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Fluorescent Bis-Calix[4]arene-Carbazole Conjugates: Synthesis and Inclusion Complexation Studies with Fullerenes C_{60} and C_{70}

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Supplementary Materials

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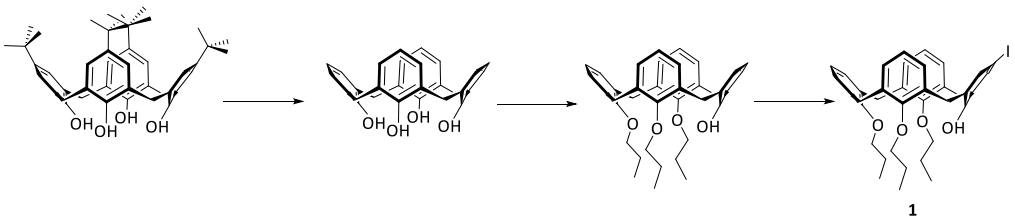
Synthesis and Structural Characterization Data of Calixarene-mono-iodo Derivative

Calix[4]arene-tripropyl-mono-iodo derivative **1** was synthesized via selective mono-iodination of 25-hydroxy-26,27,28-tripropoxycalix[4]arene [61] by an adapted synthetic procedure [38]. *p-tert*-Butyl-calix[4]arene [62] and *p*-H-calix[4]arene [63] were obtained according to reported methods.



Scheme S1. Synthesis of calix[4]arene-tripropyl-mono-iodo derivative **1**.

Compound **1:** To a solution of 25-hydroxy-26,27,28-tripropoxycalix[4]arene (950 mg, 1.725 mmol) in dry CH_3CN (27 mL) at rt, *p*-toluenesulfonic acid (297.1 mg, 1.725 mmol) was added and allowed to react during 5 min. After that period, *N*-iodosuccinimide (427 mg (1.90 mmol) was introduced in the flask and the resulting yellow suspension was stirring under argon for 17 h at rt, having the TLC control ($CHCl_3$:Hexane (1:1)) revealed the end of the reaction after that period. The solvent was removed in a rotary evaporator and the yellow residue was dissolved in CH_2Cl_2, washed with aqueous solution of $NaHCO_3$ 10% and water and dried. After solvent removal, the crude product was recrystalised from CH_2Cl_2:MeOH, affording 818.2 mg (70%) of **1** as a white solid. *m.p.*: 187-190 °C (*m.p.* lit.[64]: 172.0-172.5 °C); ν_{max}/cm^{-1} (KBr) 3530, 3060, 2963, 2921, 2871, 1588, 1459, 1385, 1292, 1248, 1200, 1158, 1085, 1043, 1005, 963, 908, 845, 799, 762, 626, 592, 554; δ_H ($CDCl_3$, 400.130 MHz) 0.92 (t, 3H, -*O*-CH_2-CH_2-C$\underline{H}_3$, *J* = 7.5 Hz), 1.11 (t, 6H, -*O*-CH_2-CH_2-C$\underline{H}_3$, *J* = 7.4 Hz), 1.82-1.96 (m, 4H, -*O*-CH_2-C$\underline{H}_2$-CH_3), 2.19-2.29 (m, 2H, -*O*-CH_2-C$\underline{H}_2$-CH_3), 3.21 (4H, d, ArC$\underline{H}_{2eq}$Ar, *J*=13.2 Hz), 3.23 (4H, d, ArC$\underline{H}_{2eq}$Ar, *J*=13.6 Hz), 3.72 (4H, t, -*O*-C$\underline{H}_2$-CH_2-CH_3, *J* = 6.7 Hz), 3.82 (t, 2H, -*O*-C$\underline{H}_2$-CH_2-CH_3, *J*=8.4 Hz), 4.30 (d, 4H, ArC$\underline{H}_{2ax}$Ar, *J*=13.8 Hz), 4.39 (d, 4H, ArC$\underline{H}_{2ax}$Ar, *J*=13.1 Hz), 4.86 (s, 1H, ArO$\underline{H}$), 6.31-6.49 (m, 6H, Ar$\underline{H}$), 6.98 (t, 1H, Ar$\underline{H}$, *J* = 7.4 Hz), 7.17 (d, 2H, Ar$\underline{H}$, *J* = 7.4 Hz), 7.40 (s, 2H, Ar$\underline{H}$).

Structural Characterization Data of Calixarene-Carbazole Conjugates

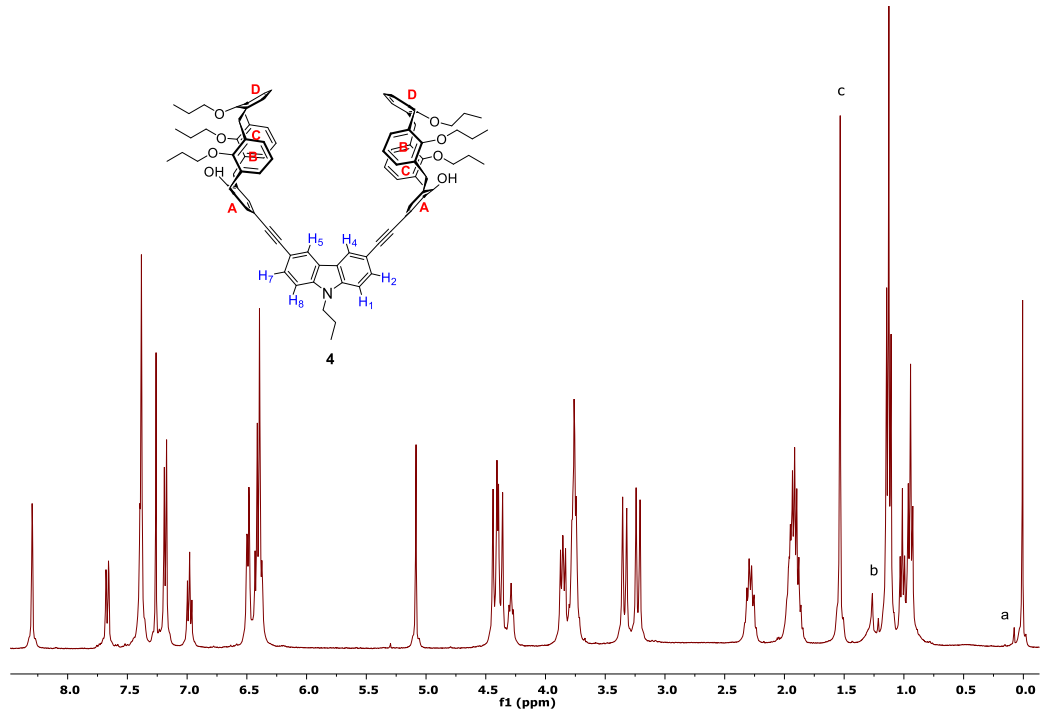


Figure S1. [1]H NMR spectrum of bis-(*p*-H-calix-triprop)-3,6-CBZ (**4**) in $CDCl_3$ (400 MHz, 25 ºC) [65]; [a]silicone grease, [b]apiezon type grease, [c]water.

