SUPPLEMENTARY INFORMATION

Complexation of 6-(4’-(toluidinyl)naphthalene-2-sulphonate by β-cyclodextrin and linked β-cyclodextrin dimers

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Fig. S1. Absorbance variation of TNS– with [βCD]total at 265 nm under the same conditions as in Fig. 3 in the main text. The solid curve represents the best fit obtained over the range 250-275 and 310-330 nm.

Fig. S2. UV-vis absorption changes by TNS– (3.00 × 10^-5 mol dm^-3) with [66βCD2su]total in the range 0, 4.00 and 8.10 × 10^-6, 1.23, 1.62, 1.99, 2.39, 2.76, 3.16, 3.55,4.50, 4.98, 5.52, 6.36, 7.21, 8.41 and 9.60 ×10^-5, 1.12, 1.27, 1.43, 1.59, 1.79 and 1.98 ×10^-5 mol dm^-3. The arrows indicate the direction of absorbance change as [66βCD2su]total increases. Isosbestic points occur at 233.5, 275, 284.5 and 308.25 nm.
**Fig. S3.** Absorbance variation of TNS\(^-\) with \([\beta CD_2 su]_{\text{total}}\) at 260 nm under the same conditions as in Fig. S2. The solid curve represents the best fit obtained over the ranges 235-275 nm.

**Fig. S4.** Absorbance variation of TNS\(^-\) with \([\beta CD_2 ur]_{\text{total}}\) at 320 nm under the same conditions as in Fig. 4 in the main text. The solid curve represents the best fit obtained over the ranges 235-270 and 310-335 nm.

**Fig. S5.** UV-vis absorption changes at 298.2 K shown by TNS\(^-\) (3.00 \times 10^{-5} \text{ mol dm}^{-3}) with \([36\beta CD_2 su]_{\text{total}}\) in the range 0, 5.08, and 7.58 \times 10^{-6}, and 1.01, 1.50, 2.22, 2.47, 2.81, 3.14, 3.52, 4.01, 4.51, 5.24, 5.98, 6.96, 7.96, 8.95, and 9.89 \times 10^{-5}, and 1.11 and 1.24 \times 10^{-4} \text{ mol dm}^{-3}. The arrows indicate the direction of absorbance change as \([36\beta CD_2 su]_{\text{total}}\) increases. Isosbestic points occur at 233.5, 277.0, and 383.5 nm.
**Fig. S6.** Absorbance variation of TNS with [36βCD₂su]_{total} at 260 nm under the same conditions as in Fig. S5. The solid curve represents the best fit obtained over the range 240-270 nm.

**Fig. S7.** UV-vis absorption changes at 298.2 K shown by TNS (3.00 × 10⁻⁵ mol dm⁻³) with [33βCD₂su]_{total} in the range 0, 5.00 × 10⁻⁶, and 1.01, 1.25, 1.50, 1.74, 1.97, 2.22, 2.48, 2.79, 3.11, 3.53, 4.00, 4.49, 5.25, 5.97, 6.95, 7.96, 89, and 9.89 × 10⁻⁵, and 1.11 and 1.23 × 10⁻⁴ mol dm⁻³. The arrows indicate the direction of absorbance change as [36βCD₂su]_{total} increases. An isosbestic point occurs at 233.5 nm.

**Fig. S8.** Absorbance variation of TNS with [33βCD₂su]_{total} at 260 nm under the same conditions as in Fig. S7. The solid curve represents the best fit obtained over the range 240-270 nm.
**Fig. S9.** UV-vis absorption changes at 298.2 K shown by TNS⁻ (3.00 × 10⁻⁵ mol dm⁻³) with [36βCD₂ur]total in the range 0, 2.50, 5.05 and 7.53 × 10⁻⁶, and 1.00, 1.25, 1.51, 1.74, 1.99, 2.24, 2.47, 2.79, 3.12, 3.46, 4.51, 5.24, 5.97, 6.93, 7.93 and 9.88 × 10⁻⁵, and 1.11 and 1.23 × 10⁻⁴ mol dm⁻³. The arrows indicate the direction of absorbance change as [36βCD₂ur]total increases. Isosbestic points occur at 234.0, 276.0 and 284.5 nm.

**Fig. S10.** Absorbance variation of TNS⁻ with [36βCD₂ur]total at 260 nm under the same conditions as in Fig. S9. The solid curve represents the best fit obtained over the range 235-275 nm.

