Supporting information

A Selective Calix[6]arene-based Fluorescent Chemosensor for Phosphatidylcholine Type Lipids

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I. Complexation studies between host **1** and DOPC

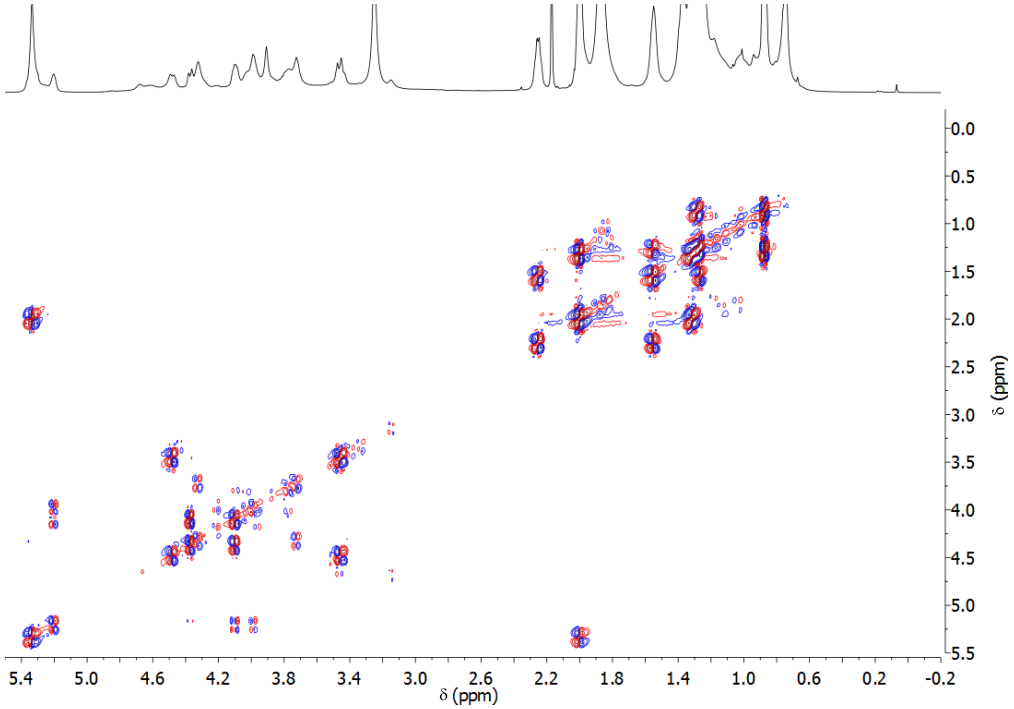


Figure S1. COSY spectrum (600 MHz, 298 K, $CDCl_3$) of compound **1** in the presence of *ca.* 3 equiv. of DOPC.

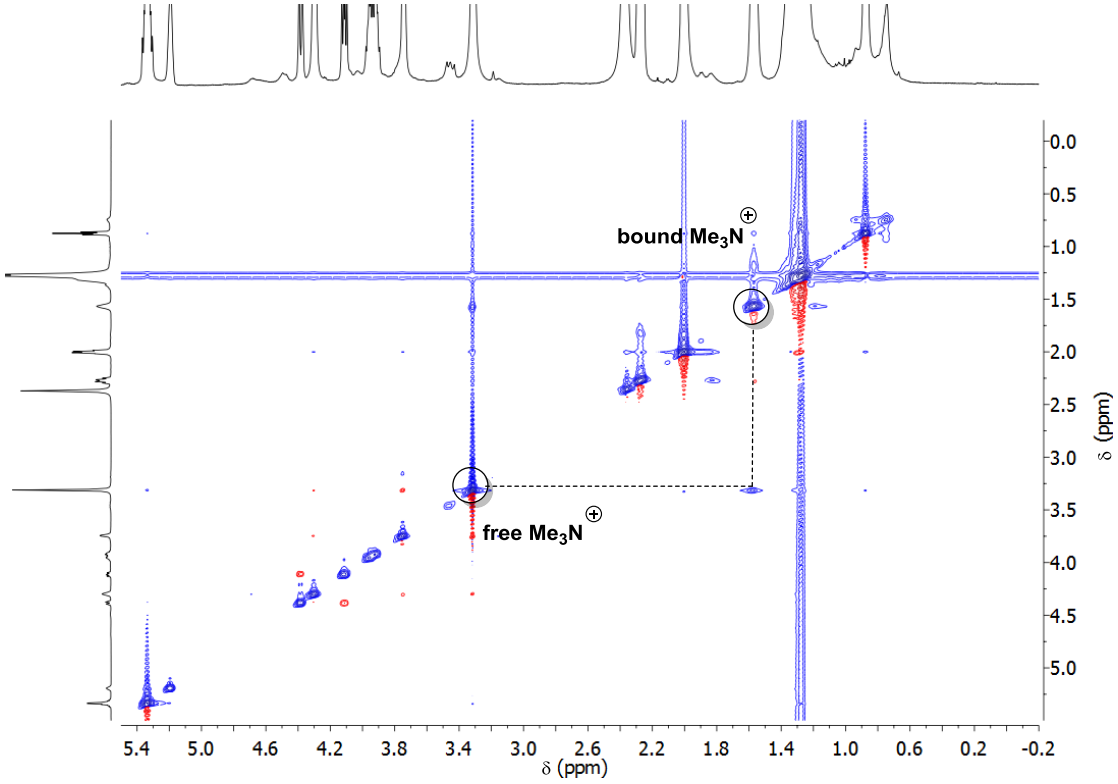


Figure S2. 2D ROESY spectrum (600 MHz, 298 K, $CDCl_3$, mixing time = 300 ms) of compound **1** in the presence of *ca.* 3 equiv. of DOPC.

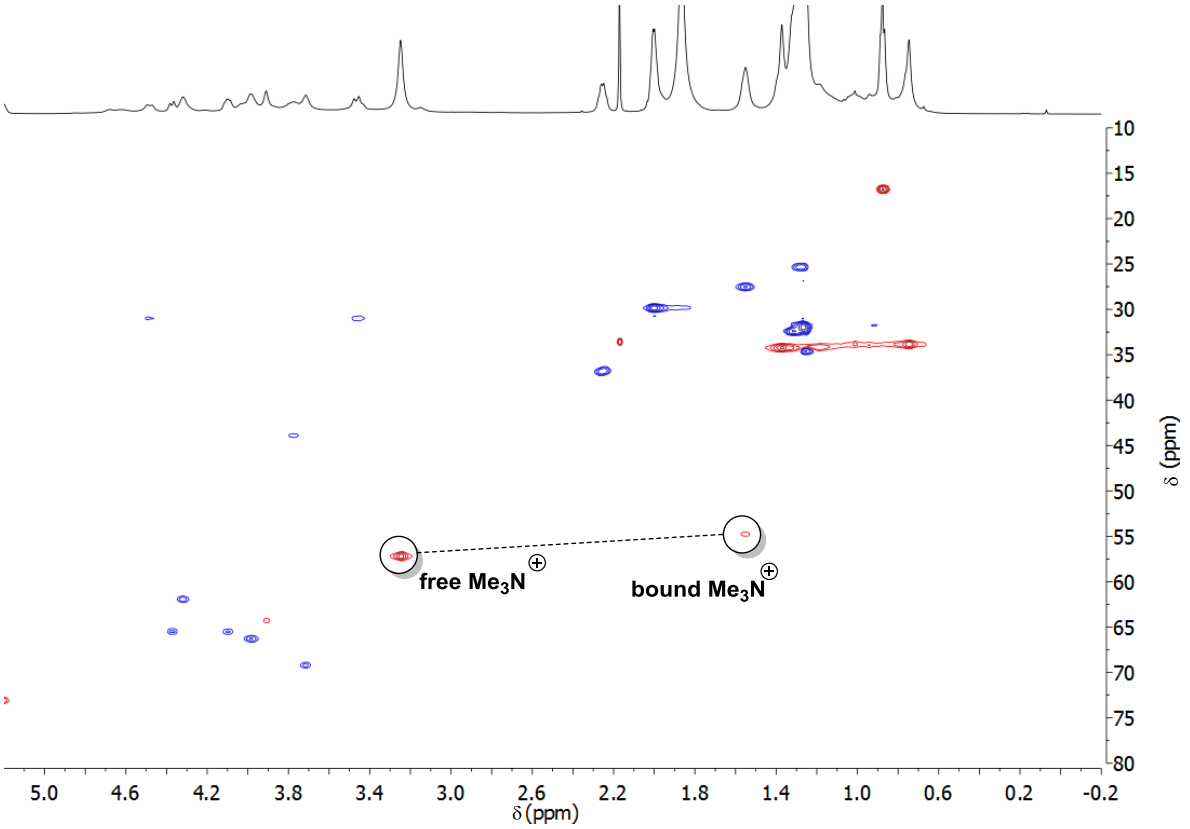


Figure S3. HSQC spectrum (600 MHz, 298 K, $CDCl_3$) of compound **1** in the presence of *ca.* 3 equiv. of DOPC.

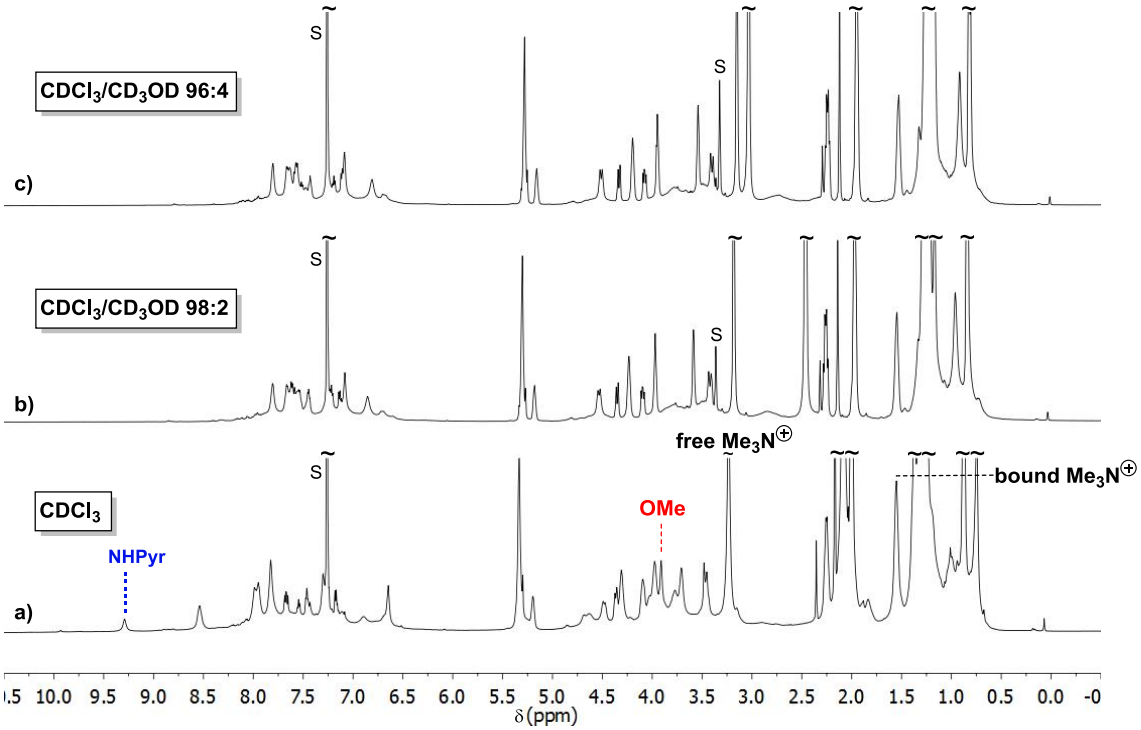


Figure S4. ^1H NMR spectra (600MHz, 298 K) of **1** in presence of *ca.* 3 equiv. of DOPC in: a) $CDCl_3$; b) in a mixture $CDCl_3/CD_3OD$ *ca.* 98:2; c) in a mixture $CDCl_3/CD_3OD$ *ca.* 96:4; s: solvent.