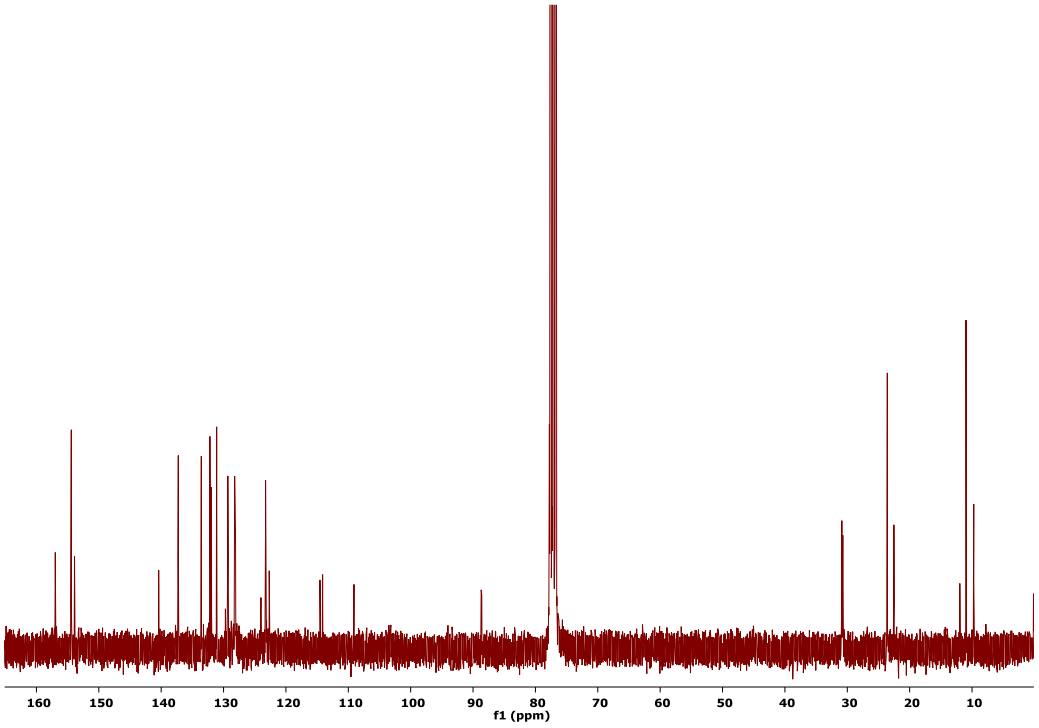


Figure S2. [13]C NMR spectrum of bis-(*p*-H-calix-triprop)-3,6-CBZ (**4**) in $CDCl_3$ (75 MHz, 25 ºC) [65].

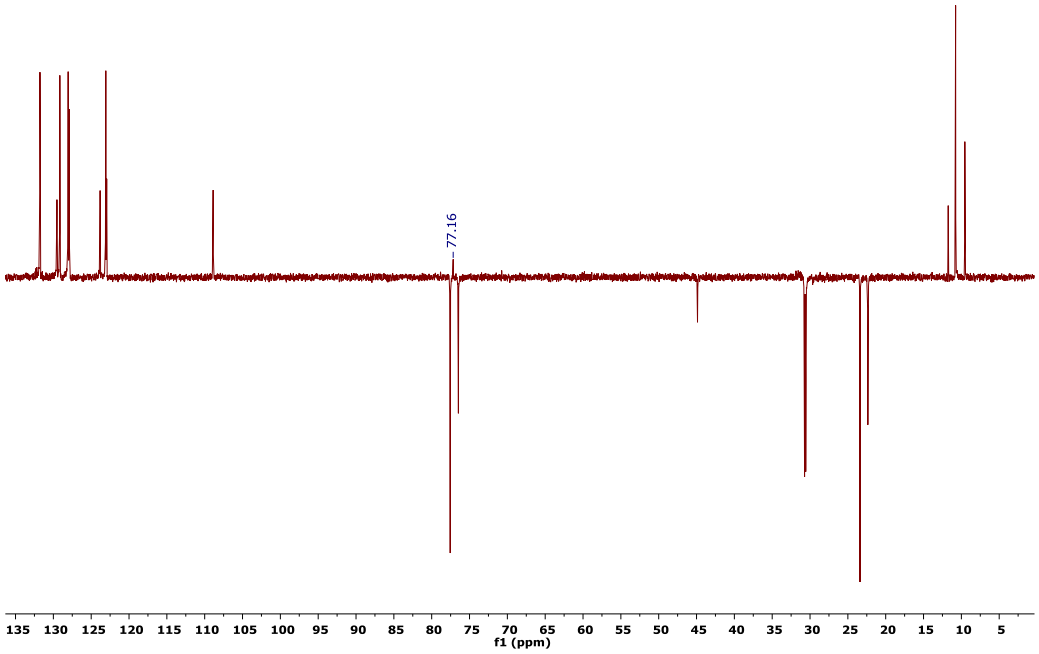


Figure S3. ^{13}C DEPT 135 NMR spectrum of bis-(*p*-H-calix-triprop)-3,6-CBZ (**4**) in $CDCl_3$ (75 MHz, 25 ºC) [65].

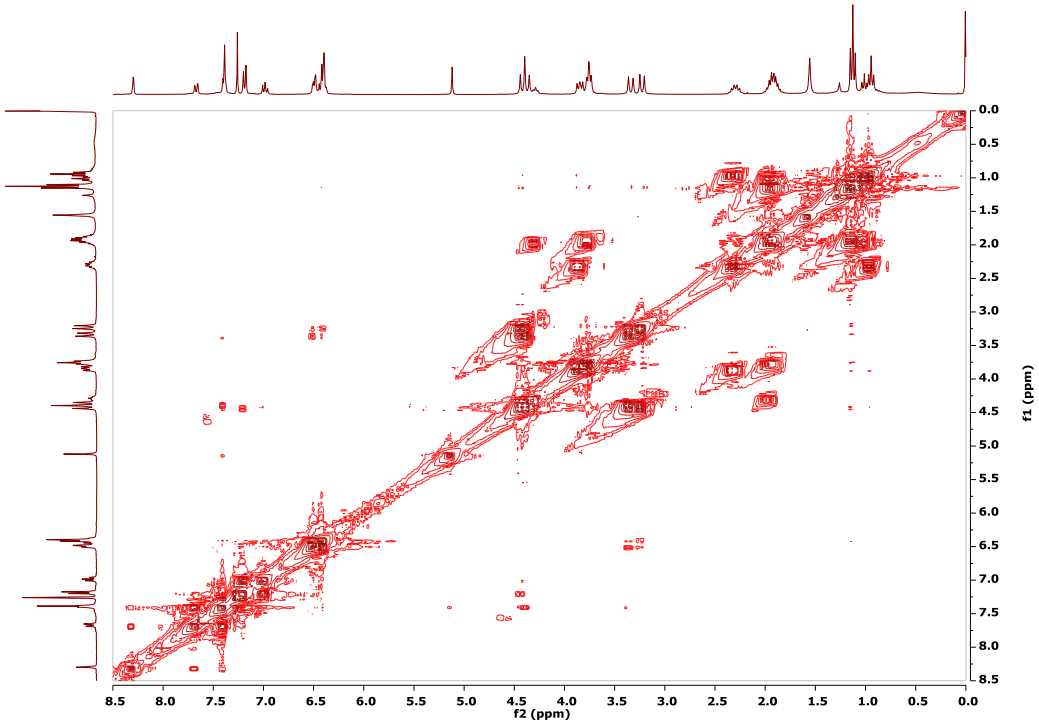


Figure S4. ^{1}H-^{1}H COSY NMR spectrum of bis-(*p*-H-calix-triprop)-3,6-CBZ (**4**) in $CDCl_3$ (400 MHz, 25 ºC) [65].

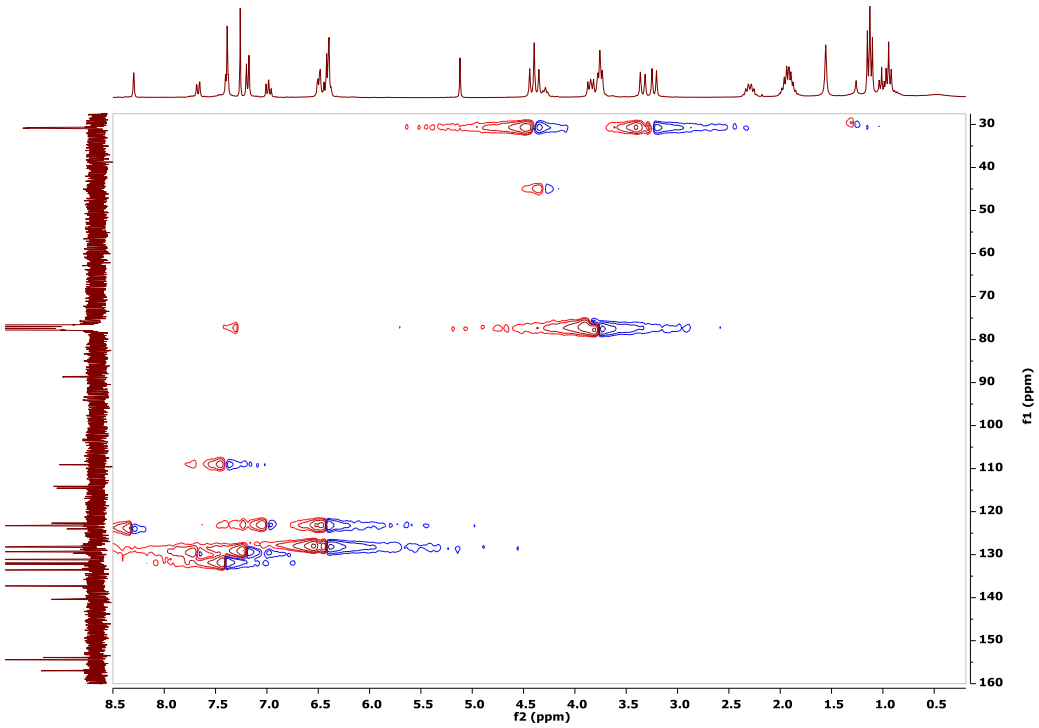


Figure S5. ^{1}H-^{13}C HSQC NMR spectrum of bis-(*p*-H-calix-triprop)-3,6-CBZ (**4**) in $CDCl_3$ (400/75 MHz, 25 ºC) [65].

