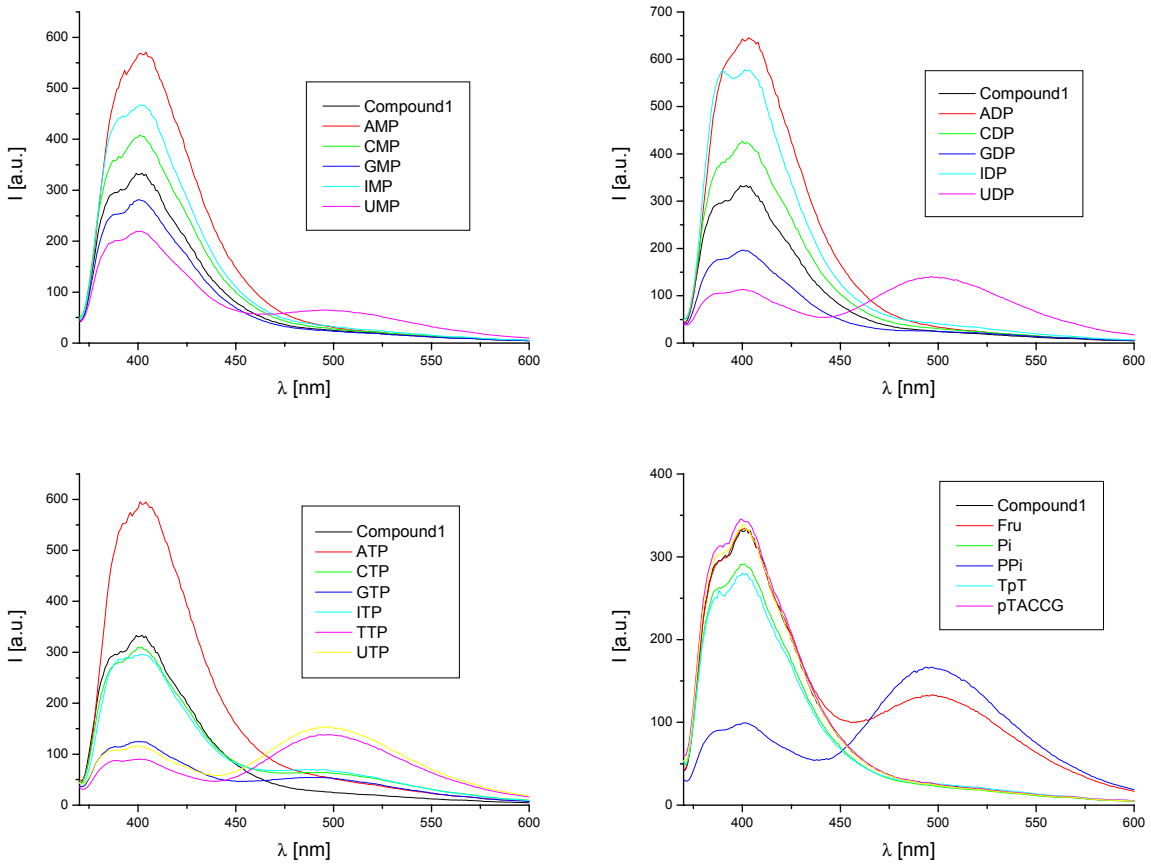



**Figure S5:** Emission spectra for analyte screening with compound **1** in HEPES buffered solution.

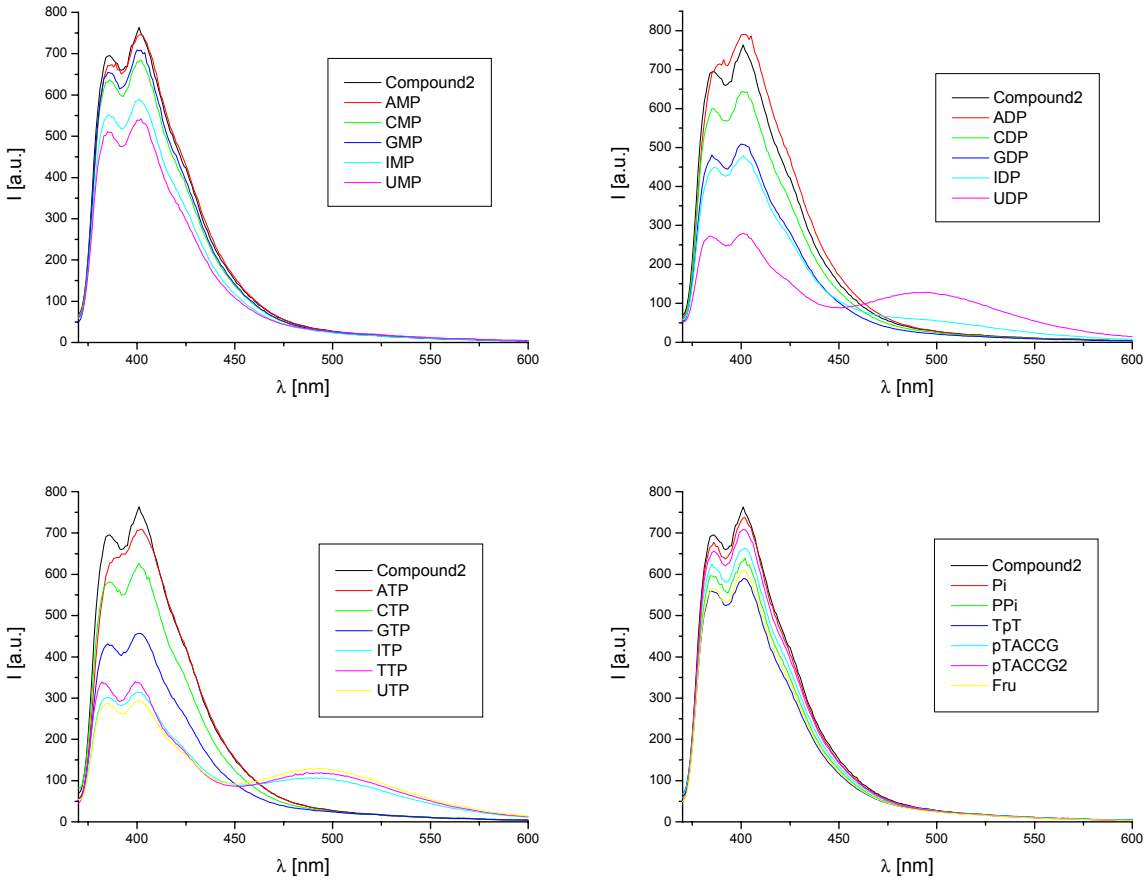



**Figure S6:** Emission spectra for analyte screening with compound **2** in HEPES buffered solution.

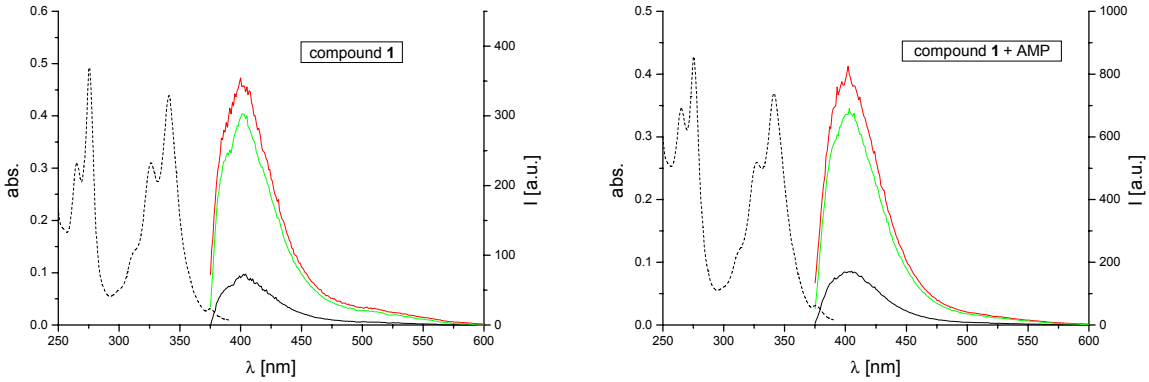



**Figure S7:** UV spectra (dashed line) and emission spectra (solid lines) for determination of fluorescence quantum yield of compound **1** alone or in combination with selected analytes in HEPES buffered solution and quinine sulfate dehydrate (in 0.1 N $H_2SO_4$) as reference. Emission spectra were