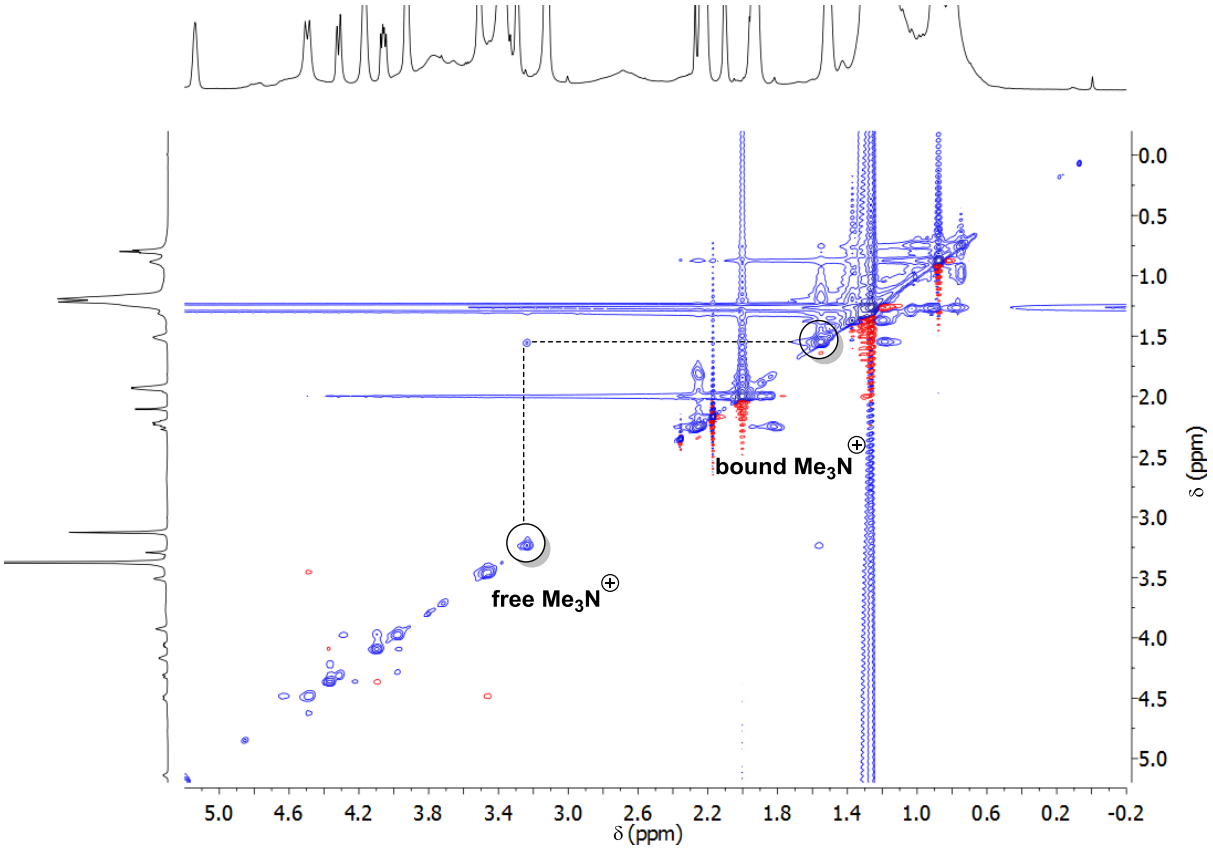


Figure S5. 2D ROESY spectrum (600 MHz, 298 K, $CDCl_3/CD_3OD$ *ca.* 96:4, mixing time = 300 ms) of compound **1** in the presence of *ca.* 3 equiv. of DOPC.

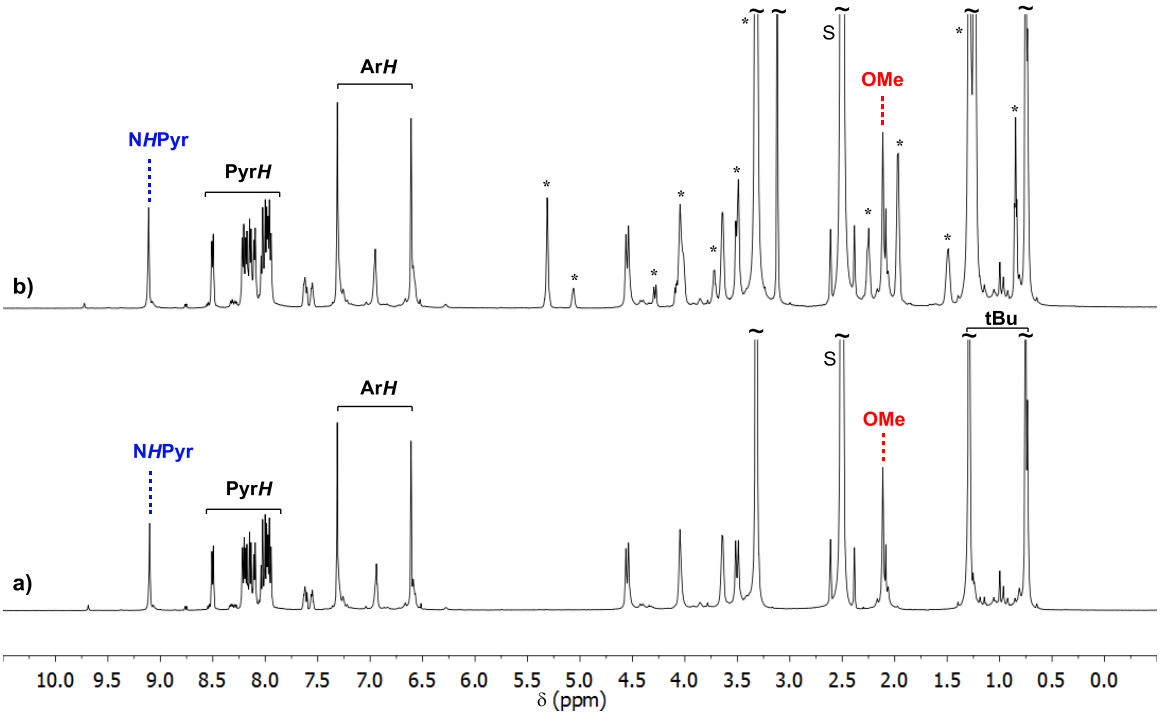


Figure S6. ^{1}H NMR spectra (600MHz, 298 K, DMSO-d_6) of: a) **1**; b) **1** in presence of *ca.* 1 equiv. of DOPC; s: solvent; *: DOPC signals.

II. Complexation studies between host **1** and POPC

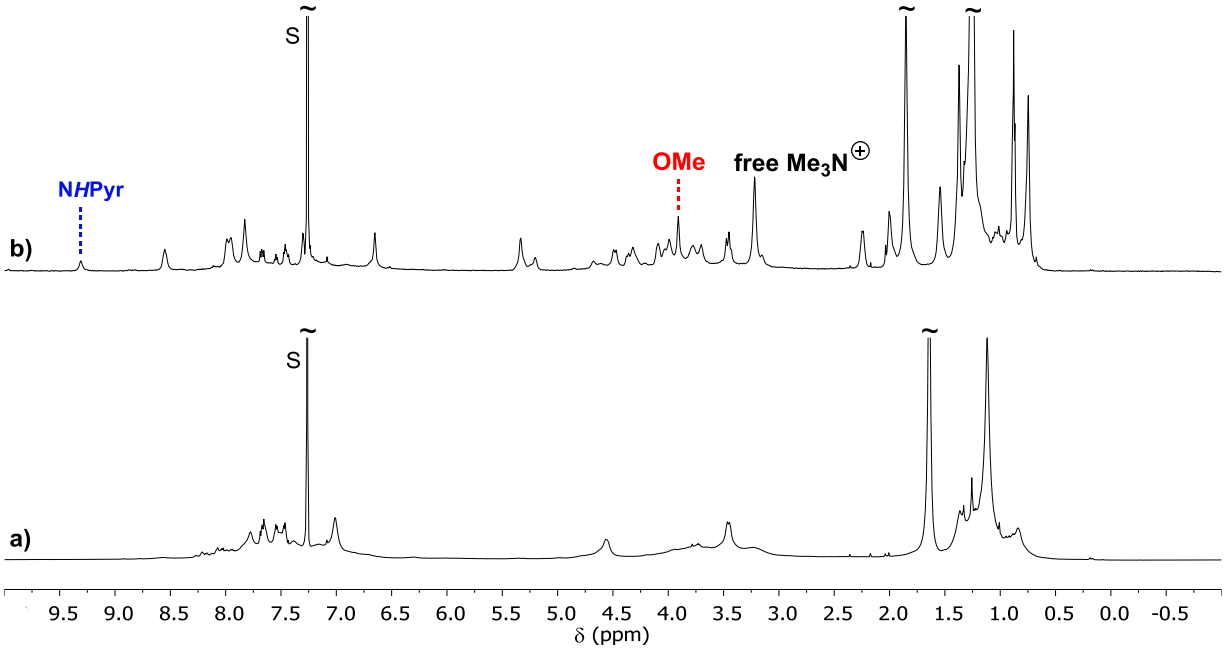


Figure S7. ^{1}H NMR spectra (600MHz, 298 K, $CDCl_3$) of: a) **1**; b) **1** in the presence of *ca.* 2.5 equiv. of POPC; s: solvent.

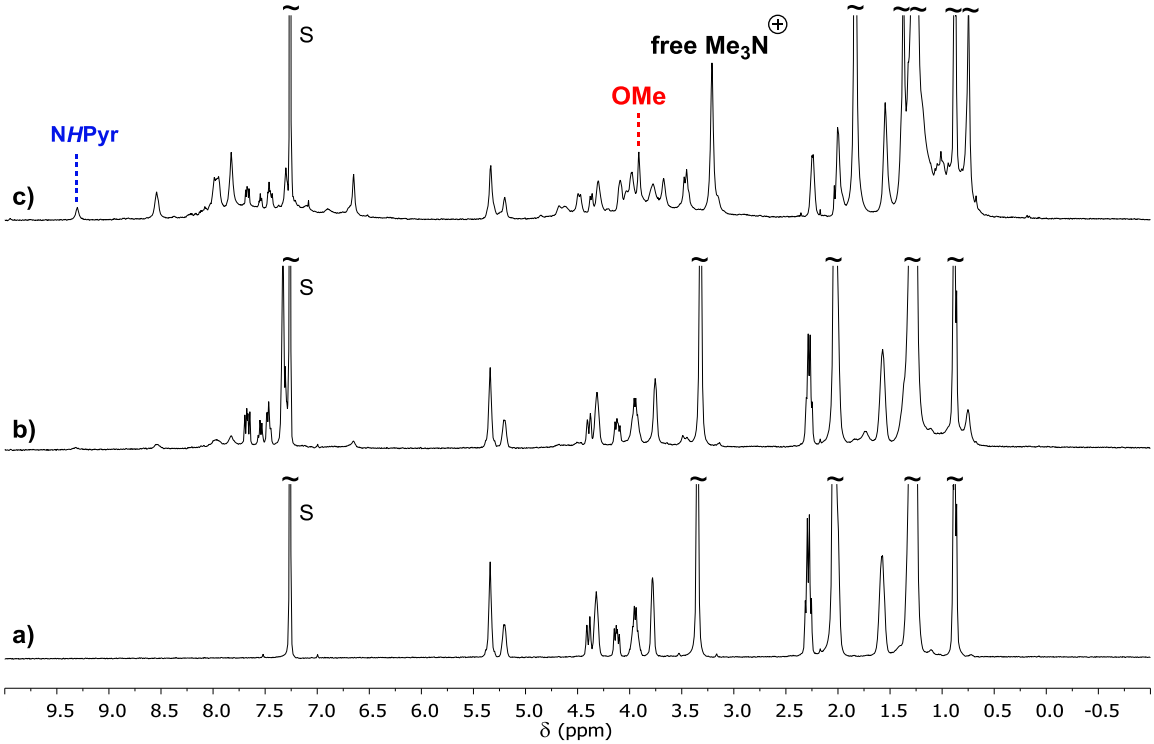
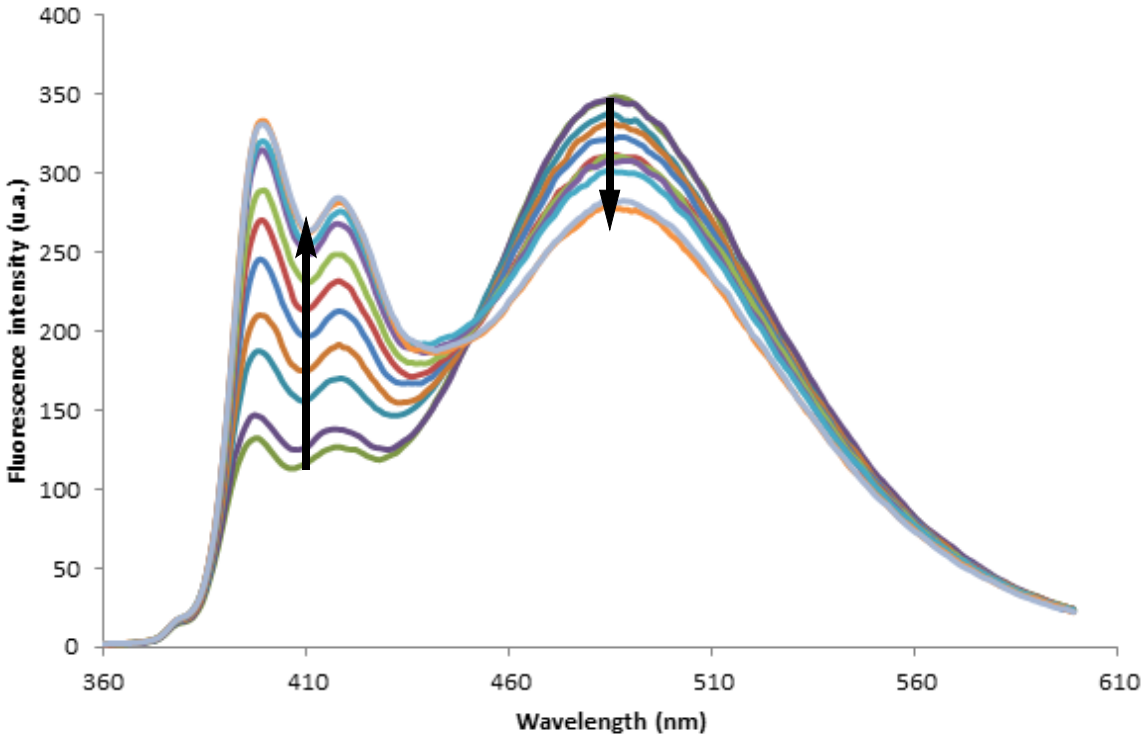


Figure S8. ^{1}H NMR spectra (600MHz, 298 K, $CDCl_3$) of: a) POPC; b) POPC in the presence of *ca.* 0.13 equiv. of **1**; c) POPC in the presence of *ca.* 0.62 equiv. of **1**; s: solvent.