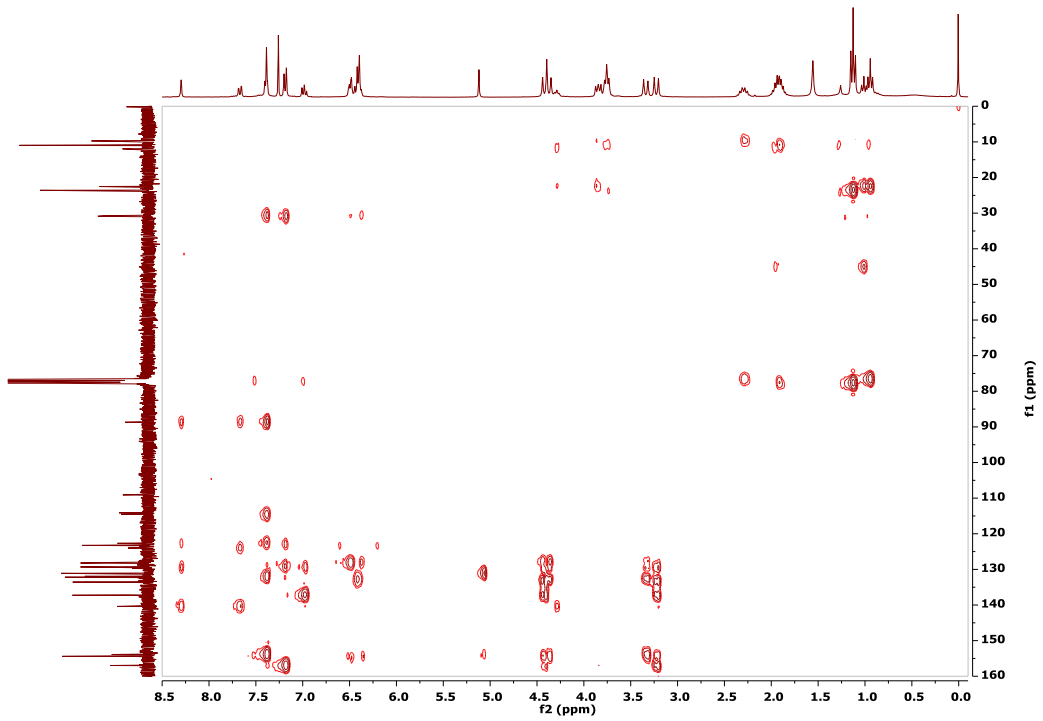


Figure S6. ^{1}H-^{13}C HMBC NMR spectrum of bis-(*p*-H-calix-triprop)-3,6-CBZ (**4**) in $CDCl_3$ (400/75 MHz, 25 ºC) [65].

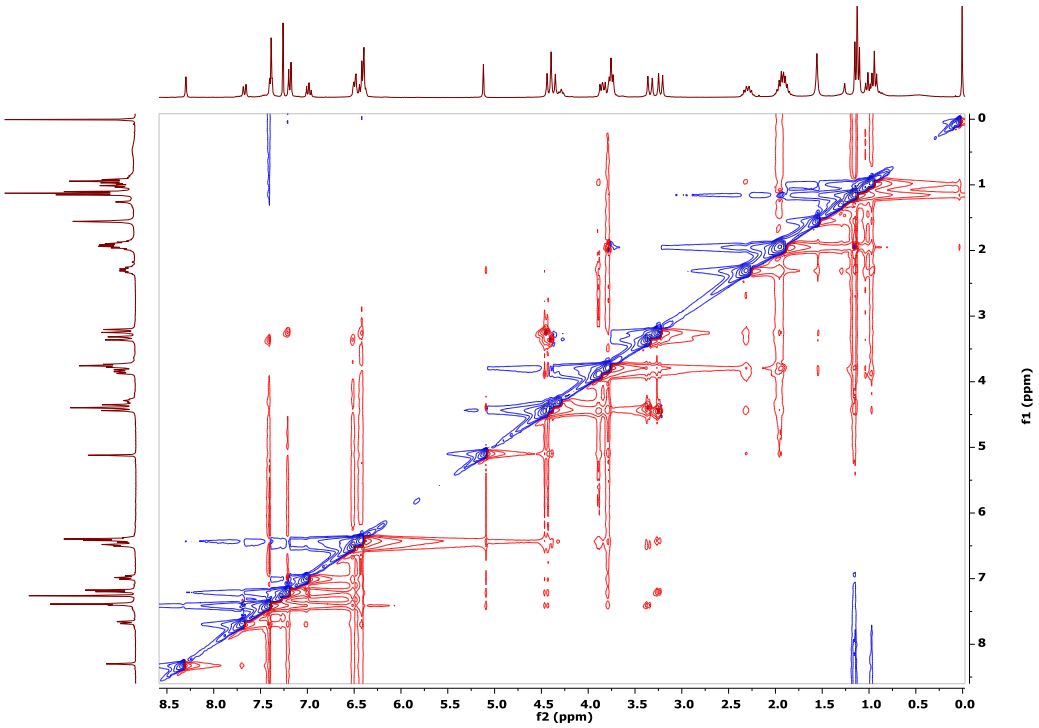


Figure S7. NOESY NMR spectrum of bis-(*p*-H-calix-triprop)-3,6-CBZ (**4**) in $CDCl_3$ (400 MHz, 25 ºC) [65].