recorded at three different combinations of emission and excitation slit widths: 5 nm / 5 nm (black), 5 nm / 10 nm (red), 10 nm / 5 nm (green)

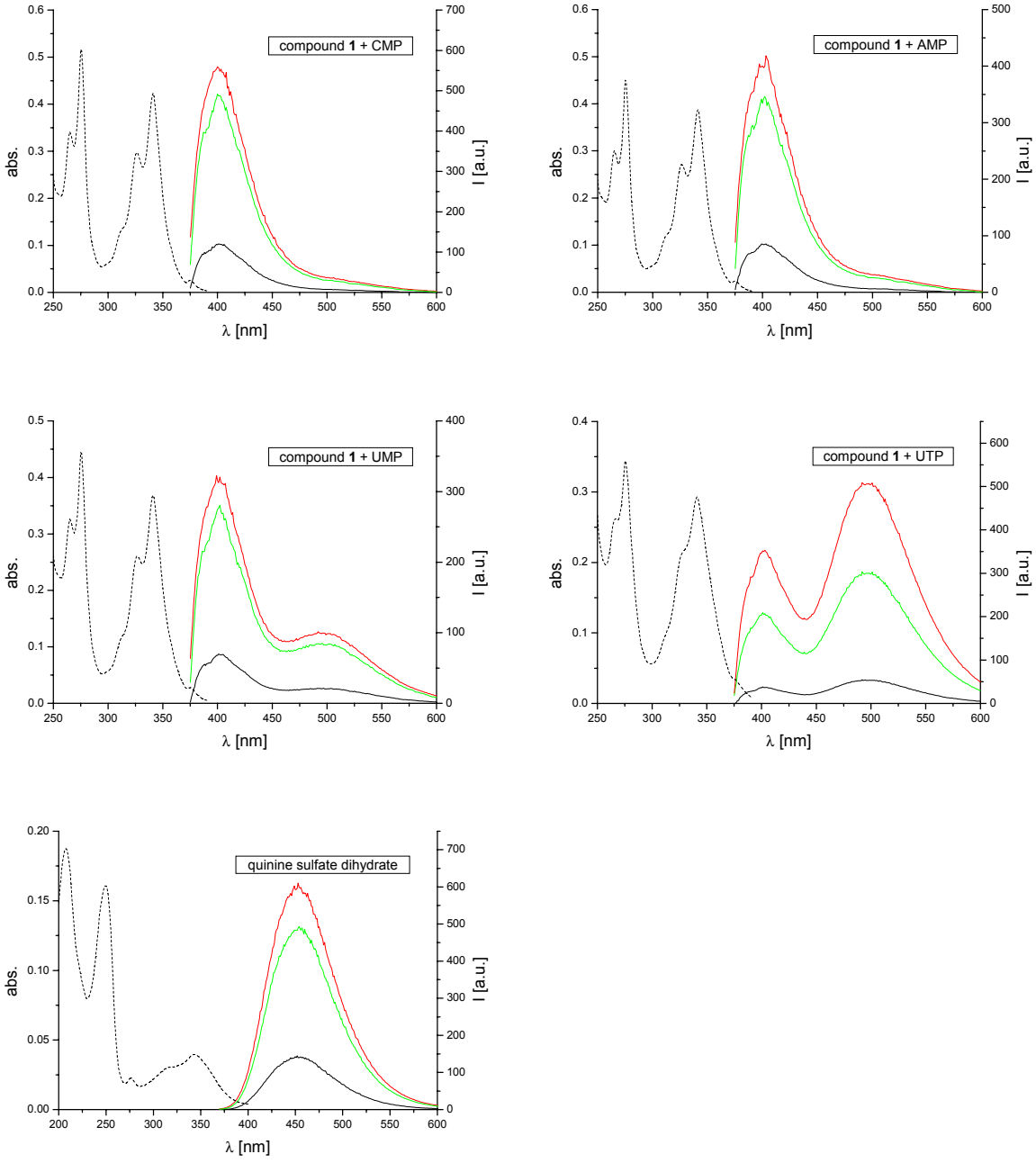



**Figure S7 (cont.):** UV spectra (dashed line) and emission spectra (solid lines) for determination of fluorescence quantum yield of compound **1** alone or in combination with selected analytes in HEPES buffered solution and quinine sulfate dehydrate (in 0.1 N $H_2SO_4$) as reference. Emission spectra were recorded at three different combinations of emission and excitation slit widths: 5 nm / 5 nm (black), 5 nm / 10 nm (red), 10 nm / 5 nm (green)