**Fig. S11.** Increase in the relative fluorescence of TNS⁻ (1.00 × 10⁻⁶ mol dm⁻³) with [βCD]total in the range 0, 4.35 and 7.50 × 10⁻⁵, and 1.07, 1.34, 1.79, 2.27, 2.97, 3.83, 4.82, 5.51, 6.50, 7.62, 8.76 and 9.98 × 10⁻⁴ and 1.11, 1.22, 1.37, 1.50, 1.68, 1.86, 2.06, 2.38, 2.72, 3.15, 3.60, 4.05, 4.50, 4.96, 5.40, 6.03, 6.75 and 7.49 mol dm⁻³. The excitation wavelength was 320 nm.
Fig. S12. The relative fluorescence increase of TNS\textsuperscript{−} with [\(\beta\text{CD}\)]\textsubscript{total} at 463 nm under the same conditions as in Fig. S11. The solid curve represents the best fit obtained over the range 400-500 nm.

Fig. S13. The relative fluorescence increase of TNS\textsuperscript{−} with [66\(\beta\text{CD}_2\text{ur}\)]\textsubscript{total} at 435 nm under the same conditions as in Fig. 5 in the text. The solid curve represents the best fit obtained over the range 400-500 nm.

Fig. S14. Increase in the relative fluorescence of TNS\textsuperscript{−} (1.00 \times 10^{-6} \text{ mol dm}^{-3}) in with [66\(\beta\text{CD}_2\text{su}\)]\textsubscript{total} in the range 0, 4.60 and 9.40 \times 10^{-6}, and 1.48, 2.10, 2.47, 3.09, 3.73, 4.42, 5.04, 5.83, 6.61, 7.39, 8.22 and 9.10 \times 10^{-5}, and 1.00, 1.12, 1.24, 1.37, 1.58, 1.80, 2.10, 2.40, 2.70, 3.00, 3.30, 3.61, 4.01, 4.50 and 5.00 \times 10^{-4} \text{ mol dm}^{-3}. The excitation wavelength was 320 nm.
**Fig. S15.** Relative fluorescence increase of TNS$^-$ with [66βCD$_{2su}$]$_{total}$ at 440 nm under the same conditions as in Fig. S14. The solid curve represents the best fit obtained over the range 400-500 nm.

**Fig. S16.** Increase in the relative fluorescence of TNS$^-$ (1.00 × 10$^{-6}$ mol dm$^{-3}$) with [36βCD$_{2su}$]$_{total}$ in the range 0, 4.90 and 9.80 × 10$^{-6}$, and 1.45, 2.01, 2.47, 3.08, 3.66, 4.26, 4.97, 5.75, 6.55, 7.33, 8.17, 9.16 and 9.96 × 10$^{-5}$, and 1.12, 1.24, 1.37, 1.58, 1.81, 2.11, 2.41, 2.70, 3.00, 3.30, 3.60, 4.00, 4.51 and 5.00 × 10$^{-4}$ mol dm$^{-3}$. The excitation wavelength was 320 nm.

**Fig. S17.** Relative fluorescence increase of TNS$^-$ with [36βCD$_{2su}$]$_{total}$ at 440 nm under the same conditions as in Fig. S16. The solid curve represents the best fit obtained over the range 400-500 nm.
Fig. S18. Increase in the relative fluorescence of TNS⁻ (1.00 × 10⁻⁶ mol dm⁻³) with [33βCD₂su]ₜotal in the range 0, 4.80 and 9.80 × 10⁻⁶, and 1.51, 2.02, 2.53, 3.12, 3.74, 4.23, 4.98, 5.86, 6.58, 7.40, 8.20, and 9.13 × 10⁻⁵, and 1.12, 1.24, 1.38, 1.50, 1.82, 2.11, 2.42, 2.73, 3.02, 3.32, 3.63, 4.51 and 5.02 × 10⁻⁴ mol dm⁻³. The excitation wavelength was 320 nm.

Fig. S19. Relative fluorescence increase of TNS⁻ with [33βCD₂su]ₜotal at 440 nm under the same conditions as in Fig. S18. The solid curve represents the best fit obtained over the range 400-500 nm.