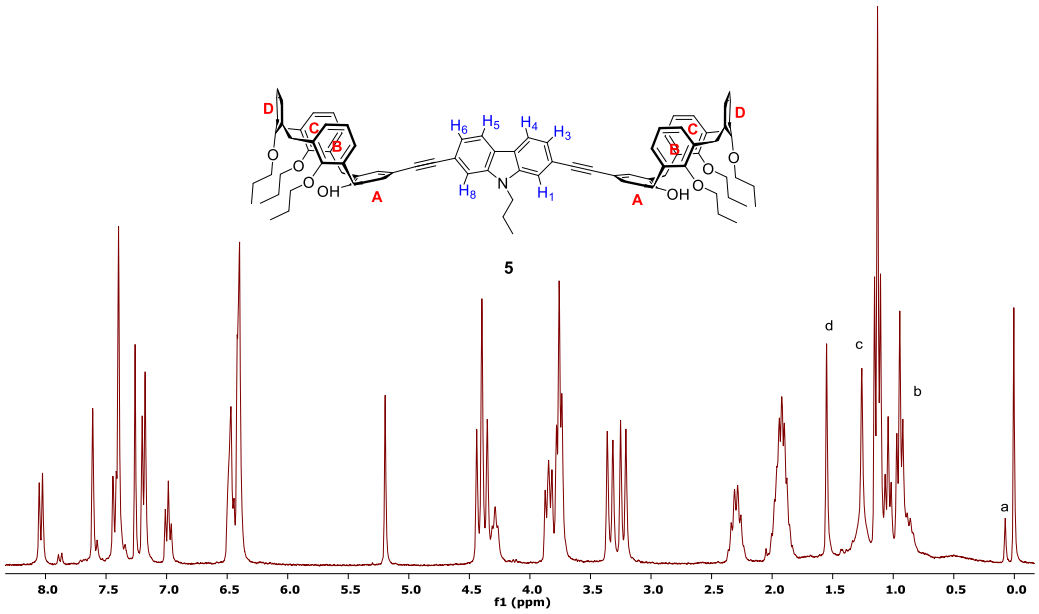
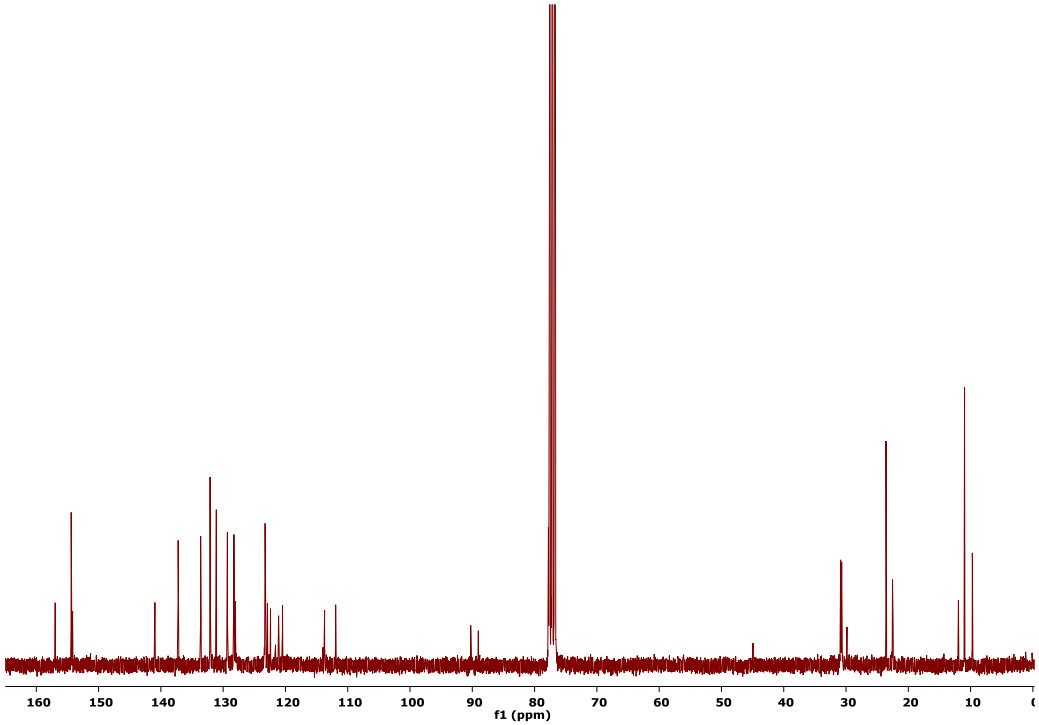
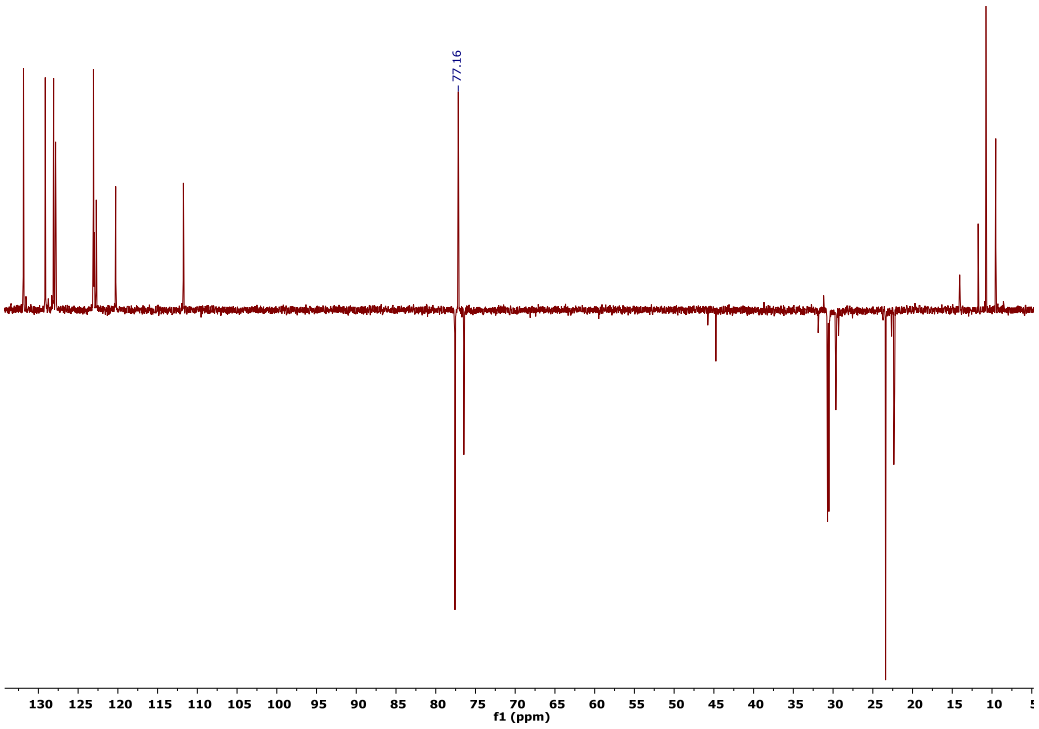


Figure S8. ^1H NMR spectrum of bis-(*p*-H-calix-triprop)-2,7-CBZ (**5**) in $CDCl_3$ (400 MHz, 25 ºC) [65]; [a]silicone grease, [b,c]apiezon type grease, [d]water.



(**a**)



(**b**)

Figure S9. ^{13}C NMR (a) and ^{13}C DEPT 135 NMR (b) spectra of bis-(*p*-H-calix-triprop)-2,7-CBZ (**5**) in $CDCl_3$ (75 MHz, 25 ºC) [65].

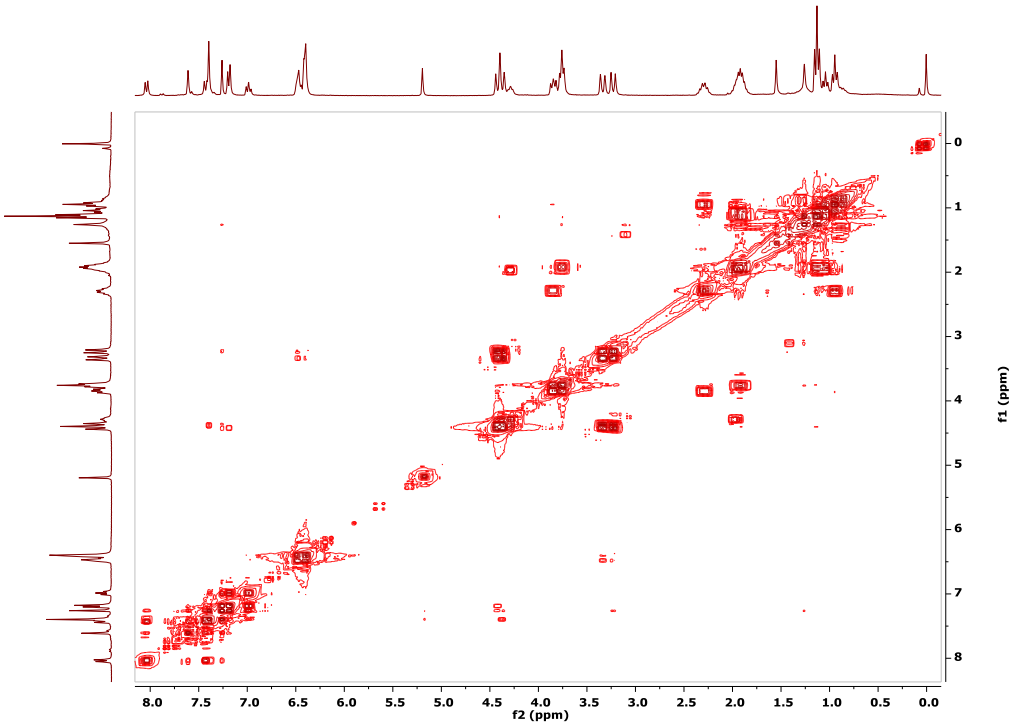


Figure S10. ^{1}H-^{1}H COSY NMR spectrum of bis-(*p*-H-calix-triprop)-2,7-CBZ (**5**) in $CDCl_3$ (300 MHz, 25 ºC) [65].