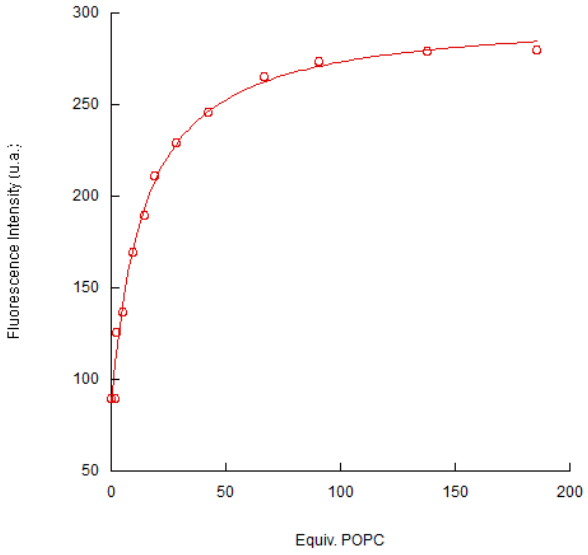


Figure S9. Top: fluorescence spectra of **1** upon the addition of POPC (0 to 185 equiv.) in chloroform. $[\mathbf{1}]_0 = 1.9 \times 10^{-6}$ M. $\lambda_{ex} = 345$ nm. Bottom: variation of fluorescence intensity at 420 nm upon the addition of POPC.

III. Complexation studies between host **1** and DPPC

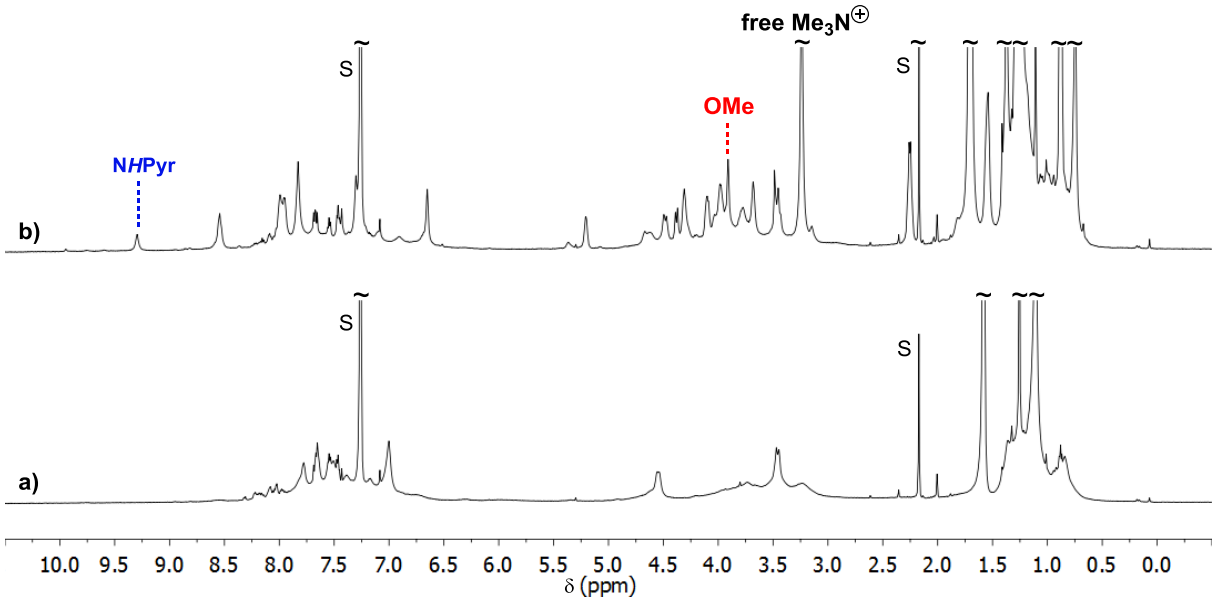


Figure S10. ^{1}H NMR spectra (600MHz, 298 K, $CDCl_3$) of: a) **1**; b) **1** in the presence of *ca.* 3 equiv. of DPPC; s: solvent.

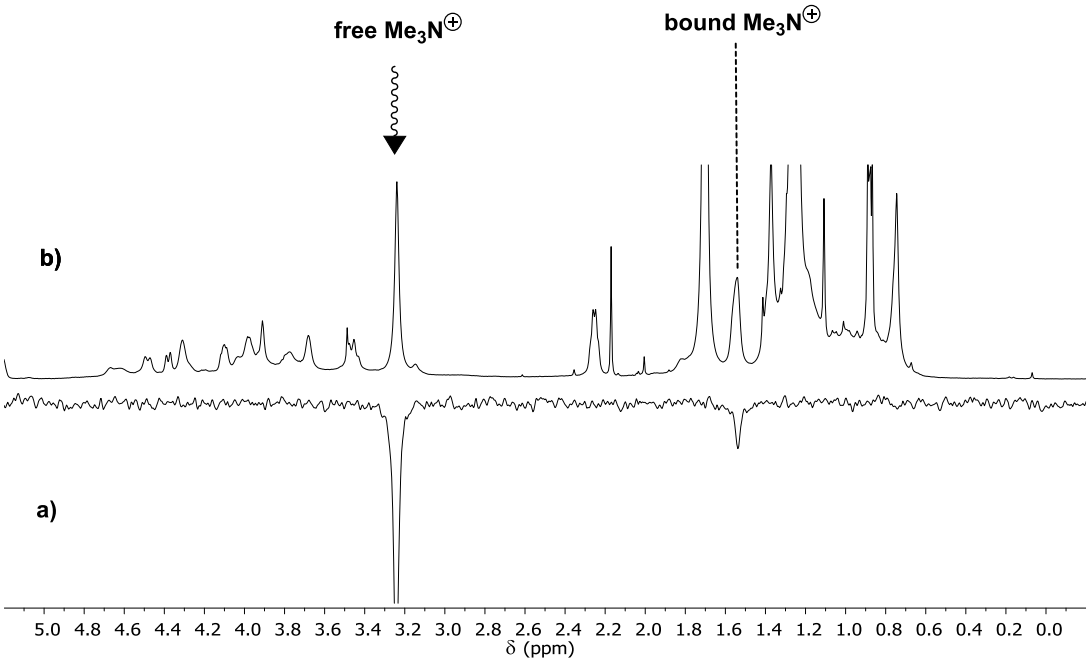


Figure S11. NMR spectra (600MHz, 298 K, $CDCl_3$) of host **1** in in the presence of *ca.* 3 equiv. of DPPC: a) 1D EXSY spectrum (mixing time = 25 ms) after selective excitation of the $^{+}NMe_3$ signal at 3.24 ppm; b) ^{1}H NMR spectrum; ▼: Pulse excitation.

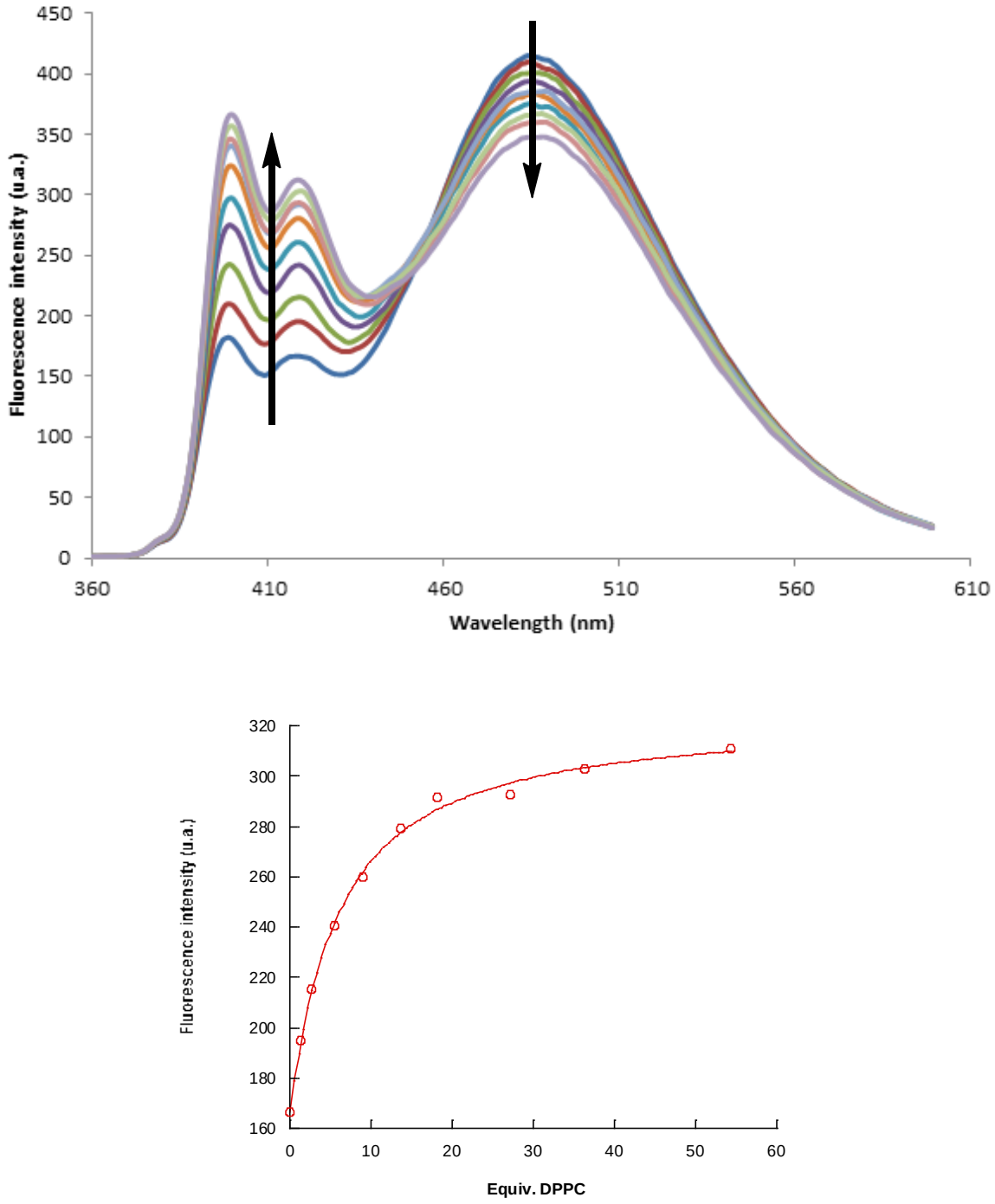


Figure S12. Top: fluorescence spectra of **1** upon the addition of DPPC (0 to 54 equiv.) in chloroform. $[\mathbf{1}]_0 = 2.6 \times 10^{-6}$ M. $\lambda_{ex} = 345$ nm. Bottom: variation of fluorescence intensity at 420 nm upon the addition of DPPC.