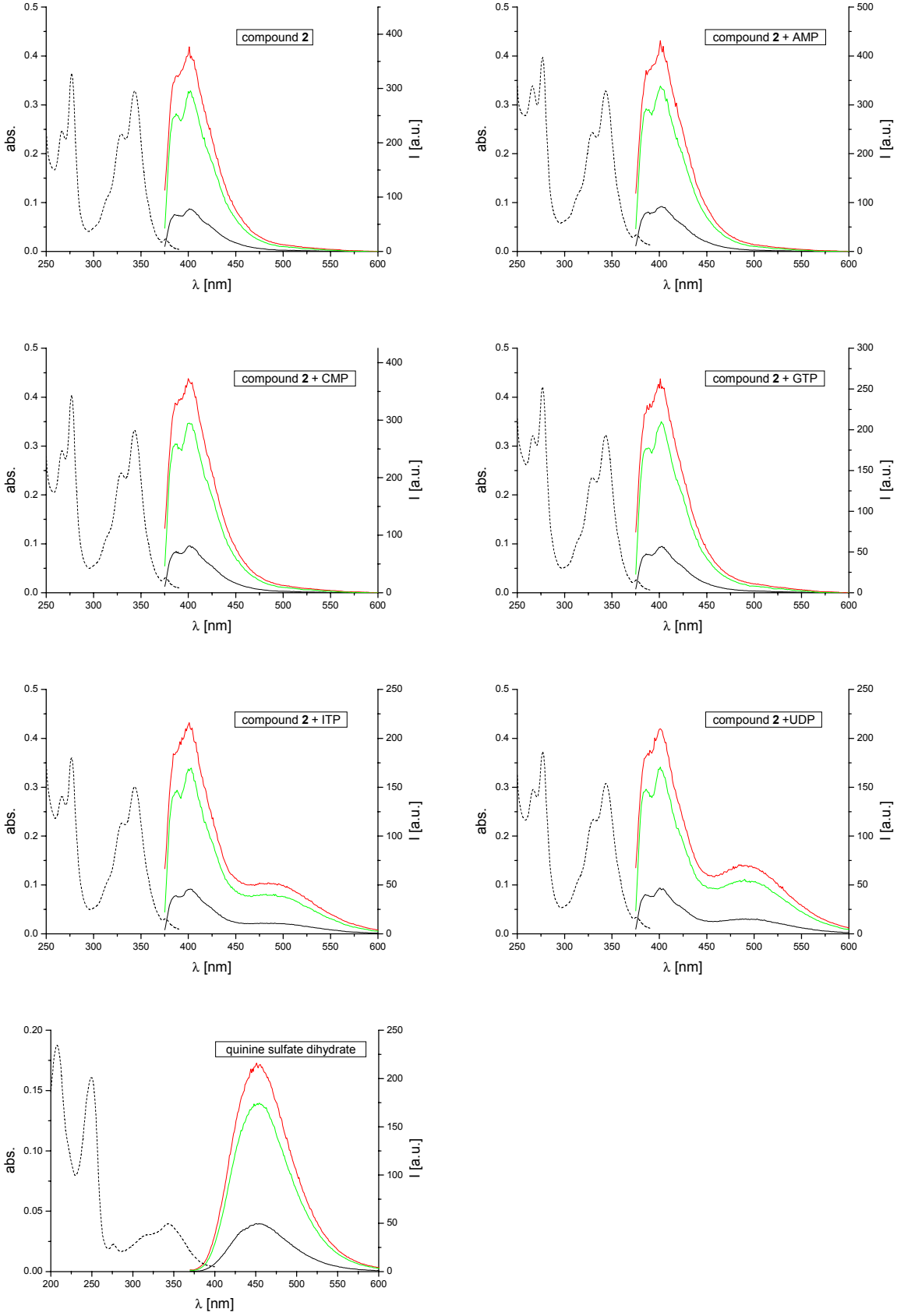
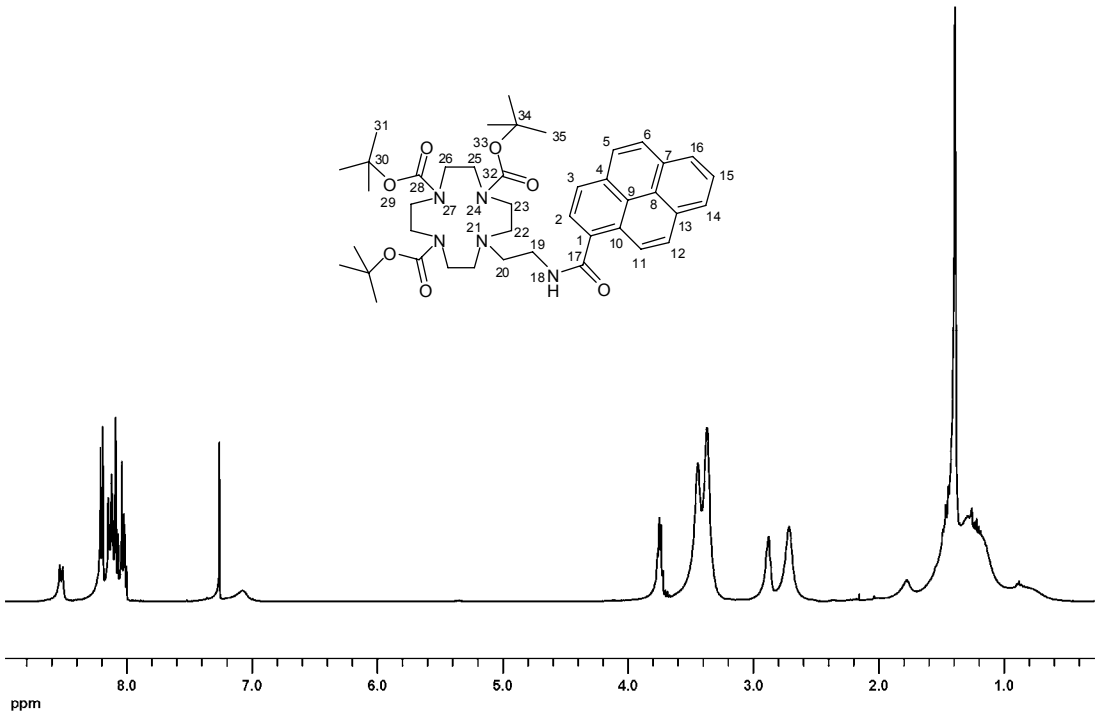
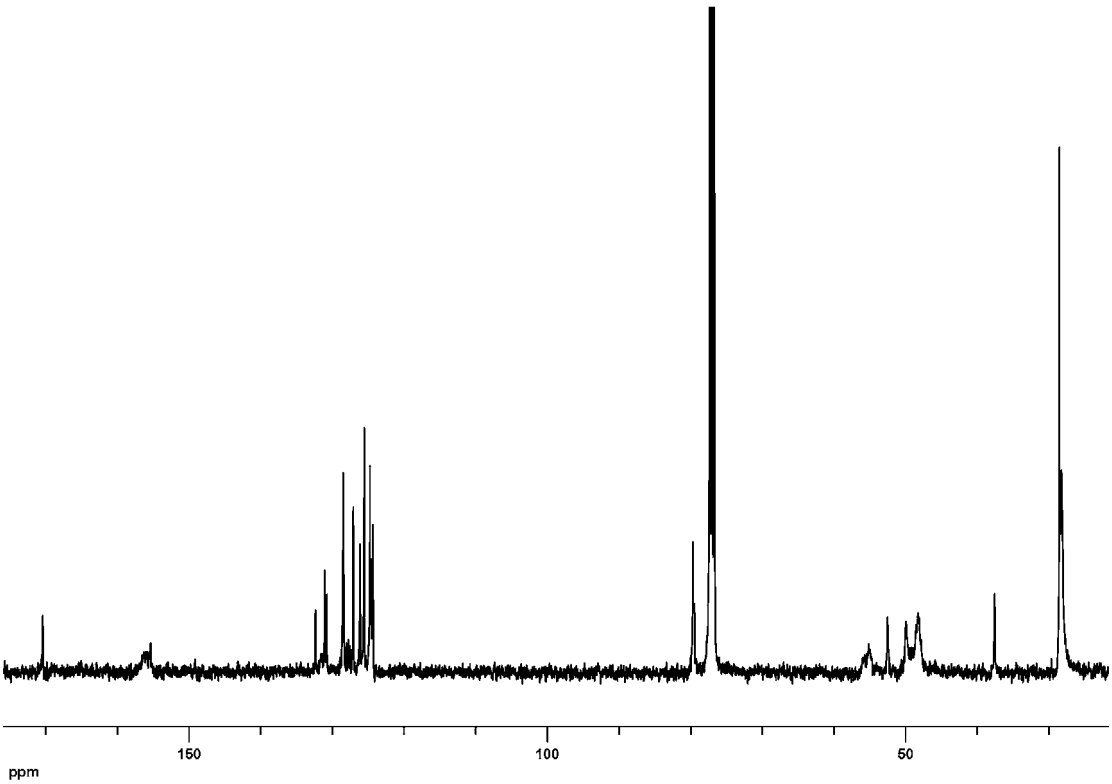