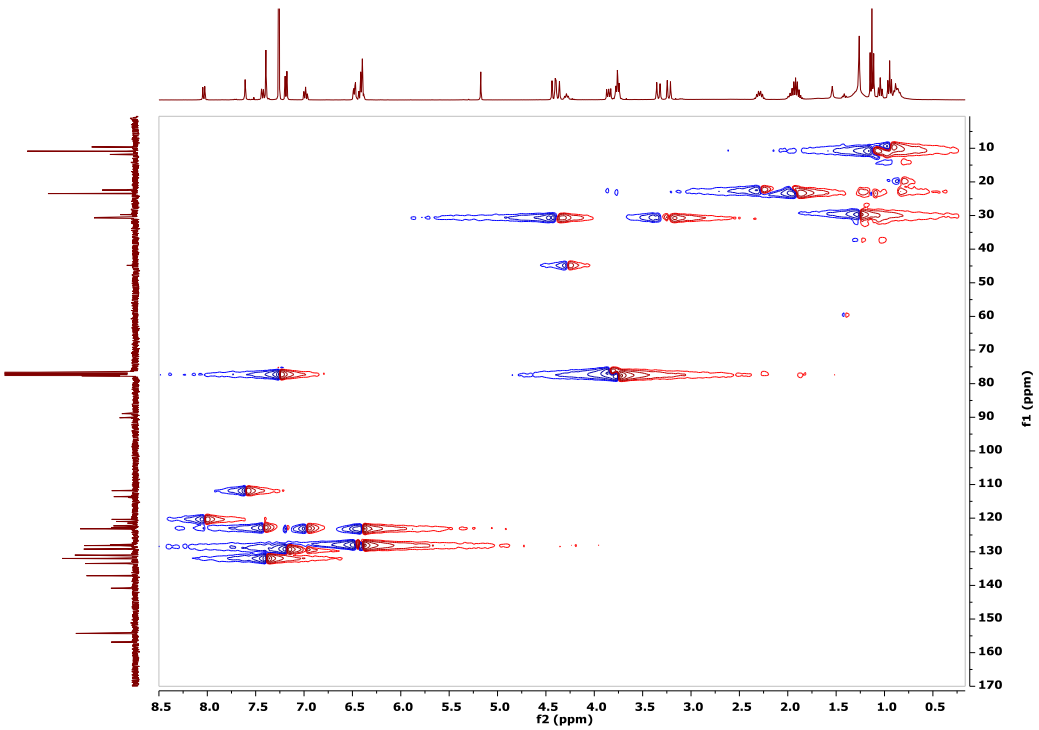
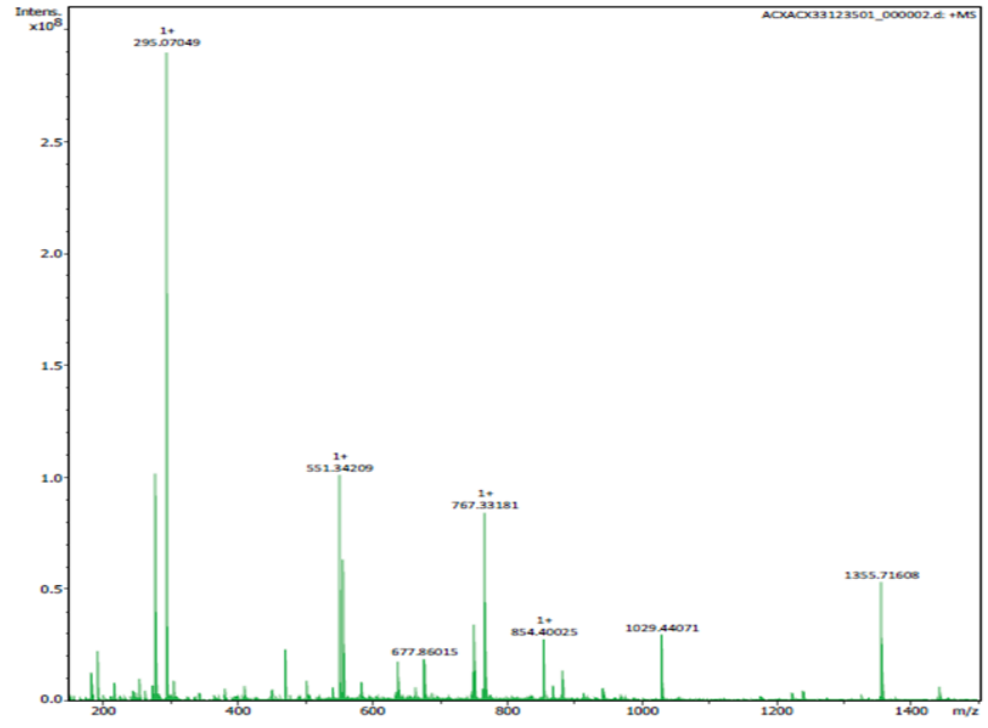
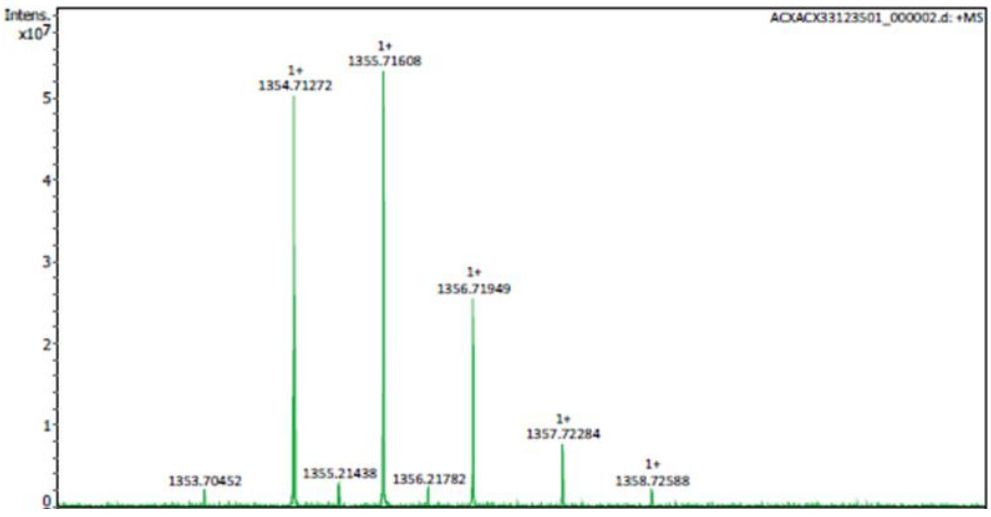


Figure S11. ^{1}H-^{13}C HSQC NMR spectrum of bis-(*p*-H-calix-triprop)-2,7-CBZ (**5**) in $CDCl_3$ (300/75 MHz, 25 ºC) [65].

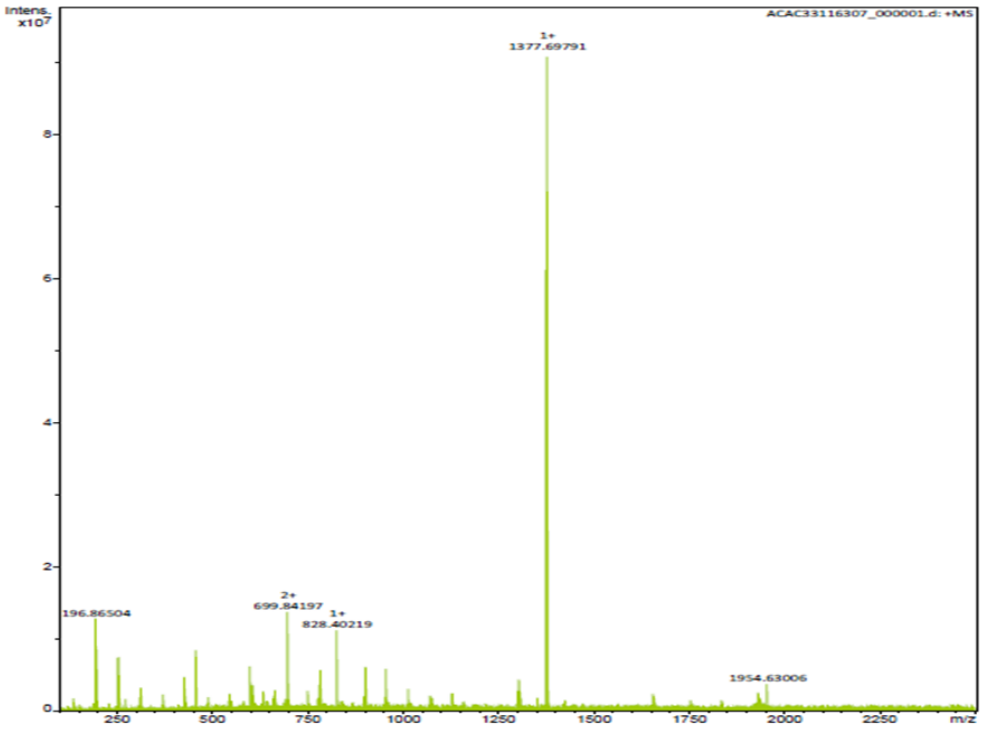


(**a**)