IV. Complexation studies between host **1** and SPH

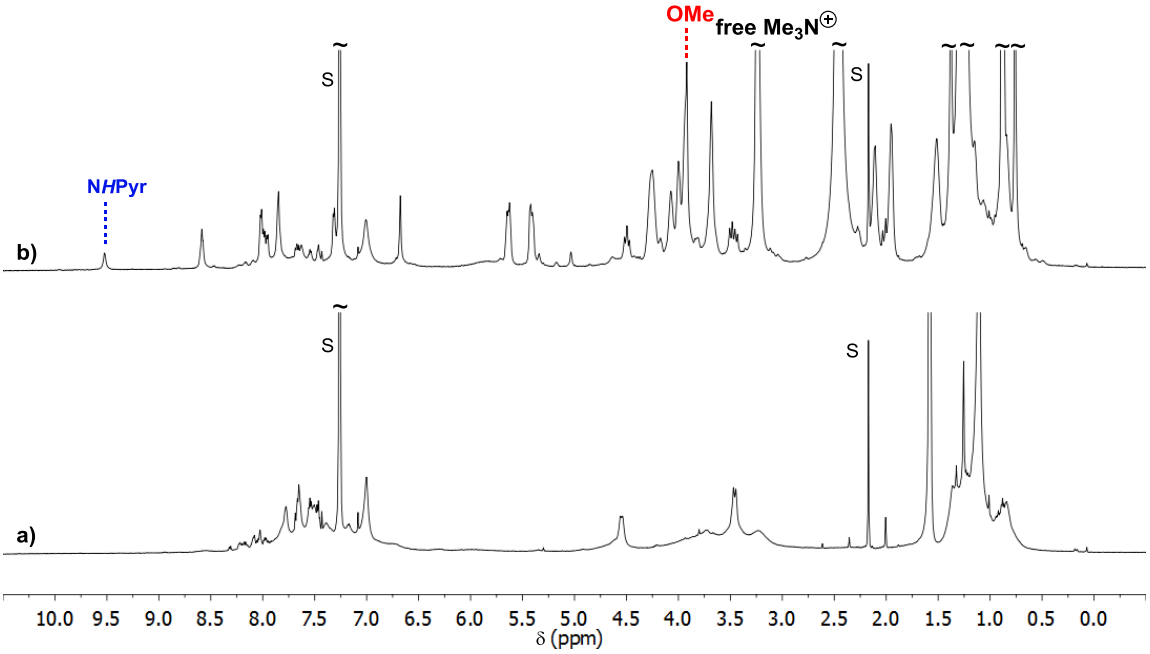


Figure S13. a) ^{1}H NMR spectra (600MHz, 298 K, $CDCl_3$) of: a) **1**; b) **1** in the presence of *ca.* 11 equiv. of SPH; s: solvent.

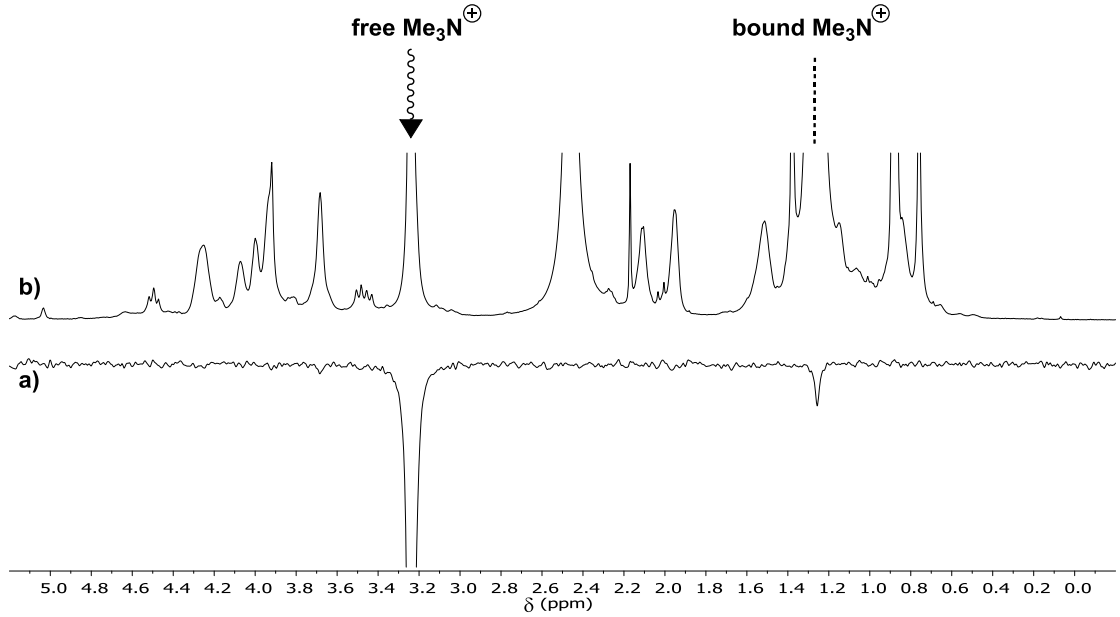


Figure S14. NMR spectra (600MHz, 298 K, $CDCl_3$) of host **1** in the presence of *ca.* 11 equiv. of SPH: a) 1D EXSY spectrum (mixing time = 25 ms) after selective excitation of the $^{+}NMe_3$ signal at 3.32 ppm; b) ^{1}H NMR spectrum; ▼: Pulse excitation.

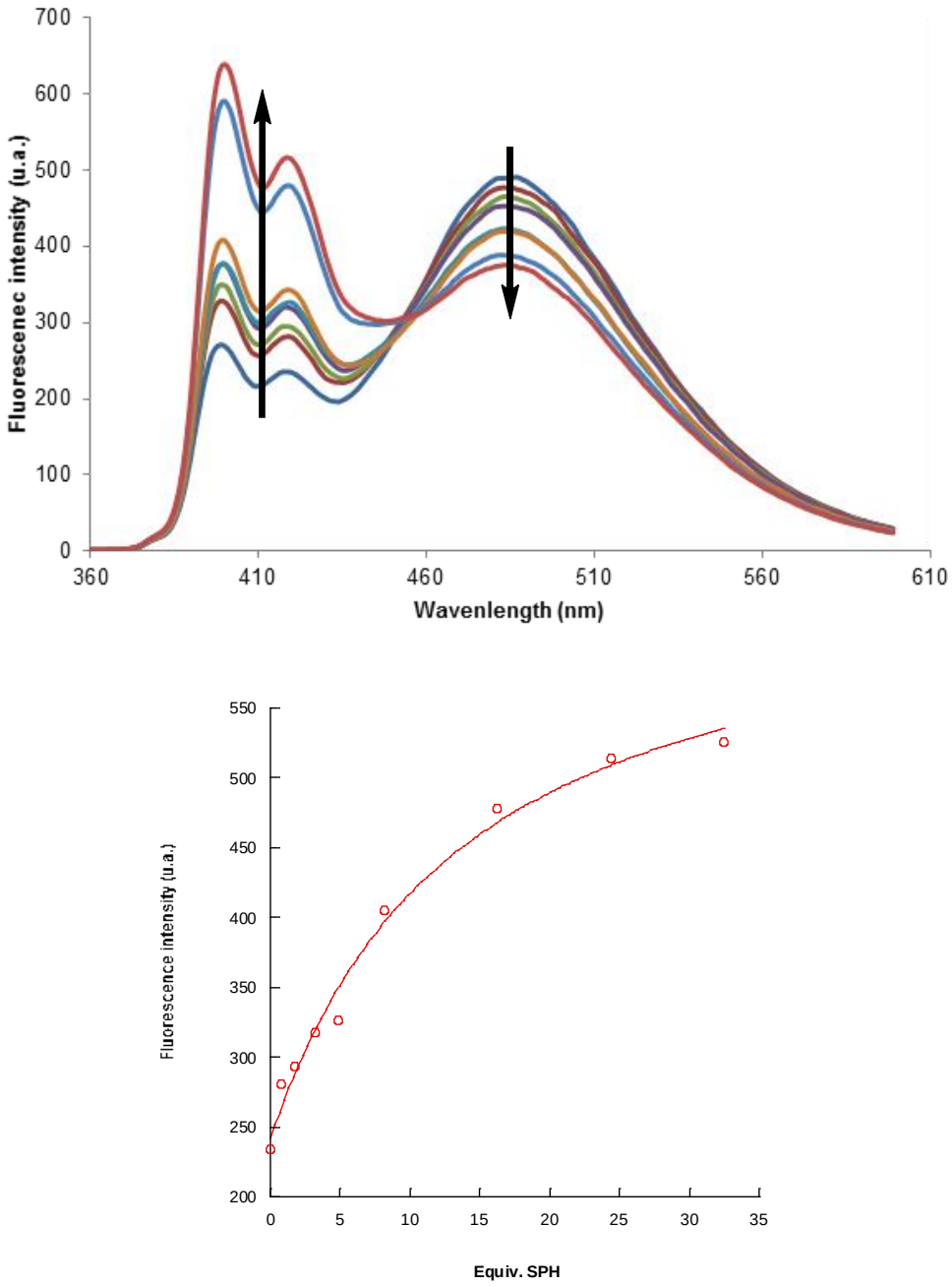


Figure S15. Top: fluorescence spectra of **1** upon the addition of SPH (0 to 32 equiv.) in chloroform. $[\mathbf{1}]_0 = 2.6 \times 10^{-6}$ M. $\lambda_{ex} = 345$ nm. Bottom: variation of fluorescence intensity at 420 nm upon the addition of SPH.

V. Complexation studies between host **1** and DPC

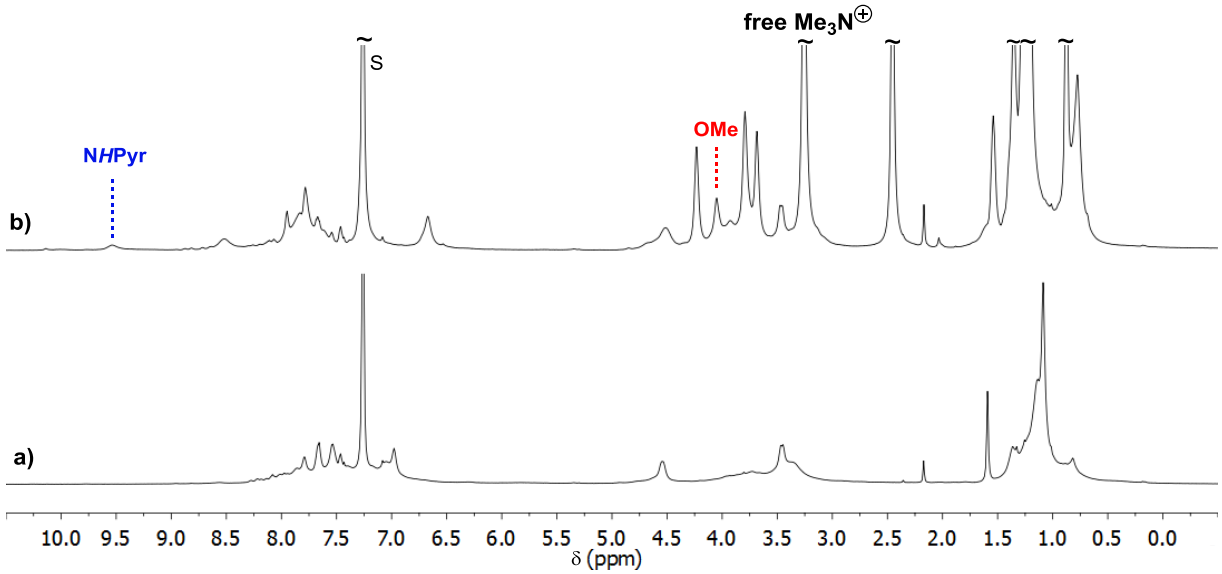


Figure S16. ^{1}H NMR spectra (600MHz, 298 K, $CDCl_3$) of: a) **1**; b) **1** in the presence of *ca.* 6 equiv. of DPC; s: solvent.