**Figure S8:** UV spectra (dashed line) and emission spectra (solid lines) for determination of fluorescence quantum yield of compound **1** alone or in combination with selected analytes in HEPES buffered solution and quinine sulfate dehydrate (in 0.1 N $H_2SO_4$) as reference. Emission spectra were recorded at three different combinations of emission and excitation slit widths: 5 nm / 5 nm (black), 5 nm / 10 nm (red), 10 nm / 5 nm (green)

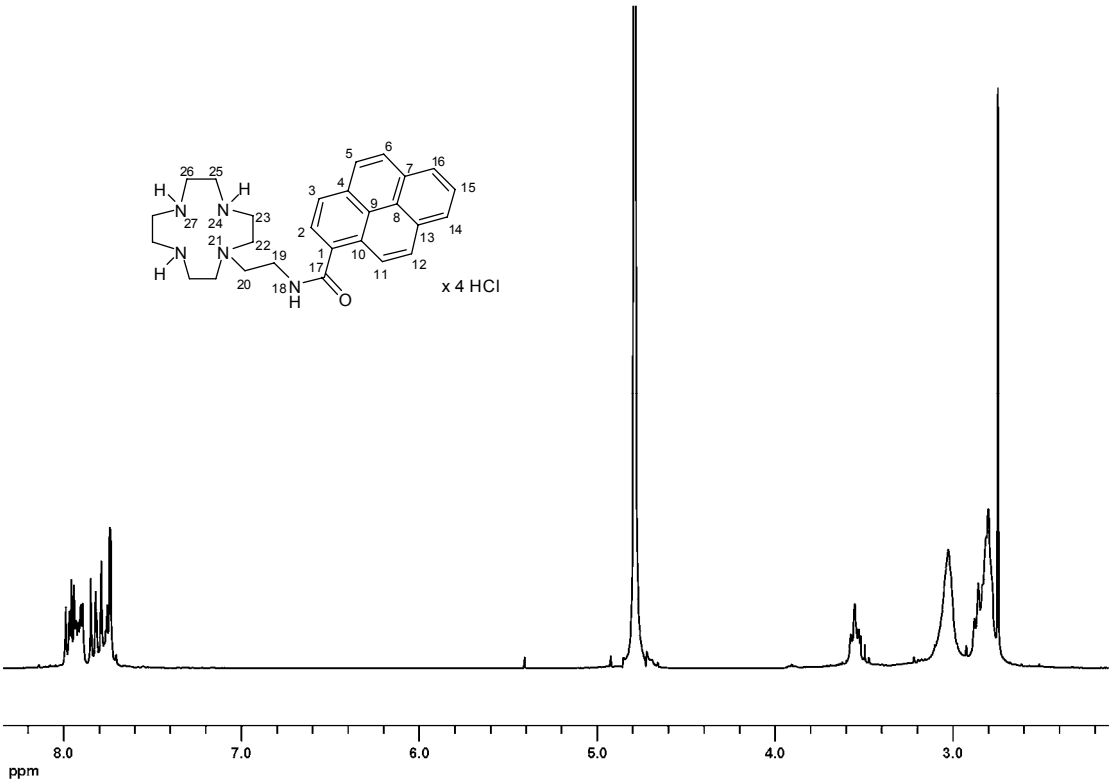
## 2. Proton and Carbon NMR Spectra of New Compounds