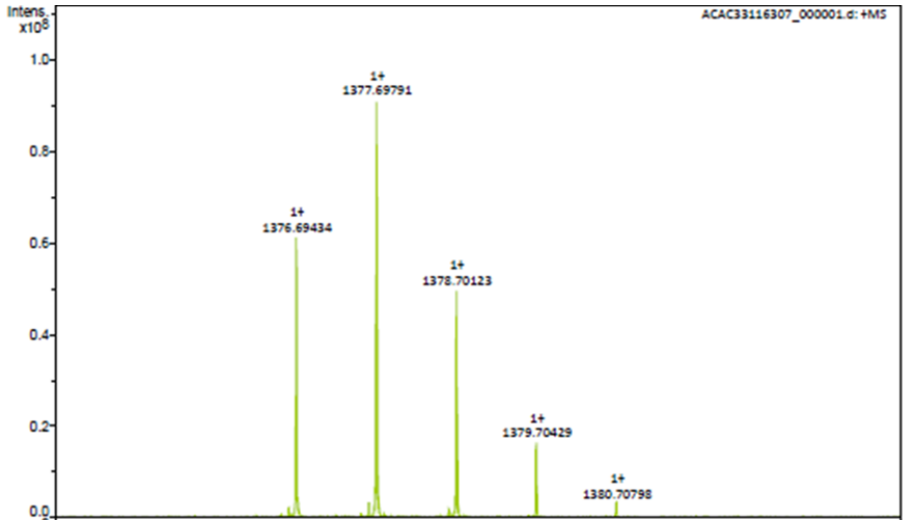


(**b**)

Figure S12. Full ESI-HRMS spectrum of bis-(*p*-H-calix-triprop)-3,6-CBZ (**4)** (**a**); ESI-HRMS spectrum of the molecular ion region (**b**).



(**a**)



(**b**)

Figure S13. Full ESI-HRMS spectrum of bis-(*p*-H-calix-triprop)-2,7-CBZ (**5**) (**a**); ESI-HRMS spectrum of the molecular ion region (**b**).

Photophysical Properties

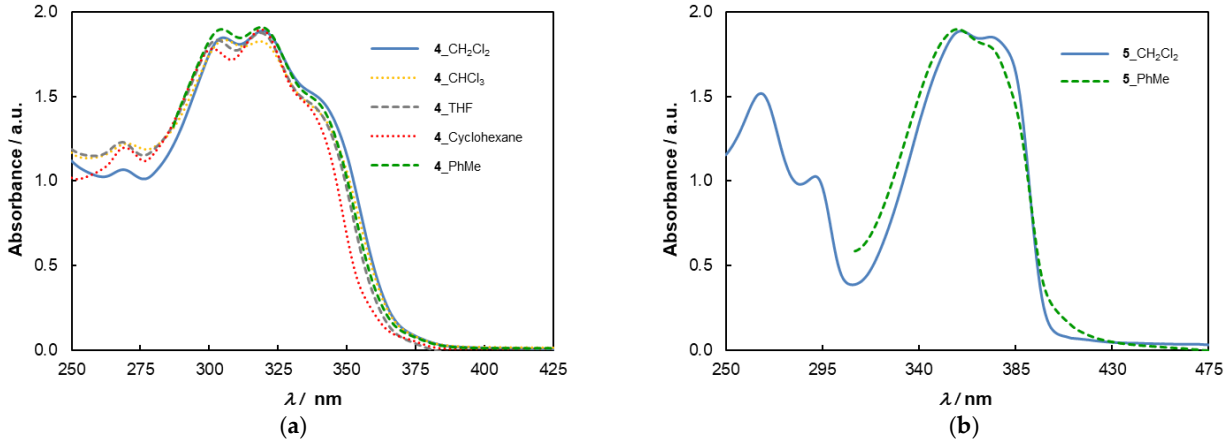


Figure S14. UV-Vis spectra of bis-(*p*-H-calix-triprop)-3,6-CBZ (**4**) (**a**) and bis-(*p*-H-calix-triprop)-2,7-CBZ (**5**) (**b**) in different solvents (2.5×10^{-5} M).

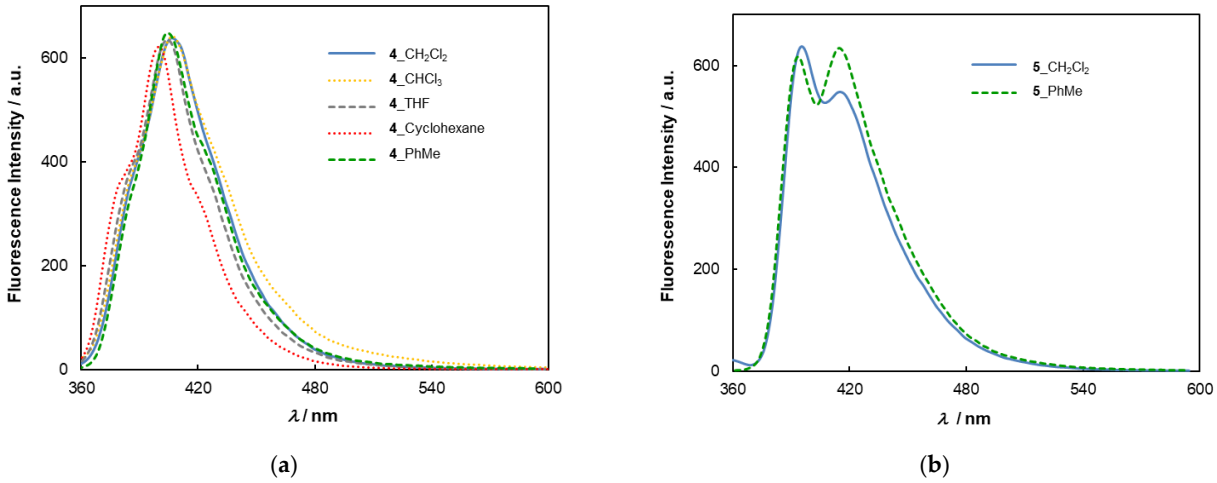


Figure S15. Emission spectra of bis-(*p*-H-calix-triprop)-3,6-CBZ (**4**) (**a**) and bis-(*p*-H-calix-triprop)-2,7-CBZ (**5**) (**b**) in different solvents (6.0×10^{-7} M).

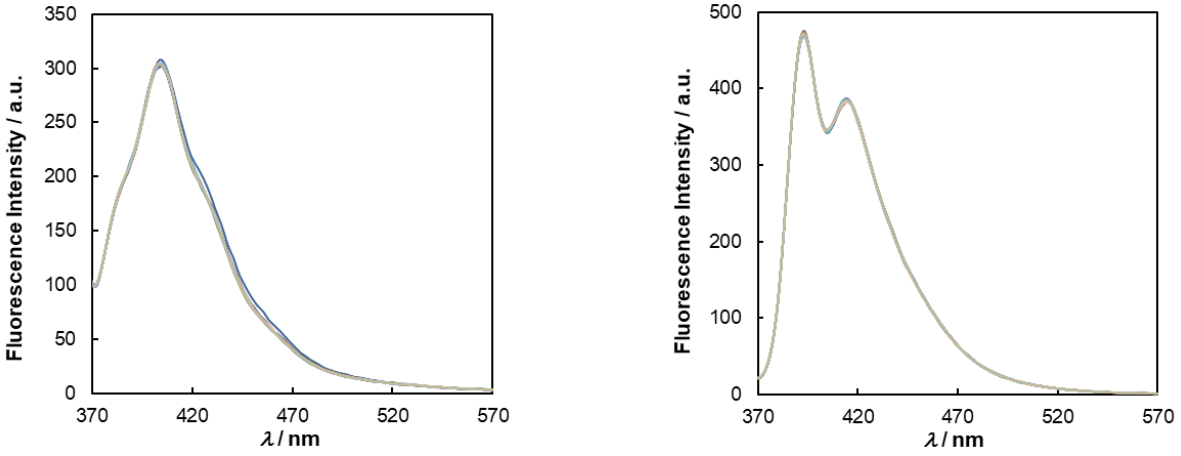


Figure S16. Emission spectra of bis-(*p*-H-calix-triprop)-3,6-CBZ (**4**) (**a**) and bis-(*p*-H-calix-triprop)-2,7-CBZ (**5**) (**b**), both in 6.0 × 10^{-7} M in toluene, upon continuous irradiation for for 20 min, under the same experimental conditions carried out on titration experiments (λ_{exc} = 357 nm).