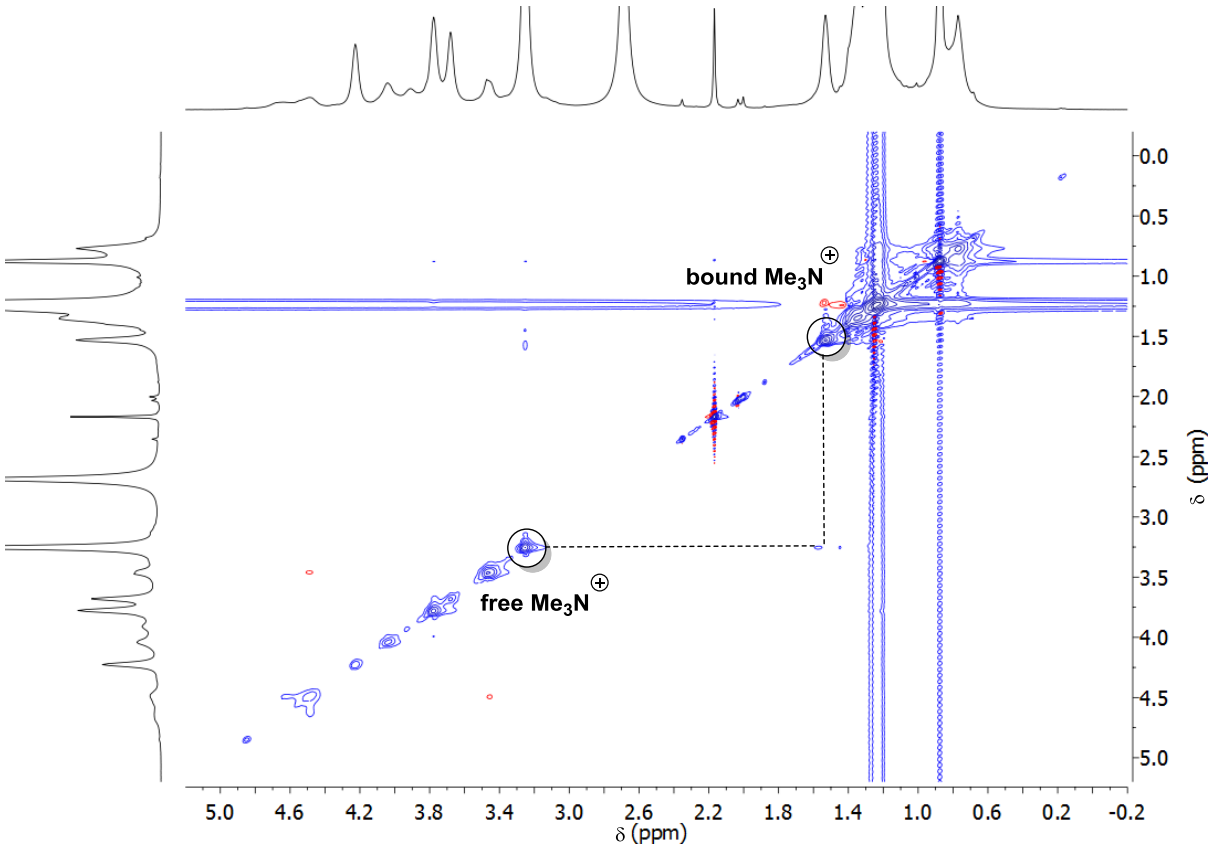


Figure S17. 2D ROESY spectrum (600 MHz, 298 K, $CDCl_3$, mixing time = 300 ms) of host **1** in the presence of *ca.* 6 equiv. of DPC.

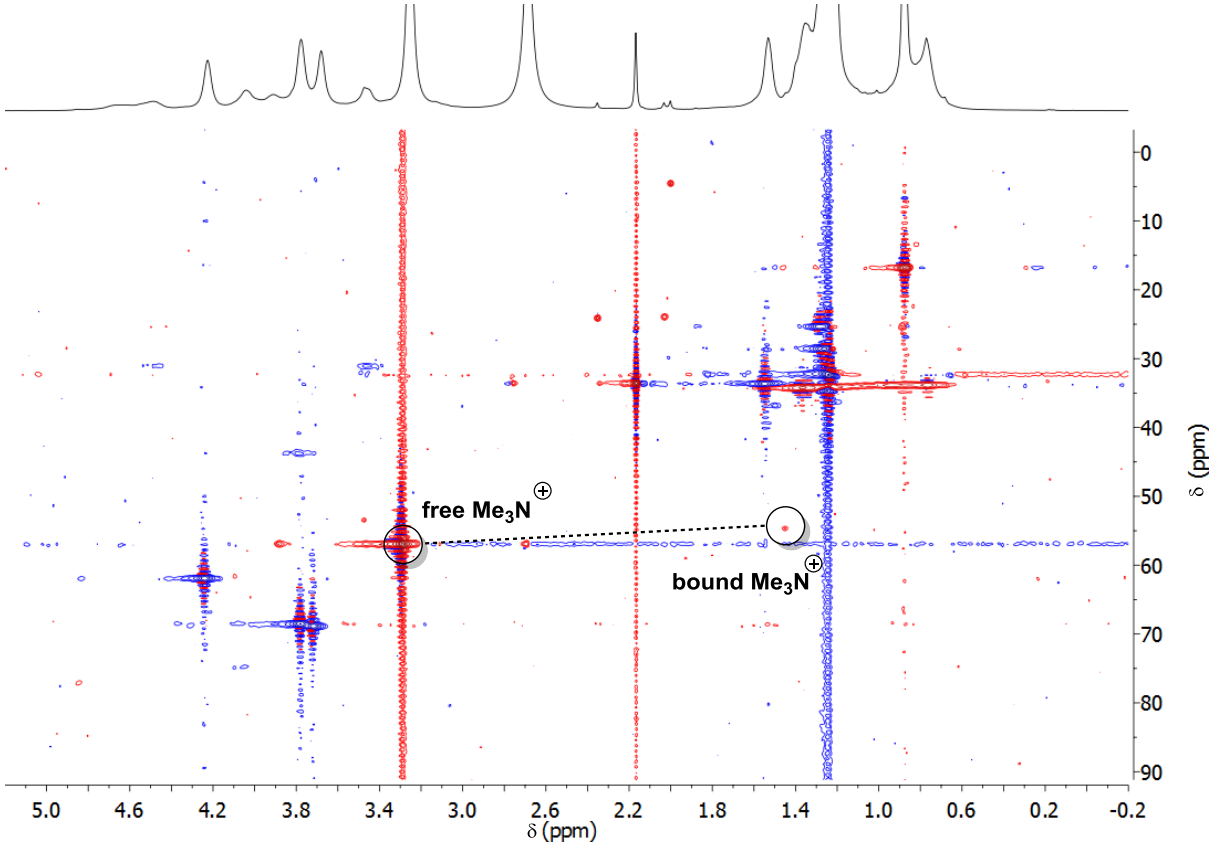


Figure S18. HSQC spectrum (600 MHz, 298 K, $CDCl_3$) of compound **1** in the presence of *ca.* 6 equiv. of DPC.

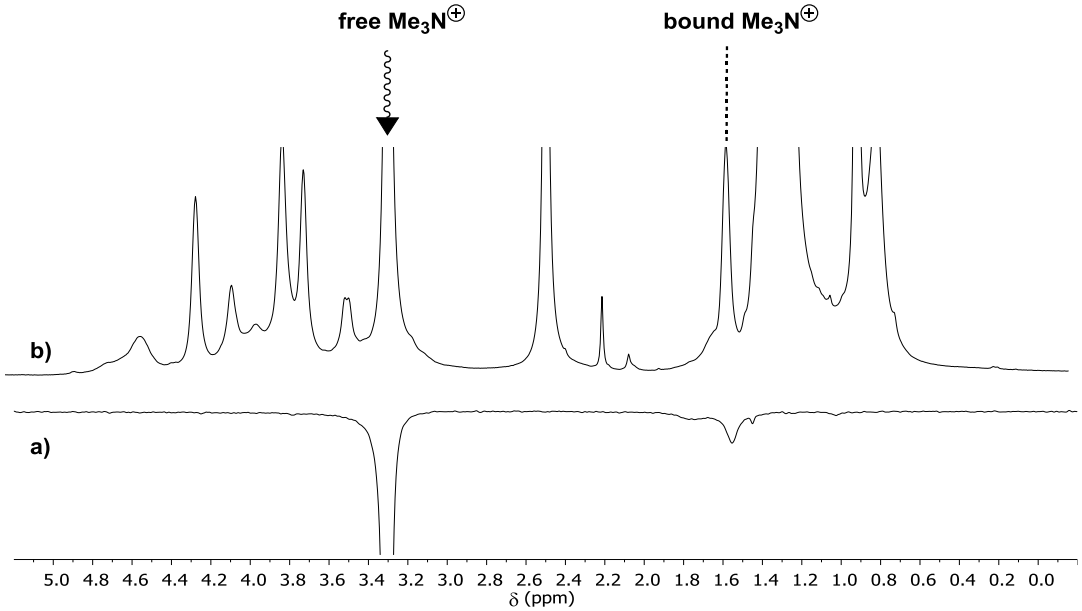


Figure S19 NMR spectra (600MHz, 298 K, $CDCl_3$) of host **1** in the presence of *ca.* 6 equiv. of DPC: a) 1D EXSY spectrum (mixing time = 25 ms) after selective excitation of the $^{+}NMe_3$ signal at 3.26 ppm; b) ^{1}H NMR spectrum; ▼: Pulse excitation.

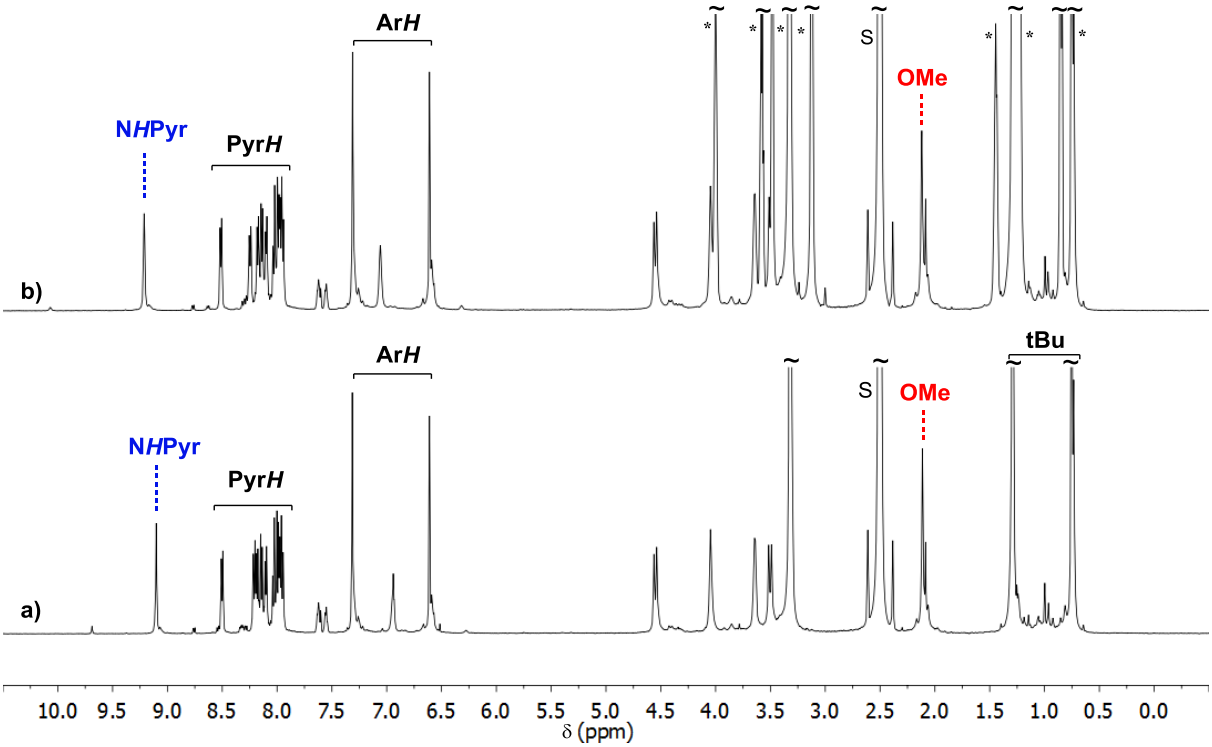


Figure S20. ^{1}H NMR spectra (600MHz, 298 K, DMSO-d_6) of: a) **1**; b) **1** in presence of *ca.*7 equiv. of DPC; s: solvent; *: DPC signals.