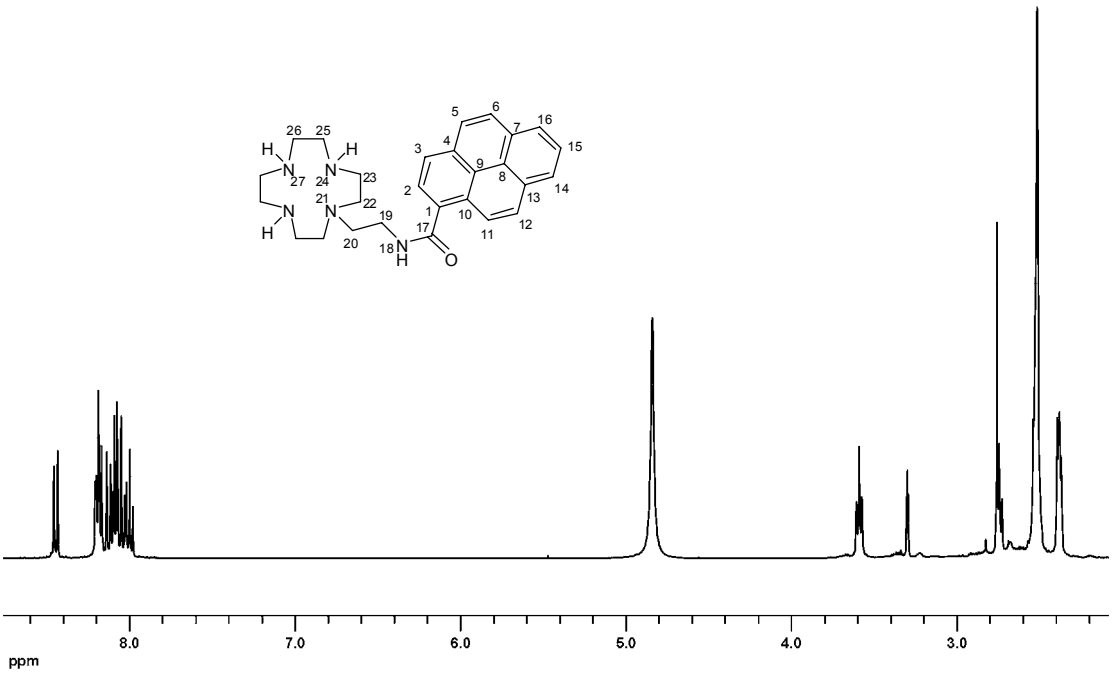

**$^{1}$H-NMR** (400 MHz, $CDCl_3$) of compound **6**



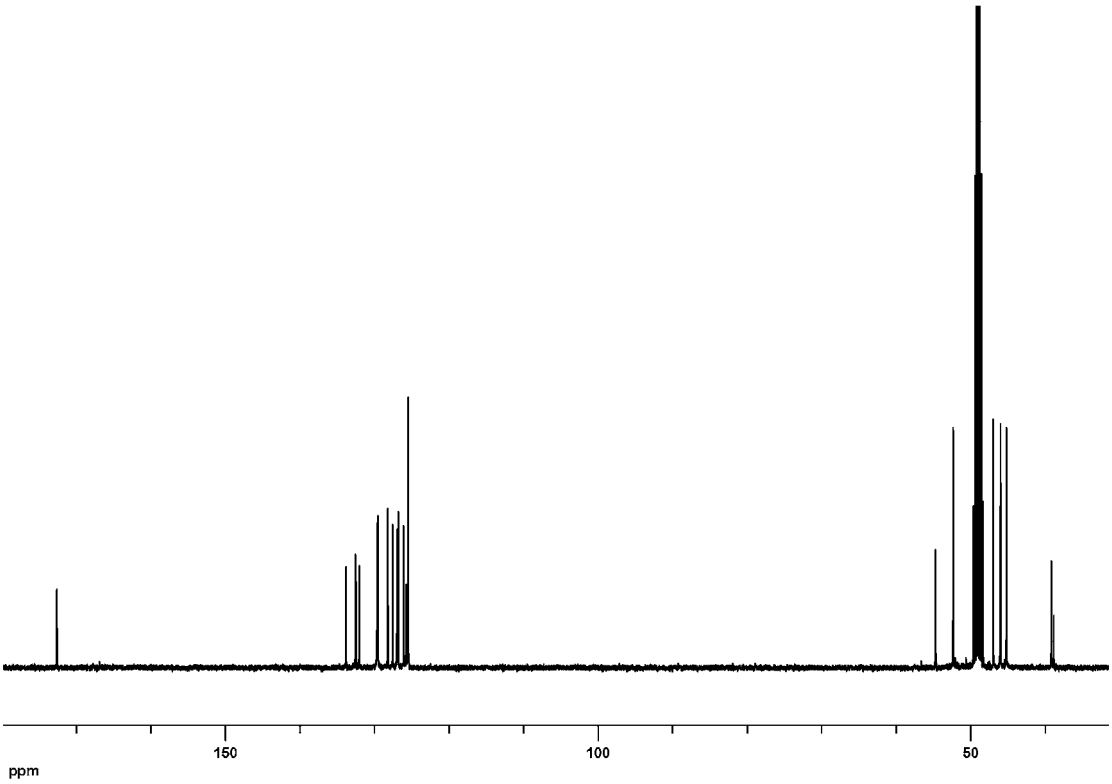

**$^{13}$C-NMR** (100 MHz, $CDCl_3$) of compound **6**



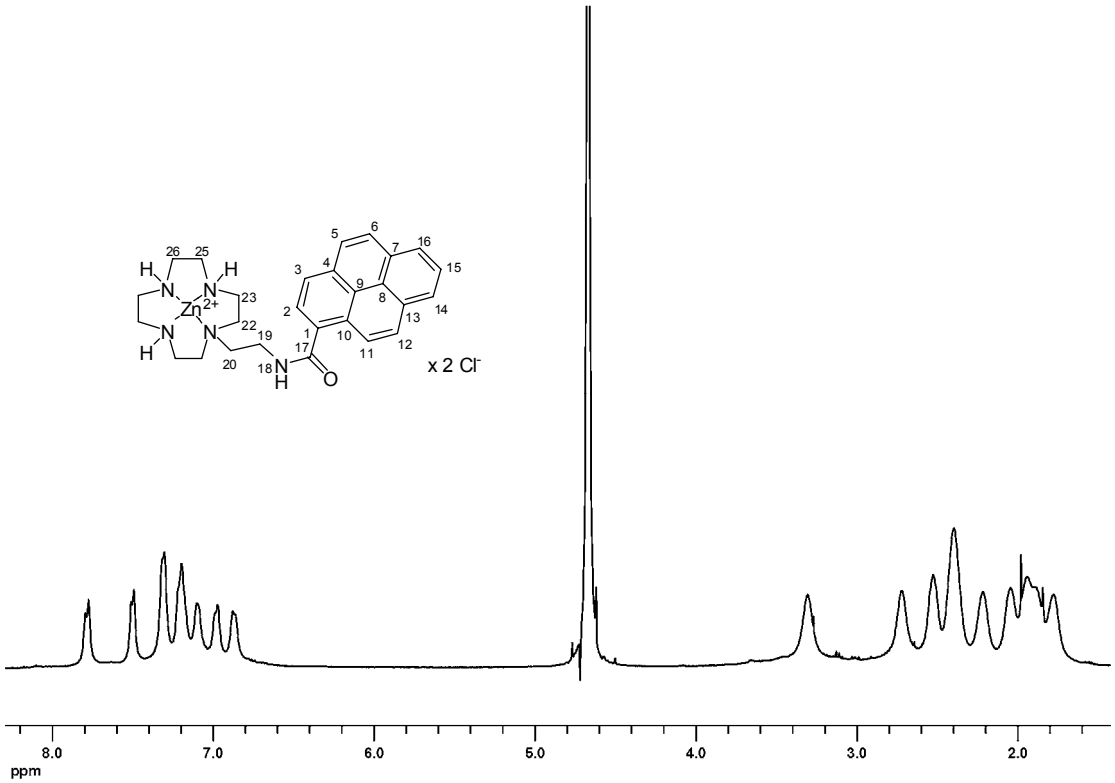

**$^1$H-NMR** (400 MHz, $D_2O$) of N-(2-(1,4,7,10-tetraazacyclododecan-1-yl)ethyl) pyrene-1-carboxamide tetrahydrochloride