Fig. S20. Increase in the relative fluorescence of TNS⁻ (1.00 × 10⁻⁶ mol dm⁻³) with [36βCD₂ur]ₜotal in the range 0, 2.00, 4.04, 6.12, 8.08, and 9.96 × 10⁻⁶, and 1.28, 1.48, 1.75, 2.02, 2.35, 2.64, 2.96, 3.28, 3.64, 3.99, 4.47, 4.97, 5.52, 6.38, 7.20, 8.42, and 9.65 × 10⁻⁵, and 1.20, 1.32, 1.44, 1.61, 1.81, and 2.00 × 10⁻⁴ mol dm⁻³. The excitation wavelength was 320 nm.
Fig. S21. Relative fluorescence increase of TNS\(^−\) with \([36\beta CD_2\text{ur}]_{\text{total}}\) at 440 nm under the same conditions as in Fig. S21. The solid curve represents the best fit obtained over the range 400-500 nm.

Fig. S22. 2D \(^1\text{H}\) ROESY NMR (600 MHz) spectrum of a D\(_2\)O solution equimolar at 2.00 × 10\(^{-3}\) mol dm\(^{-3}\) in TNS\(^−\) and 36\(\beta CD_2\text{su}\). The rectangles drawn on the spectrum, A and B, contain the cross-peaks arising from the NOE interactions between the annular H3, H5 and H6 protons of 36\(\beta CD_2\text{su}\) and the aromatic and methyl protons of TNS\(^−\), respectively.
**Fig. S23.** 2D $^1$H ROESY NMR (600 MHz) spectrum of a D$_2$O solution equimolar at 2.00 $\times$ 10$^{-3}$ mol dm$^{-3}$ in TNS$^-$ and 33βCD$_{2su}$. The rectangles drawn on the spectrum, A and B, contain the cross-peaks arising from the NOE interactions between the annular H3, H5 and H6 protons of 33βCD$_{2su}$ and the aromatic and methyl protons of TNS$^-$, respectively.

**Fig. S24.** 2D $^1$H ROESY NMR (600 MHz) spectrum of a D$_2$O solution equimolar at 2.00 $\times$ 10$^{-3}$ mol dm$^{-3}$ in TNS$^-$ and 66βCD$_{2ur}$. The rectangles drawn on the spectrum, A and B, contain the cross-peaks arising from the NOE interactions between the annular H3, H5 and H6 protons of 66βCD$_{2ur}$ and the aromatic and methyl protons of TNS$^-$, respectively.
Fig. S25. 2D $^1$H ROESY NMR (600 MHz) spectrum of a D$_2$O solution equimolar at 2.00 × 10$^{-3}$ mol dm$^{-3}$ in TNS$^-$ and 36βCD$_2$ur. The rectangles drawn on the spectrum, A and B, contain the cross-peaks arising from the NOE interactions between the annular H3, H5 and H6 protons of 36βCD$_2$ur and the aromatic protons of TNS$^-$.

Fig. S26. The energy minimized βCD.TNS$^-$ model structure of one of four possible isomers. The carbons of TNS$^-$ are shown in green for clarity.

Fig. S27. The energy minimized βCD$_2$.TNS$^-$ model structure of one of four possible isomers. The carbons of TNS$^-$ are shown in green for clarity.
**Fig. S28.** The energy minimized $36\beta$CDsu.TNS$^-$ model structure of one of two possible isomers. The carbons of TNS$^-$ are shown in green for clarity.

**Fig. S29.** The energy minimized $33\beta$CDsu.TNS$^-$ model structure. The carbons of TNS$^-$ are shown in green for clarity.

**Fig. S30.** The energy minimized $66\beta$CDur.TNS$^-$ model structure. The carbons of TNS$^-$ are shown in green for clarity.

**Fig. S31.** The energy minimized $36\beta$CDsu.TNS$^-$ model structure of one of two possible isomers. The carbons of TNS$^-$ are shown in green for clarity.
Fig. 32. The similar relative trends in $K_1$ and $K'_1$ for complexation of TNS$^-$ by $a$) $\beta$CD, $b$) 66$\beta$CD$_2$su, $c$) 36$\beta$CD$_2$su, $d$) 33$\beta$CD$_2$su, $e$) 66$\beta$CD$_2$ur, and $f$) 36$\beta$CD$_2$ur.

Figure S33. $^1$H NMR (300 MHz) spectrum of 36$\beta$CD$_2$ur in D$_2$O solution.

Figure S34. $^{13}$C NMR (300 MHz) spectrum of 36$\beta$CD$_2$ur in D$_2$O solution.