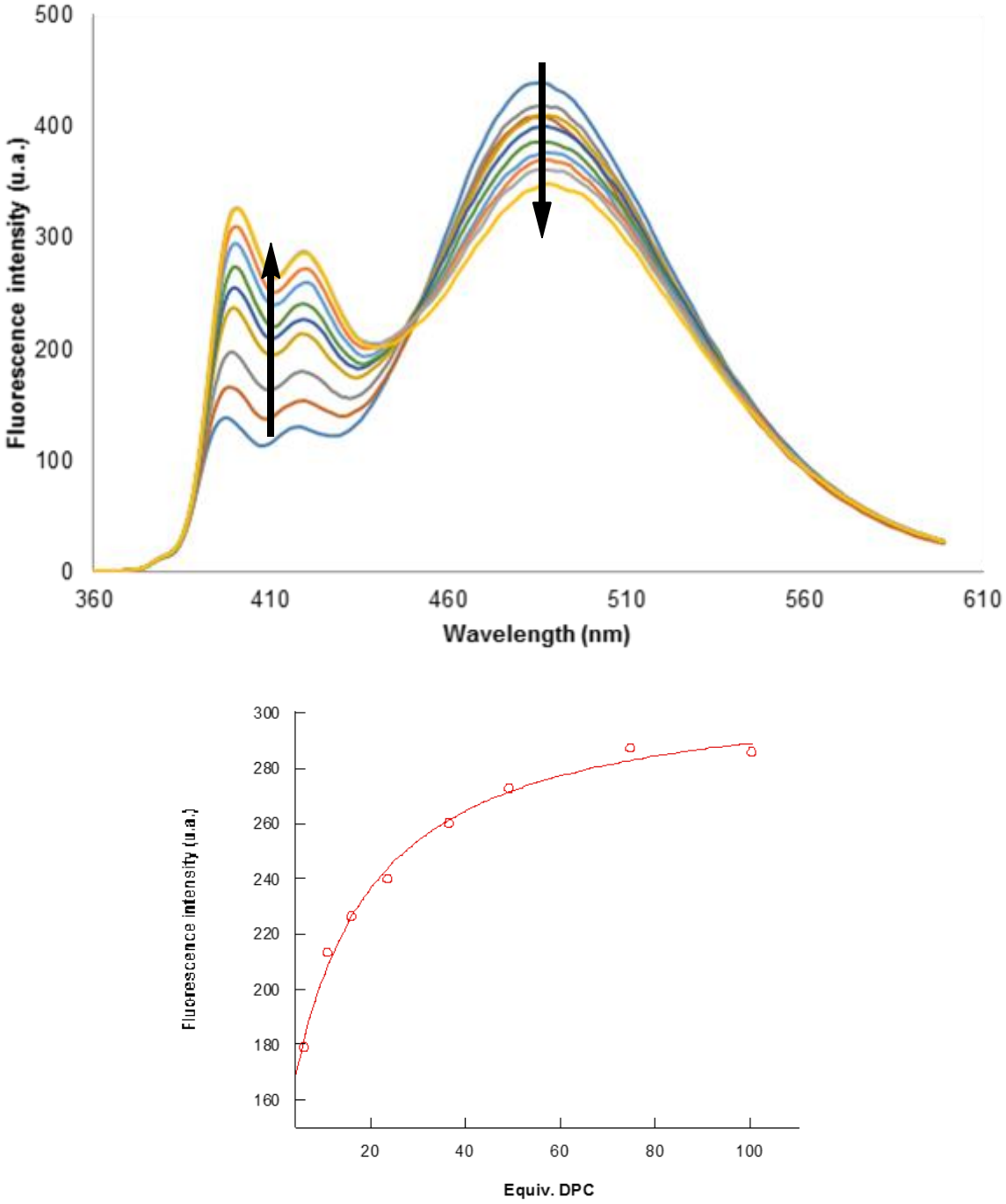


Figure S21. Top: fluorescence spectra of **1** upon the addition of DPC (0 to 100 equiv.) in chloroform. $[\mathbf{1}]_0 = 2.2 \times 10^{-6}$ M. $\lambda_{ex} = 345$ nm. Bottom: variation of fluorescence intensity at 420 nm upon the addition of DPC.

VI. Complexation studies between host **1** and MPC

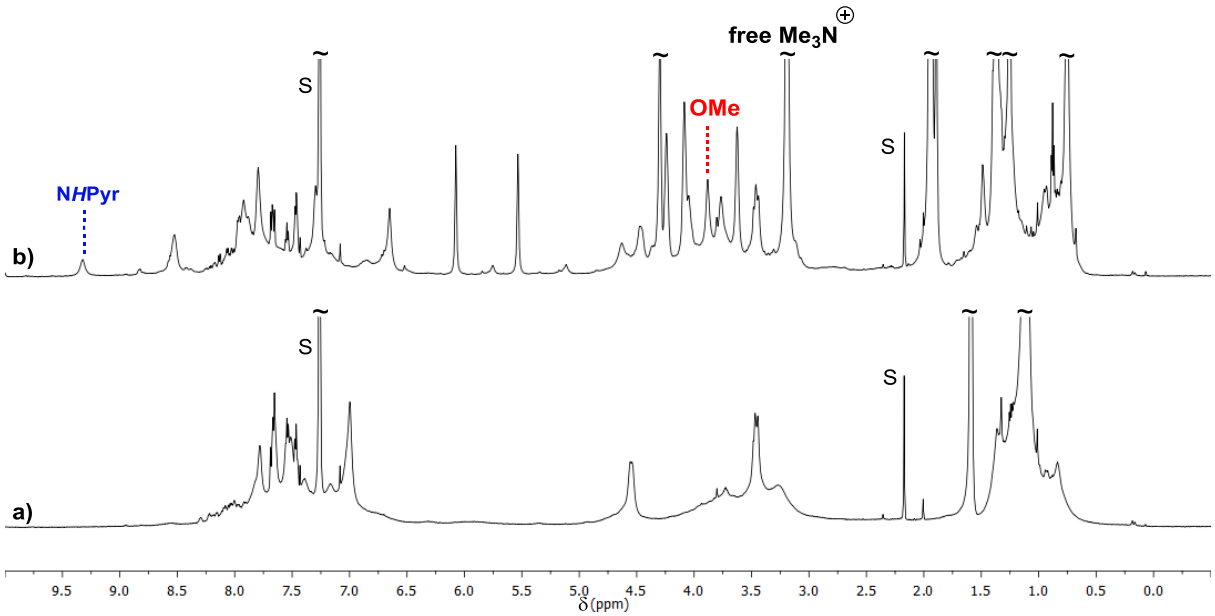


Figure S22. ^{1}H NMR spectra (600MHz, 298 K, $CDCl_3$) of: a) **1**; b) **1** in the presence of *ca.* 4.5 equiv. of MPC; s: solvent.

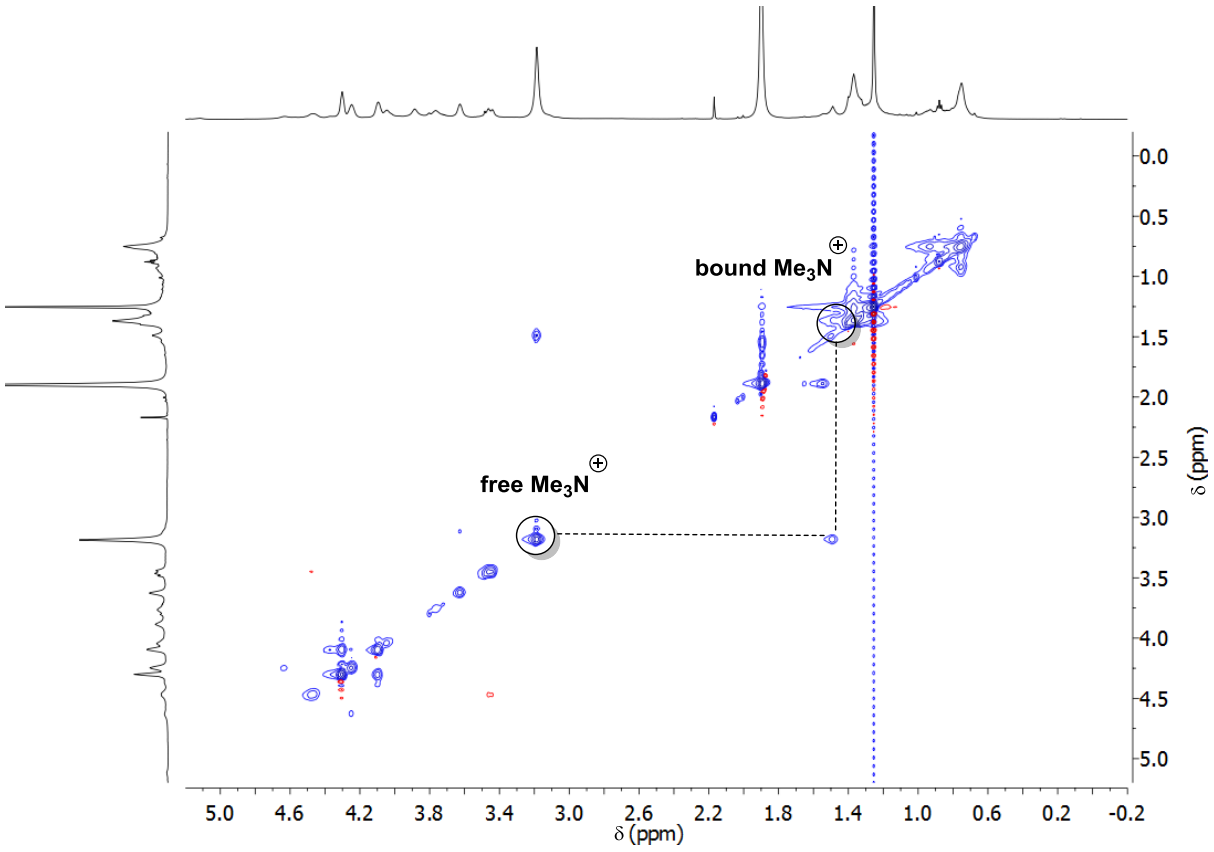


Figure S23. 2D ROESY spectrum (600 MHz, 298 K, $CDCl_3$, mixing time = 300 ms) of compound **1** in the presence of *ca.* 4.5 equiv. of MPC.

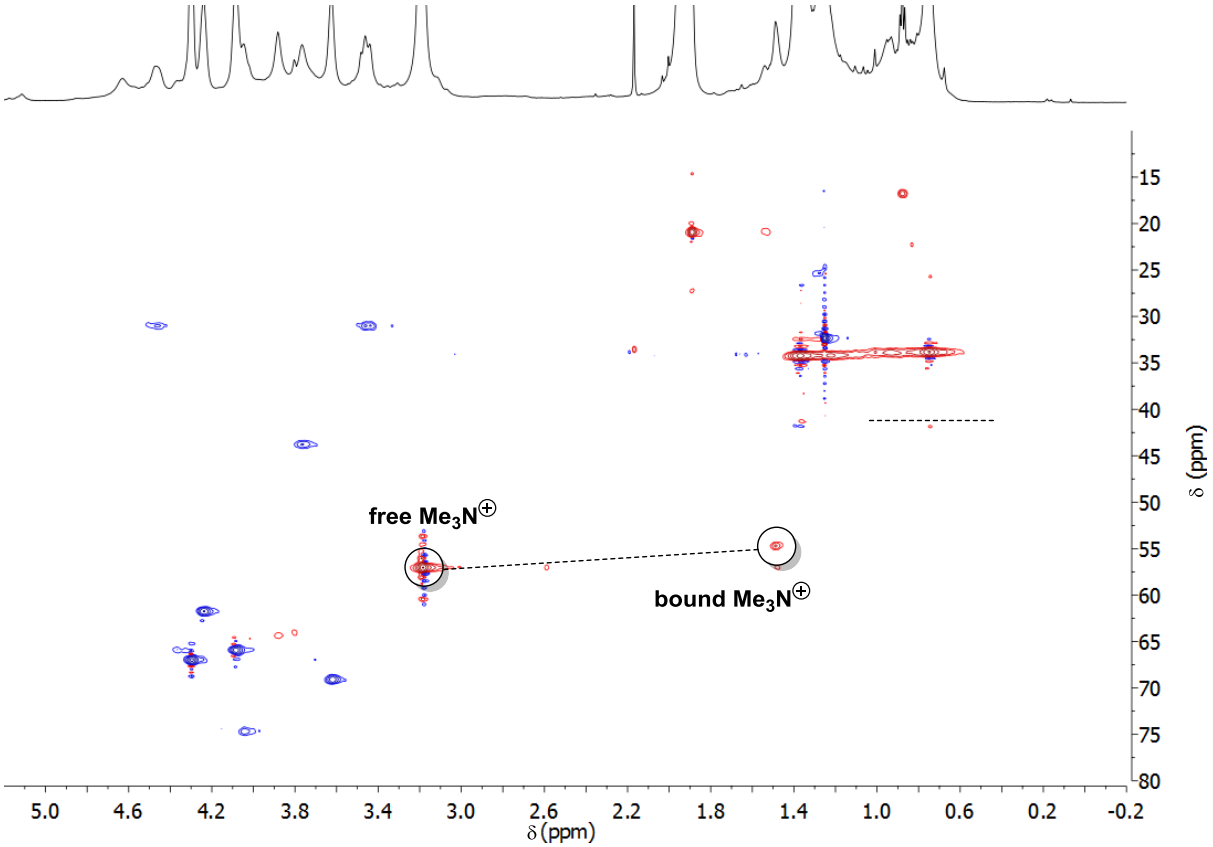


Figure S24. HSQC spectrum (600 MHz, 298 K, $CDCl_3$) of compound **1** in the presence of *ca.* 4.5 equiv. of MPC.