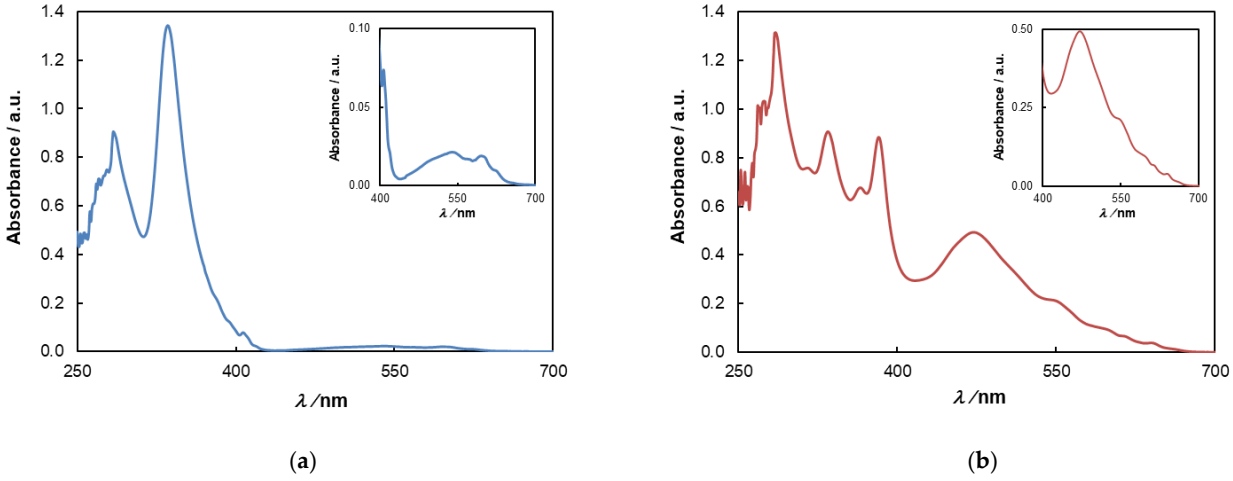
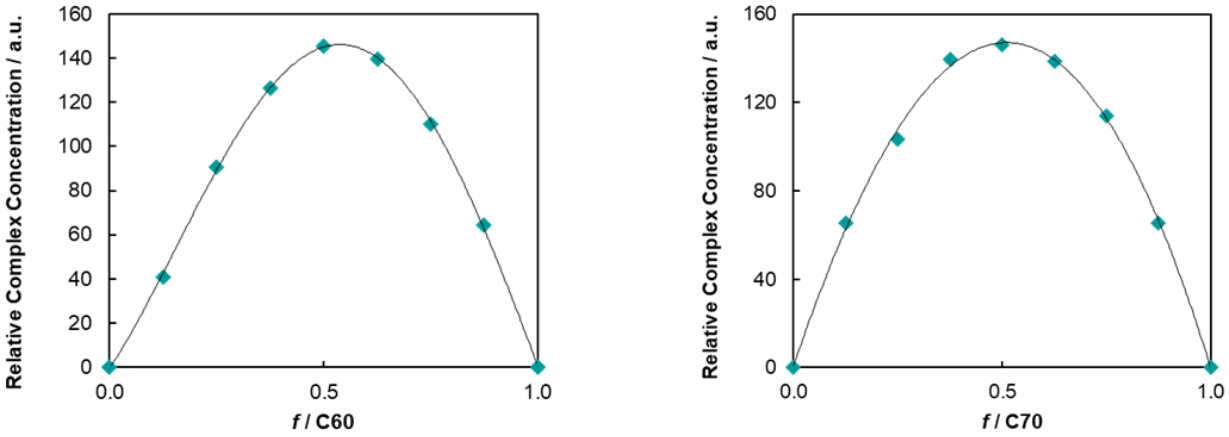


Figure S17. UV-Vis spectra of fullerenes C_{60} (**a**) and C_{70} (**b**) in toluene (2.21 x 10^{-5} M); insets: amplification of the region between 400-700 nm.

Job plots



(**a**) (**b**)

Figure S18. Job plot of complex formation between bis-(*p*-H-calix-triprop)-2,7-CBZ (**5**) and C_{60} (**a**)/C_{70} (**b**) in toluene (at constant 6.0 x 10^{-7} M total concentration) as obtained from changes in fluorescence (λ_{exc} = 357 nm).

Variable-Temperature ^{1}H NMR spectra

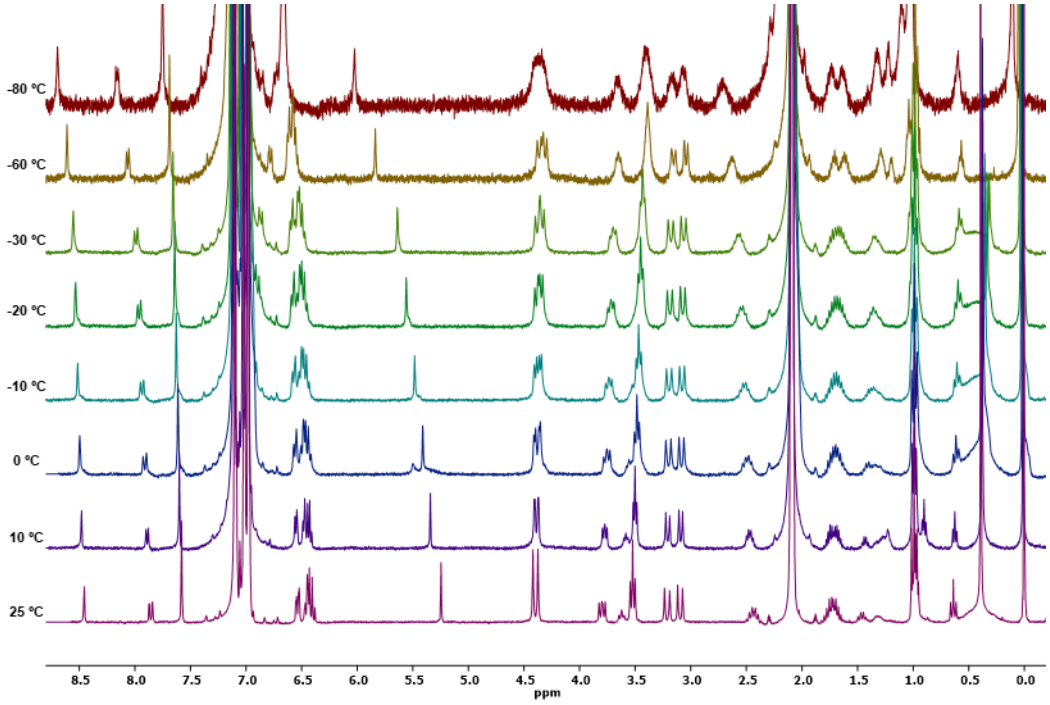


Figure S19. VT-NMR of bis-(*p*-H-calix-triprop)-3,6-CBZ (**4**) at various temperatures (400 MHz, toluene-d$_8$) [65].