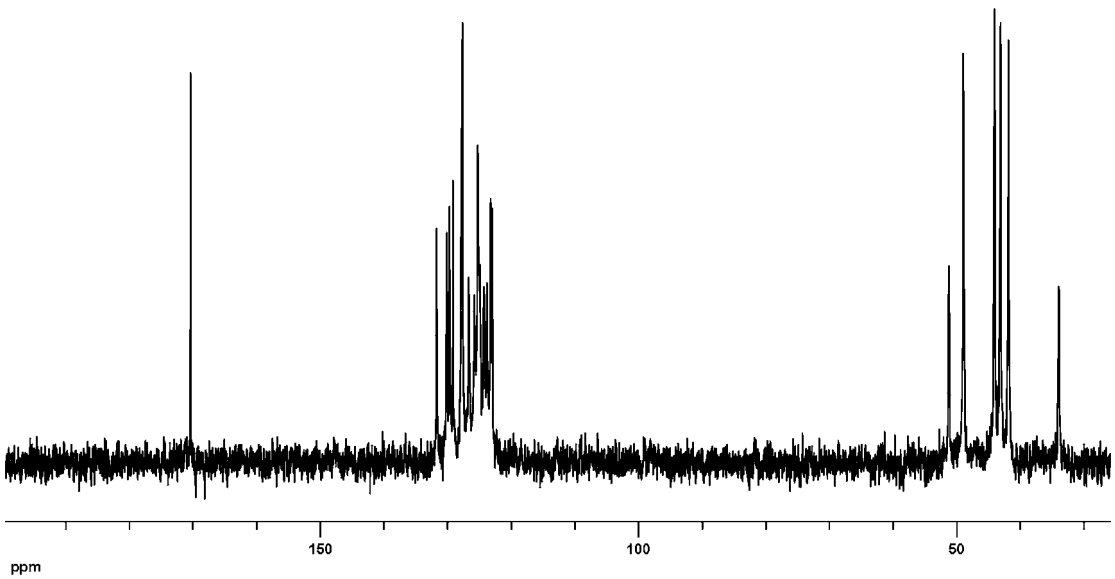

**$^{1}$H-NMR** (400 MHz, $CD_3OD$) of N-(2-(1,4,7,10-tetraazacyclo-dodecan-1-yl)ethyl) pyrene-1-carboxamide



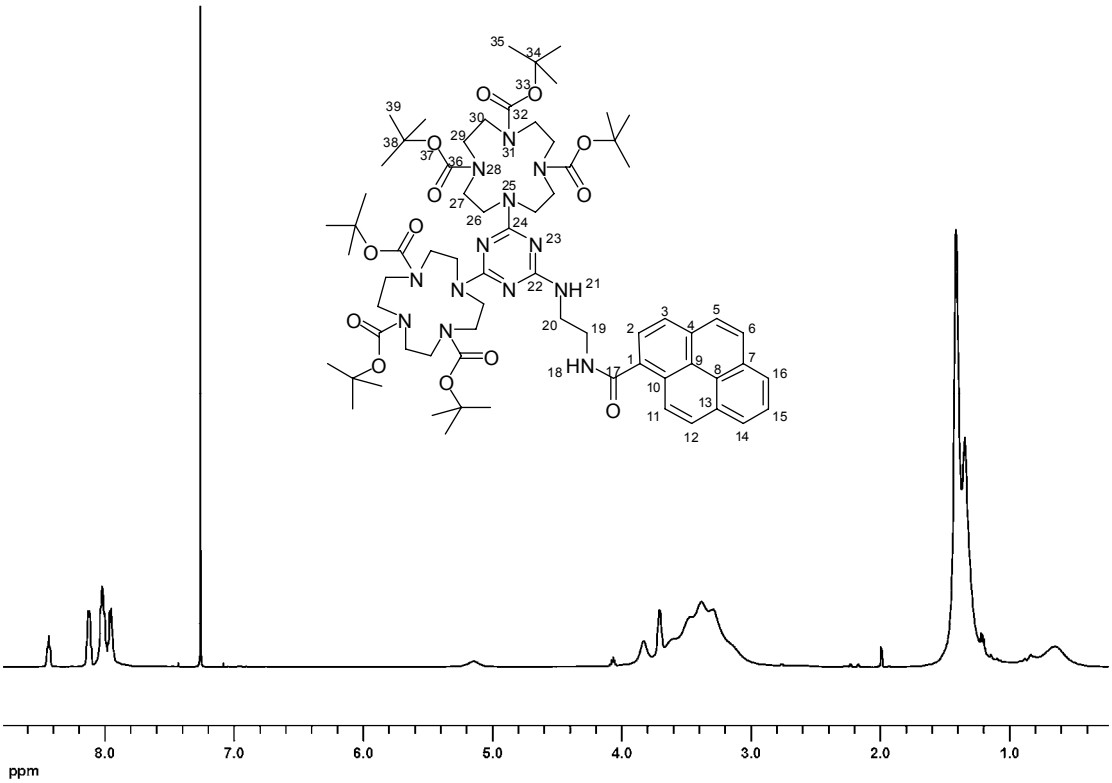

**$^{13}$C-NMR** (100 MHz, $CD_3OD$) of N-(2-(1,4,7,10-tetraazacyclo-dodecan-1-yl)ethyl) pyrene-1-carboxamide



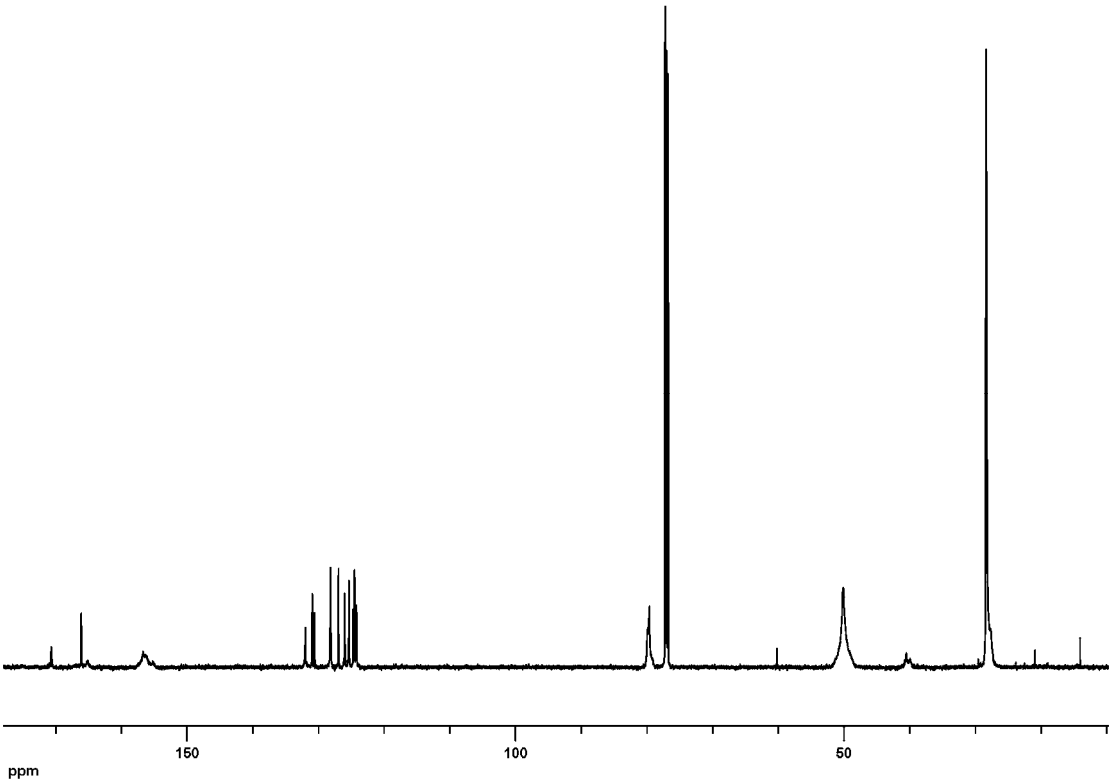

**$^{1}$H-NMR** (400 MHz, $D_2O$) of compound **1**



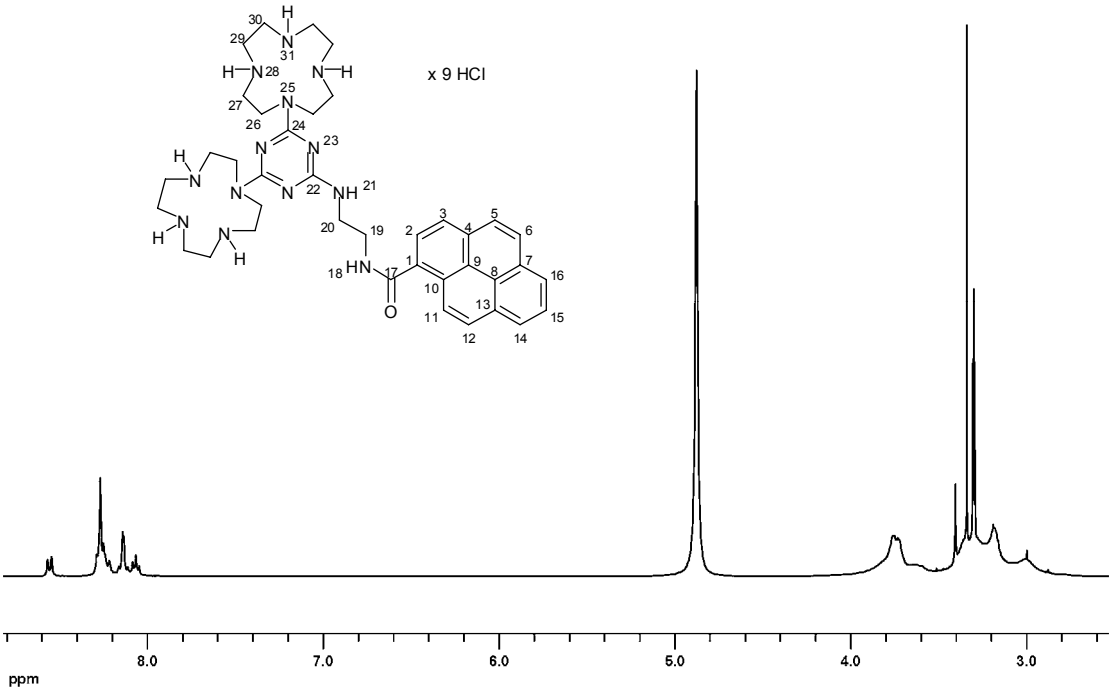

**$^{13}$C-NMR** (100 MHz, $D_2O$) of compound **1**



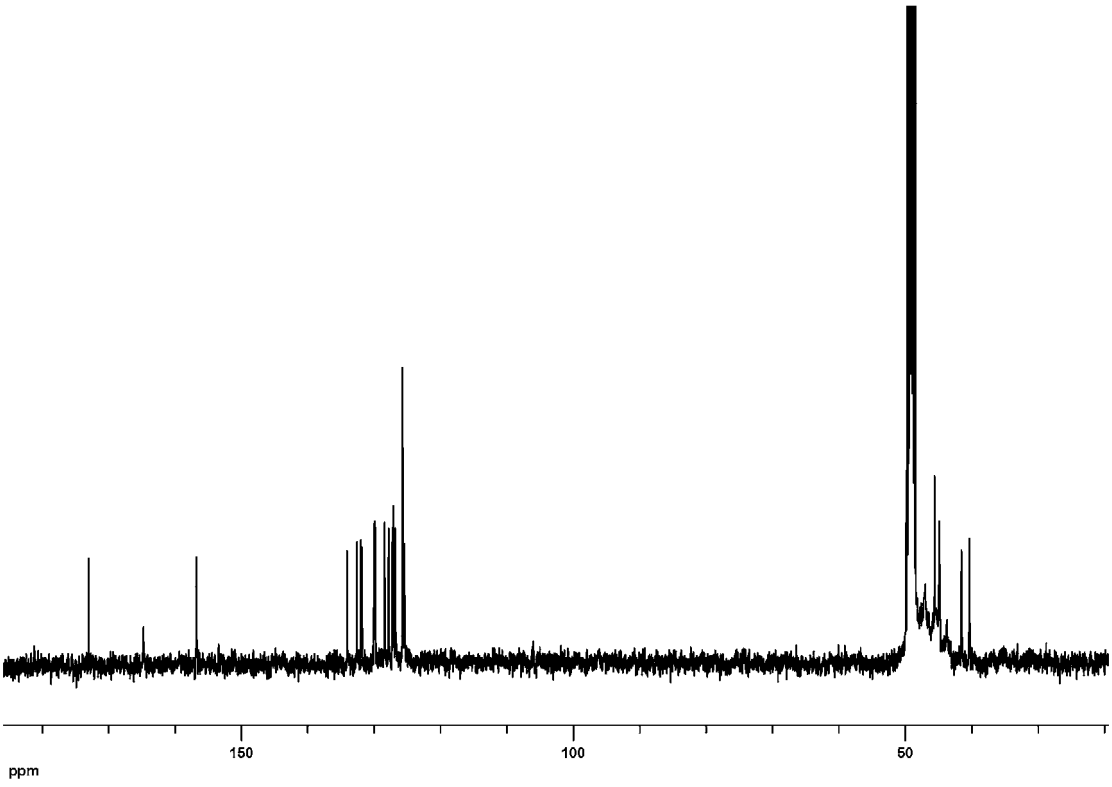