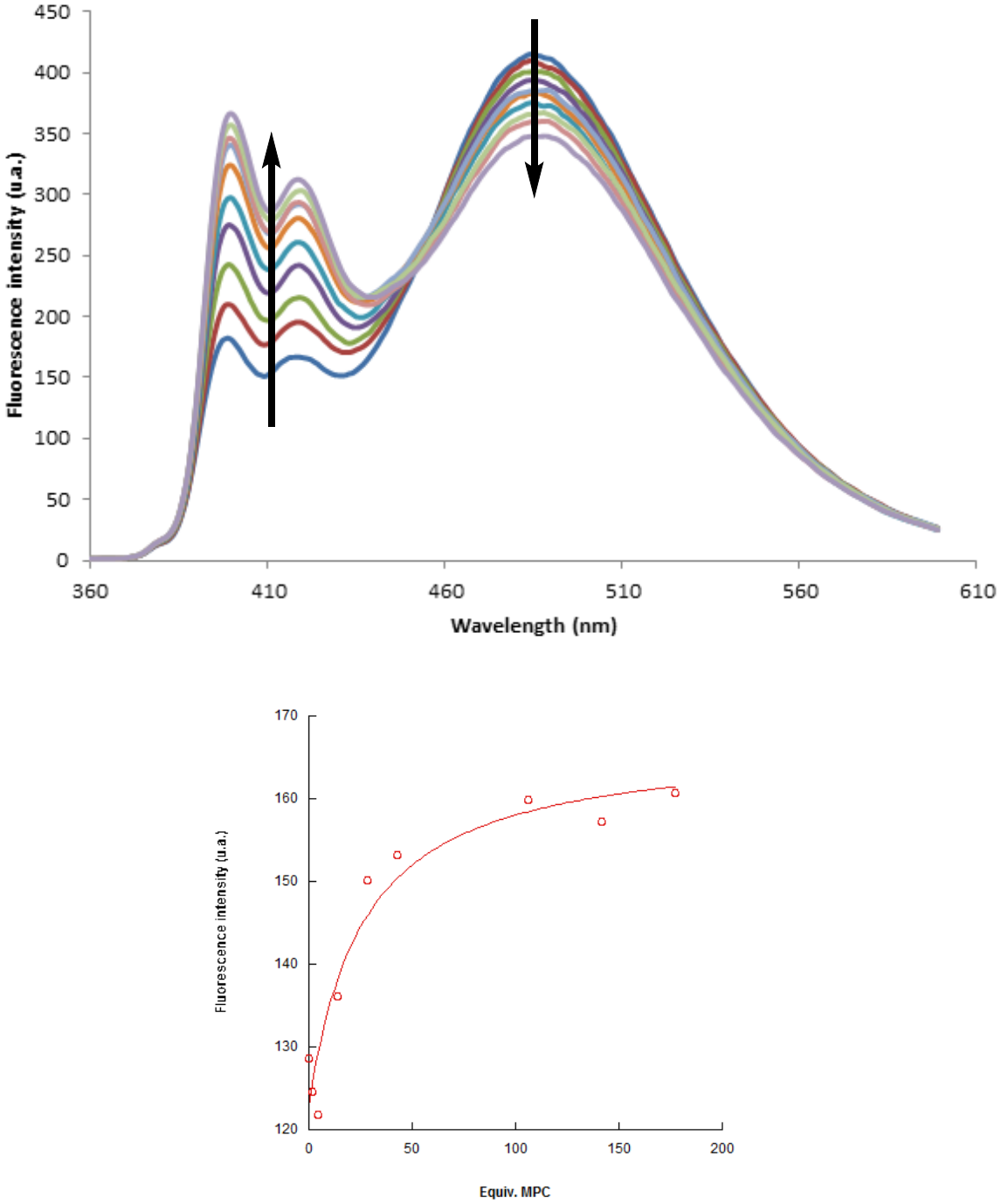


Figure S25. Top: fluorescence spectra of **1** upon the addition of MPC (0 to 71 equiv.) in chloroform. $[\mathbf{1}]_0 = 2.9 \times 10^{-6}$ M. $\lambda_{ex} = 345$ nm. Bottom: variation of fluorescence intensity at 420 nm upon the addition of MPC.

VII. Complexation studies between host **1** and DOPE

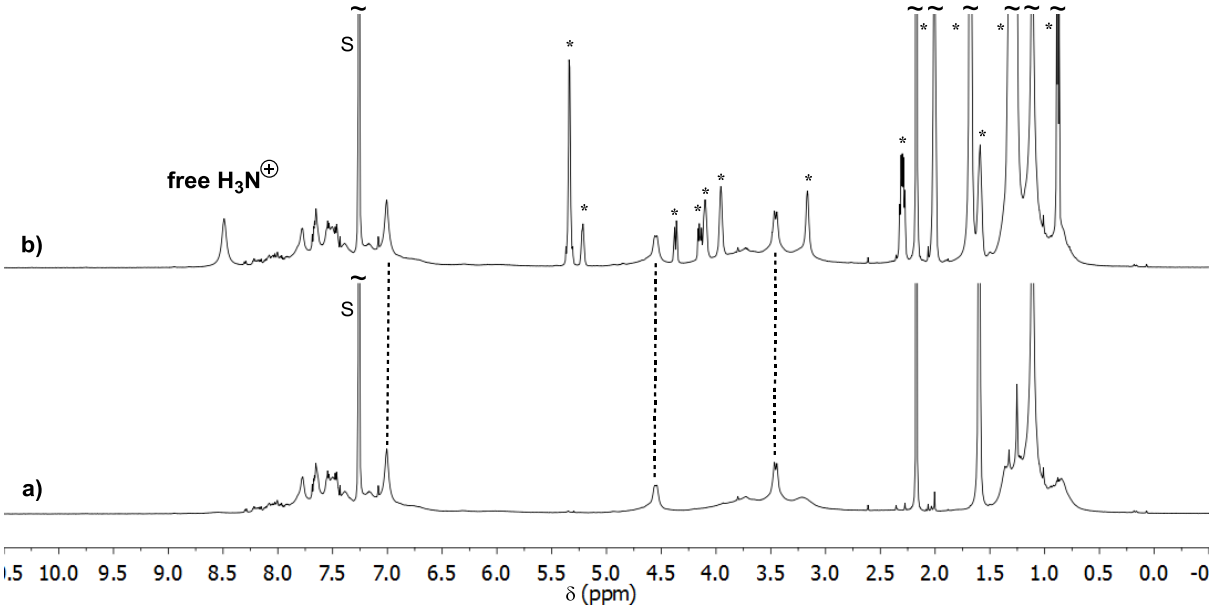


Figure S26. ^{1}H NMR spectra (600MHz, 298 K, $CDCl_3$) of: a) **1**; b) **1** in the presence of *ca.* 3 equiv. of DOPE; s: solvent; *: DOPE signals.

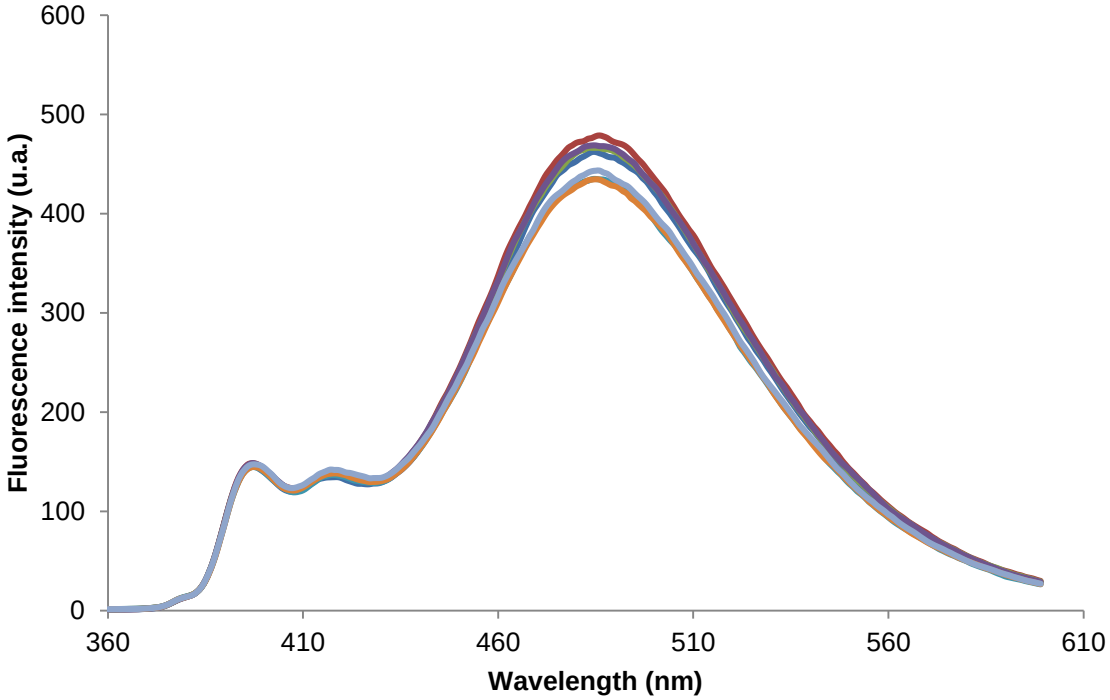


Figure S27. Fluorescence spectra of **1** upon the addition of DOPE (0 to 140 equiv.) in chloroform. $[\mathbf{1}]_0 = 2.5 \times 10^{-6}$ M. $\lambda_{ex} = 345$ nm.

VIII. ^{31}P NMR measurements

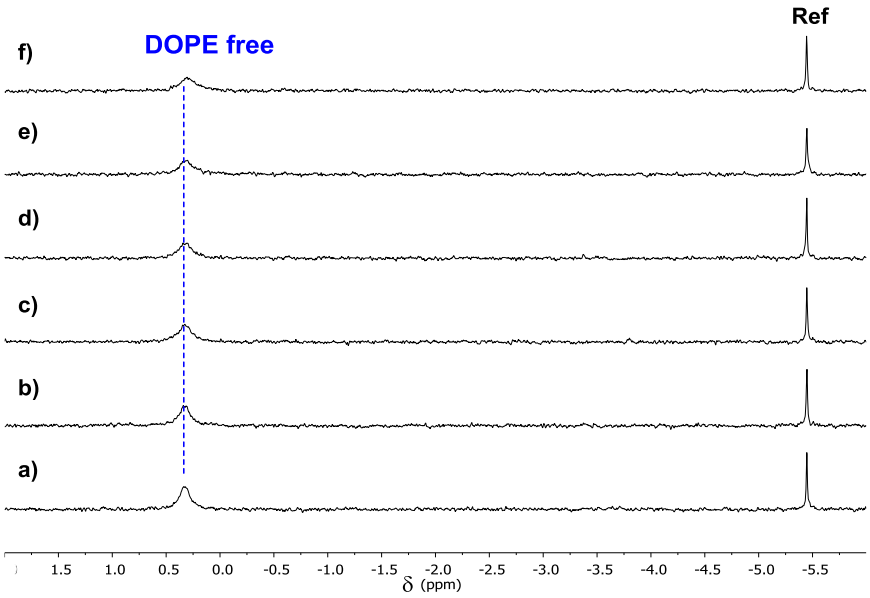


Figure S28. ^{31}P NMR spectra (400MHz, 298 K, $CDCl_3$) of: a) a solution of DOPE (*ca.* 2.9 mM); b) to f) a solution of DOPE (*ca.* 2.9 mM) after addition of host **1** up to 0.6 equiv.