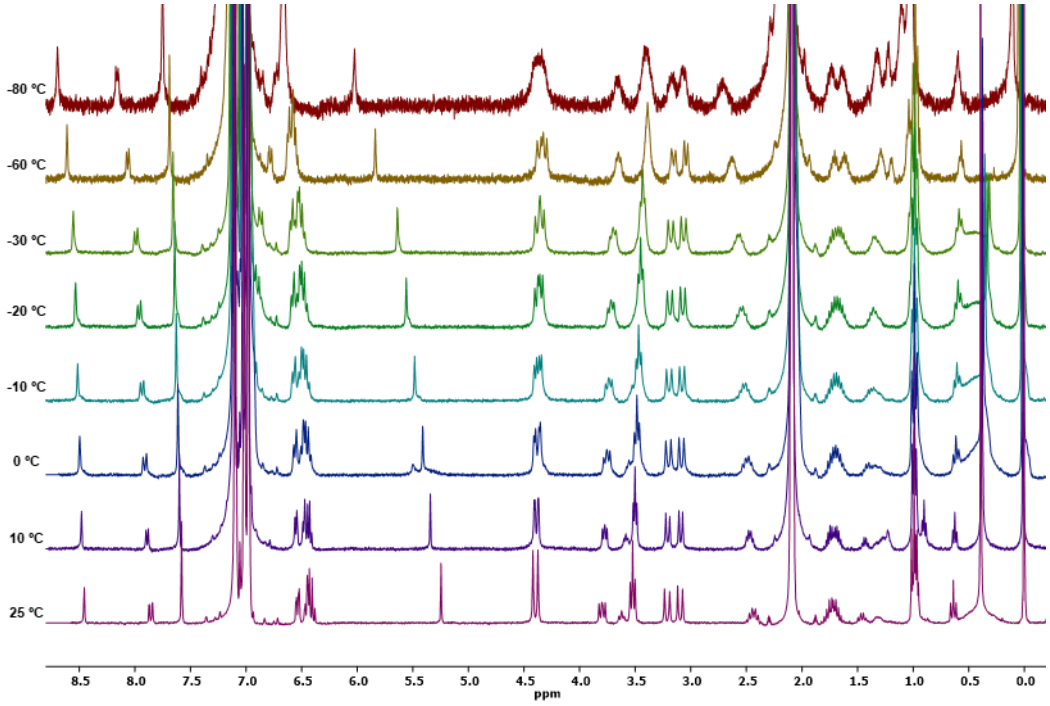


Figure S20. VT-NMR of equimolar amounts of bis-(*p*-H-calix-triprop)-3,6-CBZ (**4**) and fullerene C$_{60}$ at various temperatures (400 MHz, toluene-d$_8$) [65].

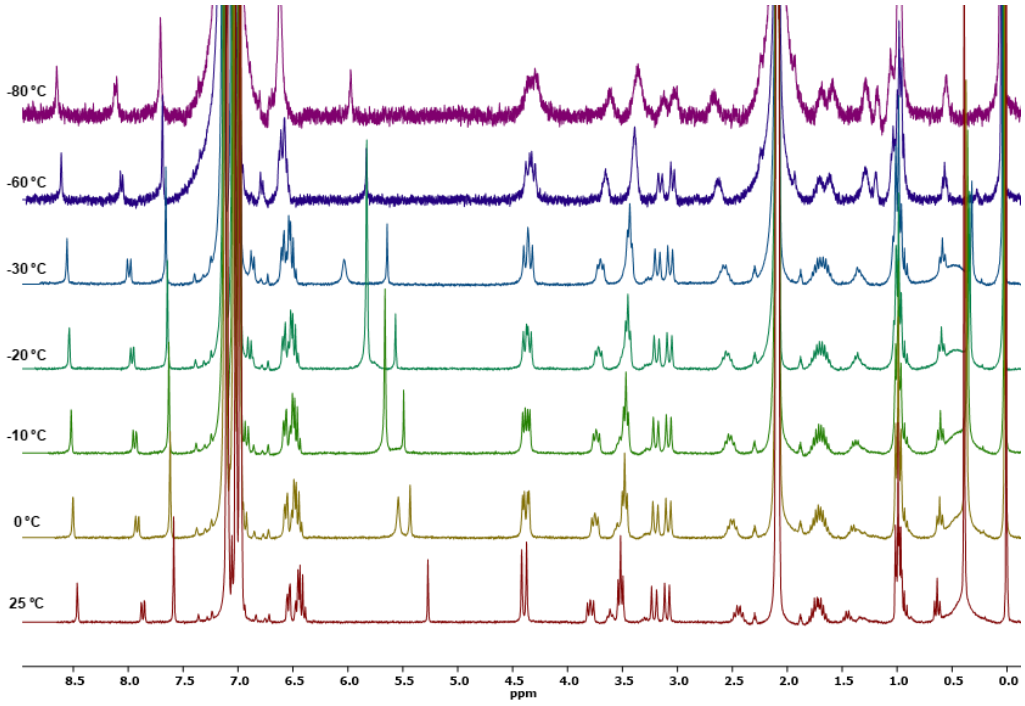


Figure S21. VT-NMR of equimolar amounts of bis-(*p*-H-calix-triprop)-3,6-CBZ (**4**) and fullerene C_{70} at various temperatures (400 MHz, toluene-d_8) [65].

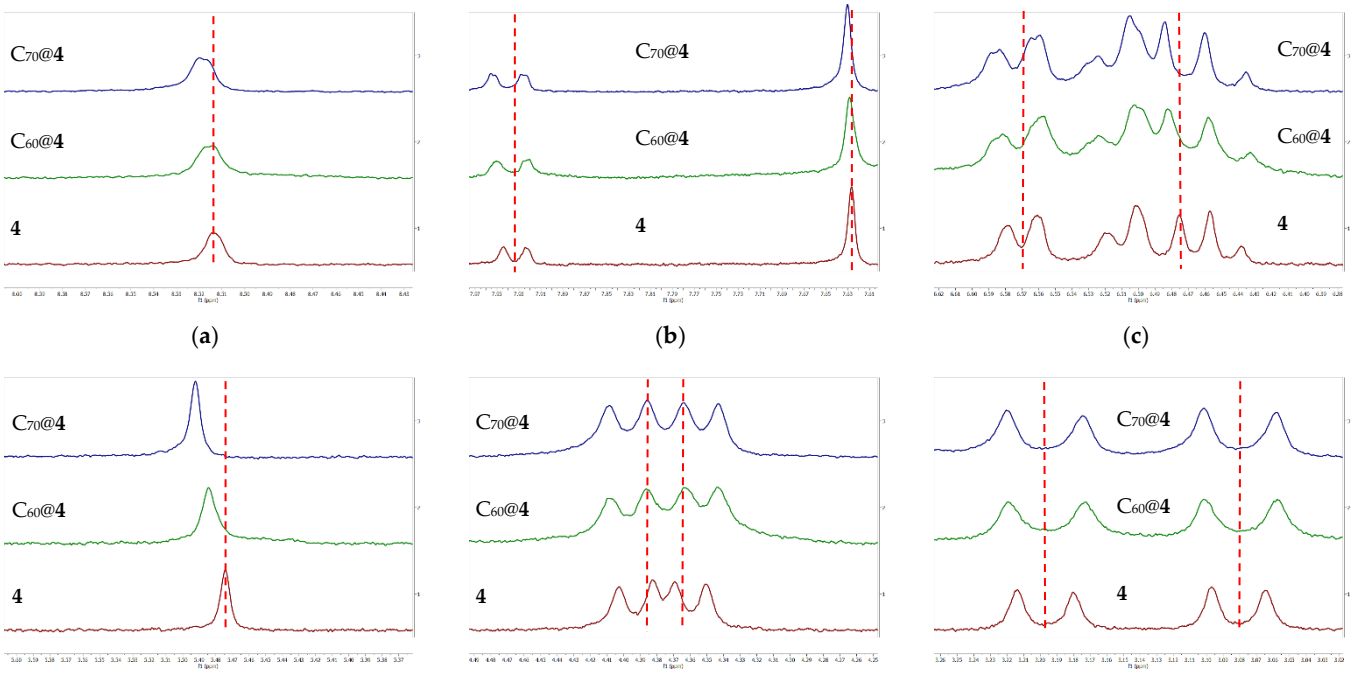


Figure S22. Stacked ^{1}H NMR spectra of **4**, C_{60}@**4**, and C_{70}@**4** at -10 °C, showing complexation-induced shifts (CIS) at several representative regions (400 MHz, toluene-d_8): (**a**) $Ar_{CBZ}\underline{H}_{(4,5)}$; (**b**) $Ar_{CBZ}\underline{H}_{(2,7)}$ and $Ar_{Calix}\underline{H}_{(ring\ A)}$; (**c**) $Ar_{Calix}\underline{H}_{(rings\ B,\ C)}$; (**d**) $ArO\underline{H}$; (**e**) $ArC\underline{H}_{2(ax)}Ar$; (**f**) $ArC\underline{H}_{2(eq)}Ar$ [65].

References

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65. All NMR spectra were post-processed by MestReNova, version: 14.1.2-25024; Mestrelab Research, S.L., 2020