**$^{1}$H-NMR** (600 MHz, $CDCl_3$) of compound **7**



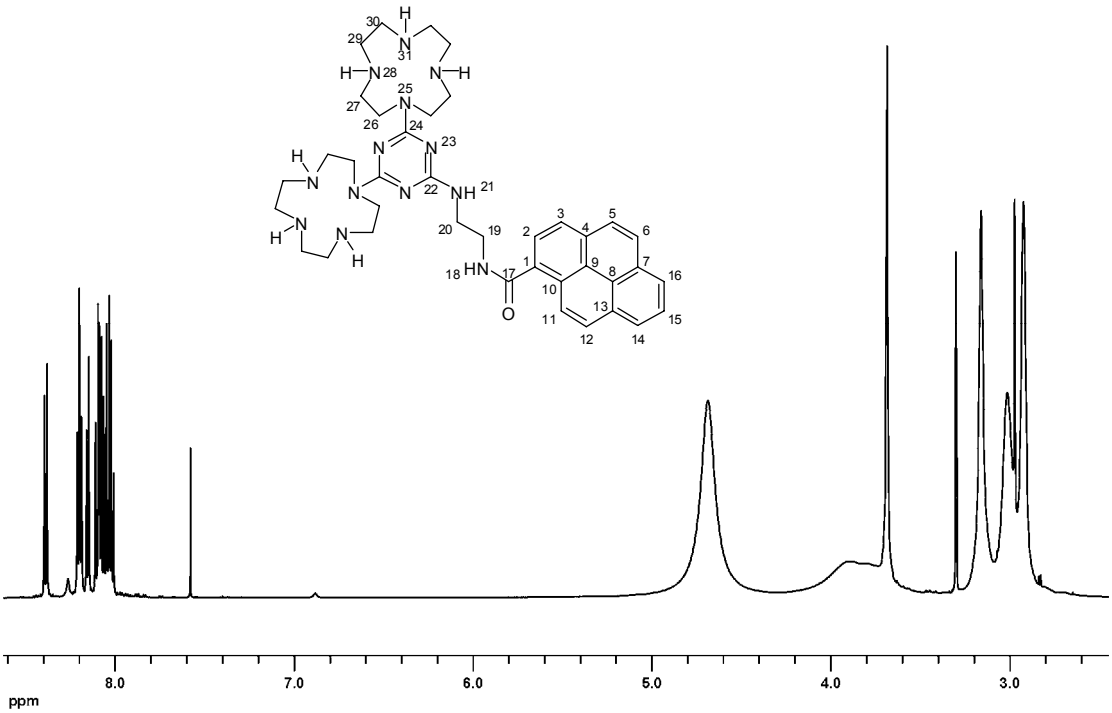

**$^{13}$C-NMR** (150 MHz, $CDCl_3$) of compound **7**



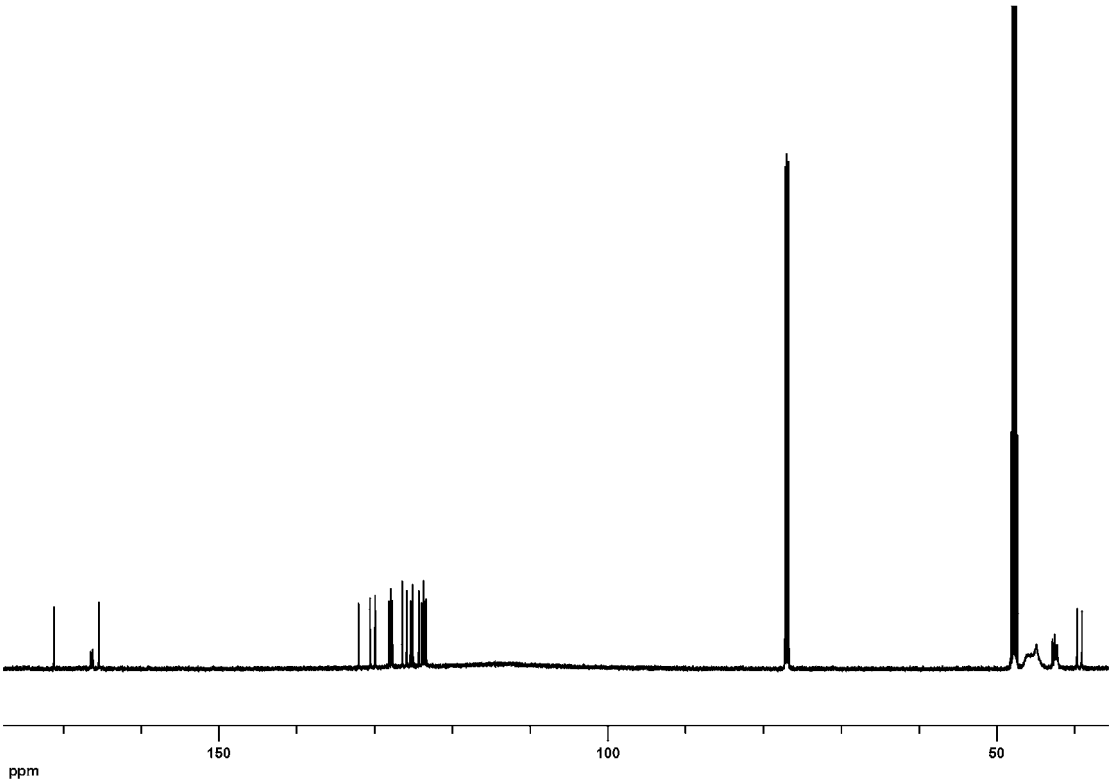

**$^{1}$H-NMR** (400 MHz, $CD_3OD$) of pyrene-1-carboxylic acid {2-[4,6-bis-(1,4,7,10-tetraaza-cyclododec-1-yl)-[1,3,5]triazin-2-ylamino]-ethyl}-amide nonahydrochloride



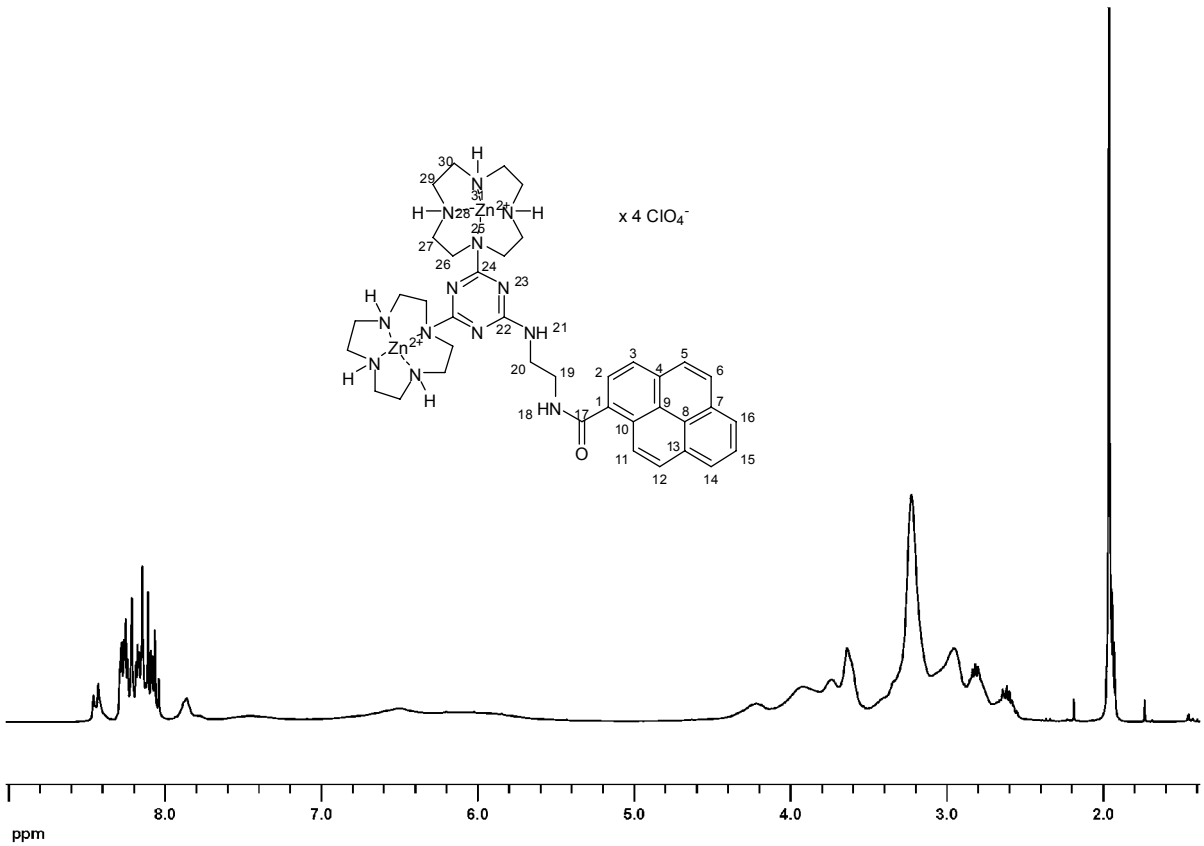

**$^{13}$C-NMR** (100 MHz, $CD_3OD$) of pyrene-1-carboxylic acid {2-[4,6-bis-(1,4,7,10-tetraaza-cyclododec-1-yl)-[1,3,5]triazin-2-ylamino]-ethyl}-amide nonahydrochloride




**$^{1}$H-NMR** (600 MHz, $CD_3CD$:$CDCl_3$ = 1:1) of pyrene-1-carboxylic acid {2-[4,6-bis-(1,4,7,10-tetraaza-cyclododec-1-yl)-[1,3,5]triazin-2-ylamino]-ethyl}-amide




**$^{13}$C-NMR** (150 MHz, $CD_3CD$:$CDCl_3$ = 1:1) of pyrene-1-carboxylic acid {2-[4,6-bis-(1,4,7,10-tetraaza-cyclododec-1-yl)-[1,3,5]triazin-2-ylamino]-ethyl}-amide




**$^{1}$H-NMR** (300 MHz, $CD_3CN$) of compound **2**