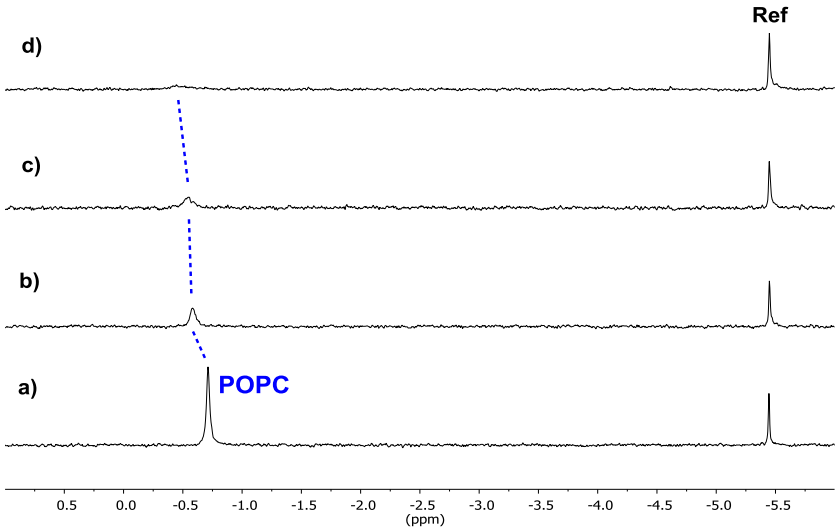


Figure S29. ^{31}P NMR spectra (400MHz, 298 K, $CDCl_3$) of: a) a solution of POPC (*ca.* 4.3 mM); b) to d) a solution of POPC (*ca.* 4.3 mM) diluted up to a concentration of 0.7 mM.

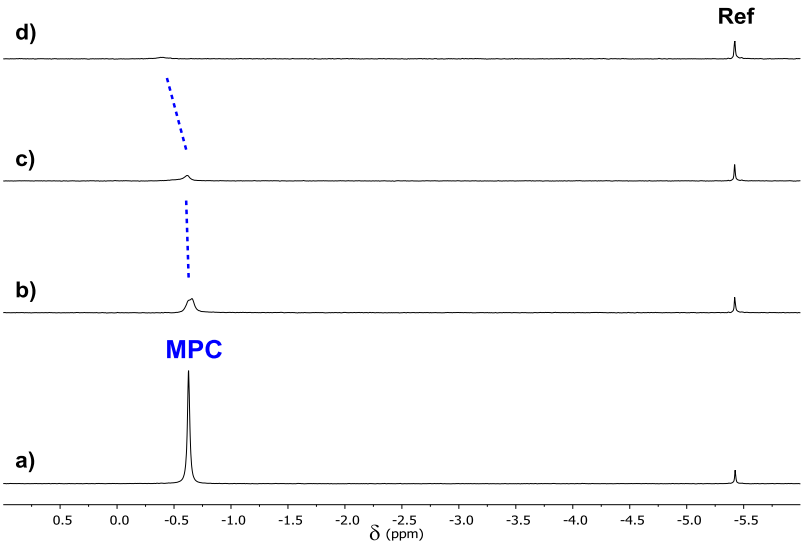


Figure S30. ^{31}P NMR spectra (400MHz, 298 K, $CDCl_3$) of: a) a solution of MPC (*ca.* 16 mM); b) to d) a solution of MPC (*ca.* 16 mM) diluted up to a concentration of 0.3 mM.

IX. Extraction experiments

1. Two liquid-liquid extraction experiments were conducted preparing two different 20µL water solutions of 2 known DOPC concentration. After adding these solutions to a solution of **1** in chloroform, the resulting fluorescence intensity was monitored.

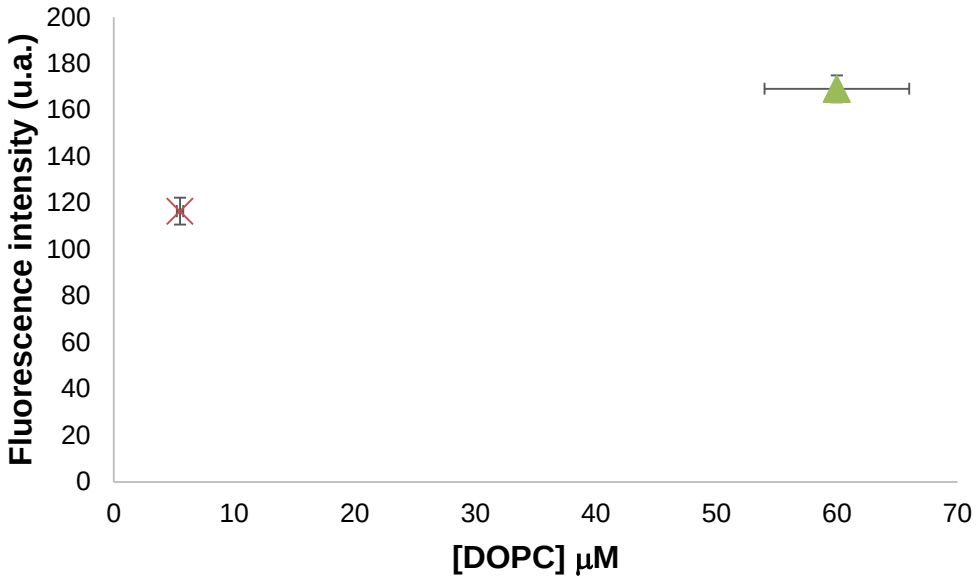


Figure S31. Red cross: fluorescence intensity of a solution of **1⊃DOPC** upon addition of a solution of DOPC in water (*ca.* 5.5 µM) to a solution of **1 (***ca.* 2 µM in 2 mL) in $CHCl_3$. Green triangle: fluorescence intensity of a solution of **1⊃DOPC** upon addition of a solution of DOPC in water (*ca.* 60 µM) to a solution of **1 (***ca.* 2 µM in 2 mL) in $CHCl_3$. λ_{ex} = 345 nm. Errors estimated of ± 10% for the equivalents of DOPC and ± 5 % for the fluorescence intensity.

2. NMR experiments

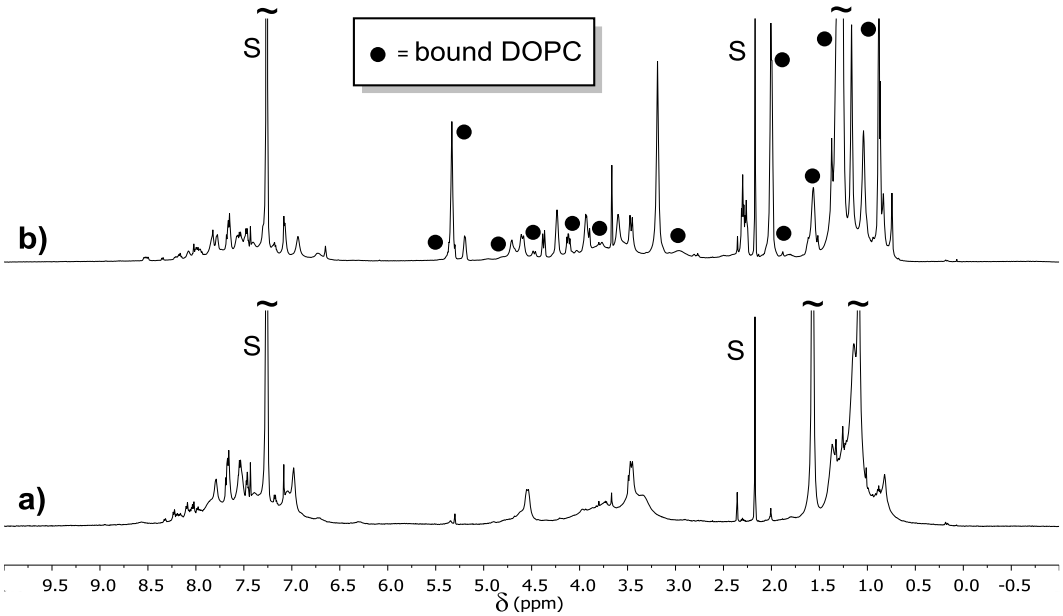


Figure S32. ^{1}H NMR spectrum (600MHz, 298 K, $CDCl_3$) of: a) 1.1 mM solution of **1** in $CDCl_3$ (600 μL); b) after addition of 100 μL of a 12 mM solution of DOPC in D_2O after mixing; s: solvent.

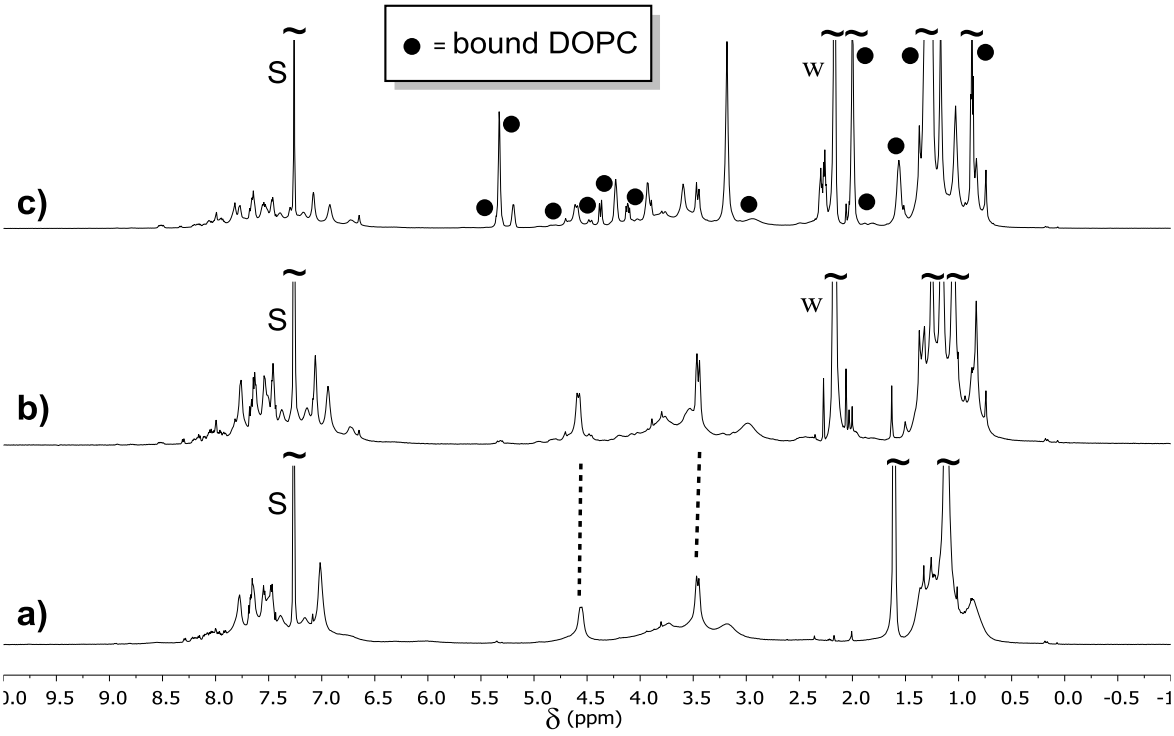


Figure S33. ^{1}H NMR spectra (600MHz, 298 K, $CDCl_3$) of: a) **1**; b) **1** after addition of a solution of DOPC liposomes prepared D_2O; c) **1** after addition of a solution of DOPC liposomes prepared D_2O and after heating and stirring for 16h at 50°C; s: solvent; w: water.

3. Fluorescence titration

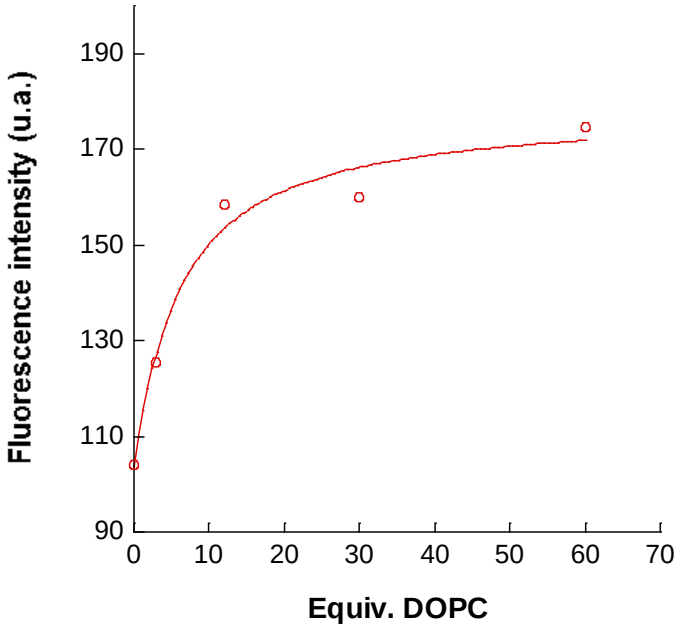


Figure S34. Variation of fluorescence intensity at 397 nm upon the addition of DOPC in chloroform to a 1.9×10^{-6} M solution of **1** in 2 mL chloroform in the presence of 20 μL of water. Solid line corresponds to 1:1 binding which yields a log $K = 4.5 \pm 0.2$; $\lambda_{ex} = 345$ nm.