Supporting information

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

Emilio Brunetti, Steven Moerkerke, Johan Wouters, Kristin Bartik* and Ivan Jabin*

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I. Complexation studies between host 1 and DOPC

Figure S1. COSY spectrum (600 MHz, 298 K, CDCl₃) of compound 1 in the presence of ca. 3 equiv. of DOPC.

Figure S2. 2D ROESY spectrum (600 MHz, 298 K, CDCl₃, mixing time = 300 ms) of compound 1 in the presence of ca. 3 equiv. of DOPC.
Figure S3. HSQC spectrum (600 MHz, 298 K, CDCl₃) of compound 1 in the presence of *ca.* 3 equiv. of DOPC.

Figure S4. $^1$H NMR spectra (600MHz, 298 K) of 1 in presence of *ca.* 3 equiv. of DOPC in: a) CDCl₃; b) in a mixture CDCl₃/CD₃OD *ca.* 98:2; c) in a mixture CDCl₃/CD₃OD *ca.* 96:4; s: solvent.
Figure S5. 2D ROESY spectrum (600 MHz, 298 K, CDCl<sub>3</sub>/CD<sub>3</sub>OD ca. 96:4, mixing time = 300 ms) of compound 1 in the presence of ca. 3 equiv. of DOPC.

Figure S6. <sup>1</sup>H NMR spectra (600MHz, 298 K, DMSO-<em>d</em><sub>6</sub>) 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. \([1]_0 = 1.9 \times 10^{-6} \text{ M.} \ \lambda_{ex} = 345 \text{ nm.} \) 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 $^3$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. \([1]_0 = 2.6 \times 10^{-6} \text{ M. } \lambda_{ex} = 345 \text{ nm.}\) 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 $^+\text{NMe}_3$ 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. $[1]_0 = 2.6 \times 10^{-6}$ 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 (600 MHz, 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. [1]₀ = 2.2 × 10⁻⁶ M. λₑₓ = 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 (600 MHz, 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. $[1]_0 = 2.9 \times 10^{-6}$ 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. [1]$_0$ = 2.5 × 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.

\[ \text{Fluorescence intensity (u.a.)} \]

\[ [\text{DOPC}] \mu\text{M} \]

Figure S31. Red cross: fluorescence intensity of a solution of 1\( \supset \)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 CHCl₃. Green triangle: fluorescence intensity of a solution of 1\( \supset \)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 CHCl₃. \( \lambda_{\text{ex}} = 345 \) 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$_2$O 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$_2$O; c) 1 after addition of a solution of DOPC liposomes prepared D$_2$O 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 $1.9 \times 10^{-6}$ 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.