Supplementary Material (ESI) for Chemical Communications

Suppporting Information for Manuscript Entitled: Exploring the limits of encapsulation within hexameric pyrogallol[4]arene nano-capsules

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Information comprises:

- Materials and experimental methods
- ^{1}H NMR assignments for PgC_6:guest ratio
- Crystal data: Unit cell dimensions for the crystals containing encapsulated benzo[α]pyrene and pentacene
- Figures for modeling studies / calculations.

Materials and experimental methods

C-Hexylpyrogallol[4]arene was synthesized according to literature procedures.[5] Single crystal X-ray diffraction experiments were performed on a Bruker SMART 1000 CCD diffractometer operating with Mo Kα radiation at 173K.

^{1}H NMR assignments for PgC_6:guest ratio

Given that it was not possible to identify atomic positions for the encapsulated guest species (due to low capsule occupancies), 1H NMR on (washed and dried) single crystals dissolved in $CDCl_3$ was used to calculate the guest:capsule ratio although the integrals for the guest species were small. To arrive at a ratio, indicative peaks of B[α]P and pentacene have been used against the signal for the bridging methylene hydrogen signal of *C*-hexylpyrogallol[4]arene. Calibration of indicative peaks against the integral for the bridging methylene protons divided by 24 (number per nano-capsule) affords the guest:capsule ration. For pentacene, some peaks corresponding to the PAH have been shrouded by the larger and broader signals for PgC_6. Although the intensity of the signals for the pentacene in particular were very small, it is indicative that both molecular components are present in the crystalline material. Furthermore, given that *C*-hexylpyrogallol[4]arene crystallizes without room for co-crystallization of other species on the exterior of the capsules (as there are no solvent sites large enough to accommodate a pentacene molecule for example), and that the single crystals are strongly colored red (compared to colorless for 'guest-free'), we are confident that the probe molecules are encapsulated prior to dissolution of the crystals. This is supported by the fact that full data collection on these two crystals shows the typical structure of the acetonitrile solvate with no such voids present on the exterior of the assembly. Furthermore, both crystal types are strongly colored (organge and red for B[α]P and pentacene respectively).

^{1}H NMR of orange crystals of the host-guest arrangement, B[α]P⊂(*C*-hexylpyrogallol[4]arene)$_6$.

δ_H ($CDCl_3$) 500 MHz: 9.06 (d, 2H, B[α]P Ar**H**), 8.77 (s, 336H, 336 × PgC_6 O**H**), 8.55 (s, 1H, B[α]P Ar**H**), 8.31 (d, 1H, B[α]P Ar**H**), 8.28 (d, 1H, B[α]P Ar**H**), 8.24 (d, 1H, B[α]P Ar**H**), 8.10

(d, 1H, B[α]P Ar**H**), 8.00 (t, 2H, B[α]P Ar**H**), 7.93 (d, 1H, B[α]P Ar**H**), 7.81 (m, 2H, B[α]P Ar**H**), 7.46 (s, 334H, 334 × PgC_6 O**H**), 6.88 (s, 334H, 334 × PgC_6 Ar**H**), 6.83 (s, 334H, 334 × PgC_6 O**H**), 4.37 (t, 334H, 334 × PgC_6 Ar-C**H**-Ar), 2.24 (m, 668H, 334 × PgC_6 ArCHC**H_2**), 1.43 (m, 668H, 334 × PgC_6 $ArCHCH_2C$**H_2**), 1.34 (m, 2004H, 1002 × PgC_6 $ArCHCH_2CH_2C$**$H_2C H_2C H_2$**), 0.90 (t, 1002H, 334 × PgC_6 C**H_3**).

Calculation of occupancy: 336H / 24H = 13.91 (~14)

^{1}H NMR of deep red crystals of the host-guest arrangement, Pentacene⊂(*C*-hexylpyrogallol[4]arene)$_6$.

δ_H ($CDCl_3$) 300MHz: 9.25 (s, 4H, Pent Ar**H**), 8.49 (m, 4H, Pent Ar**H**), 8.80 (s, 968H, 968 × PgC_6 O**H**) 7.49 (s, 600H, 600 × PgC_6 O**H**), 6.90 (s, 968H, 968 × PgC_6 Ar**H**), 6.87 (s, 968H, 968 × PgC_6 O**H**), 4.39 (t, 968H, 968 × PgC_6 Ar-C**H**-Ar), 2.27 (m, 1936H, 968 × PgC_6 ArCHC**H_2**), 1.46 (m, 1936H, 968 × PgC_6 $ArCHCH_2C$**H_2**), 1.34 (m, 5808H, 1800 × PgC_6 $ArCHCH_2CH_2C$**$H_2C H_2C H_2$**), 0.93 (t, 2904H, 968 × PgC_6 C**H_3**).

Calculation of occupancy: 968H / 24H = 40.33 (~40)

Crystal data

Unit cell dimensions for orange crystals containing encapsulated benzo[α]pyrene:

Triclinic, a = 19.321(6), b = 22.389(6), c = 23.150(7) Å, α = 69.791(6), β = 70.068(5), γ = 72.049(5) °, U = 8626(8) Å^3.

Unit cell dimensions for deep red crystals containing encapsulated pentacene:

Triclinic, a = 19.556(6), b = 22.629(8), c = 23.596(8) Å, α = 69.289(6), β = 69.594(7), γ = 72.031(6) °, U = 8948(9) Å^3.

These cell dimensions (and subsequent structural solutions) show that these crystals are isostructural to the acetonitrile solvate of PgC_6. Due to the low capsule occupancies, it was not possible to resolve the positions of the guest species within the electron density map. As no structural information can be gained from these studies, only unit cell dimensions are reported. Unit cell dimensions for the acetonitrile solvate of PgC6 are as follows: Triclinic, a = 19.573(3), b = 22.624(4), c = 23.425(4) Å, α = 69.761(3), β = 69.973(3), γ = 71.867(3) °, U = 8922(3) Å^3.

Figures for modeling studies / calculations

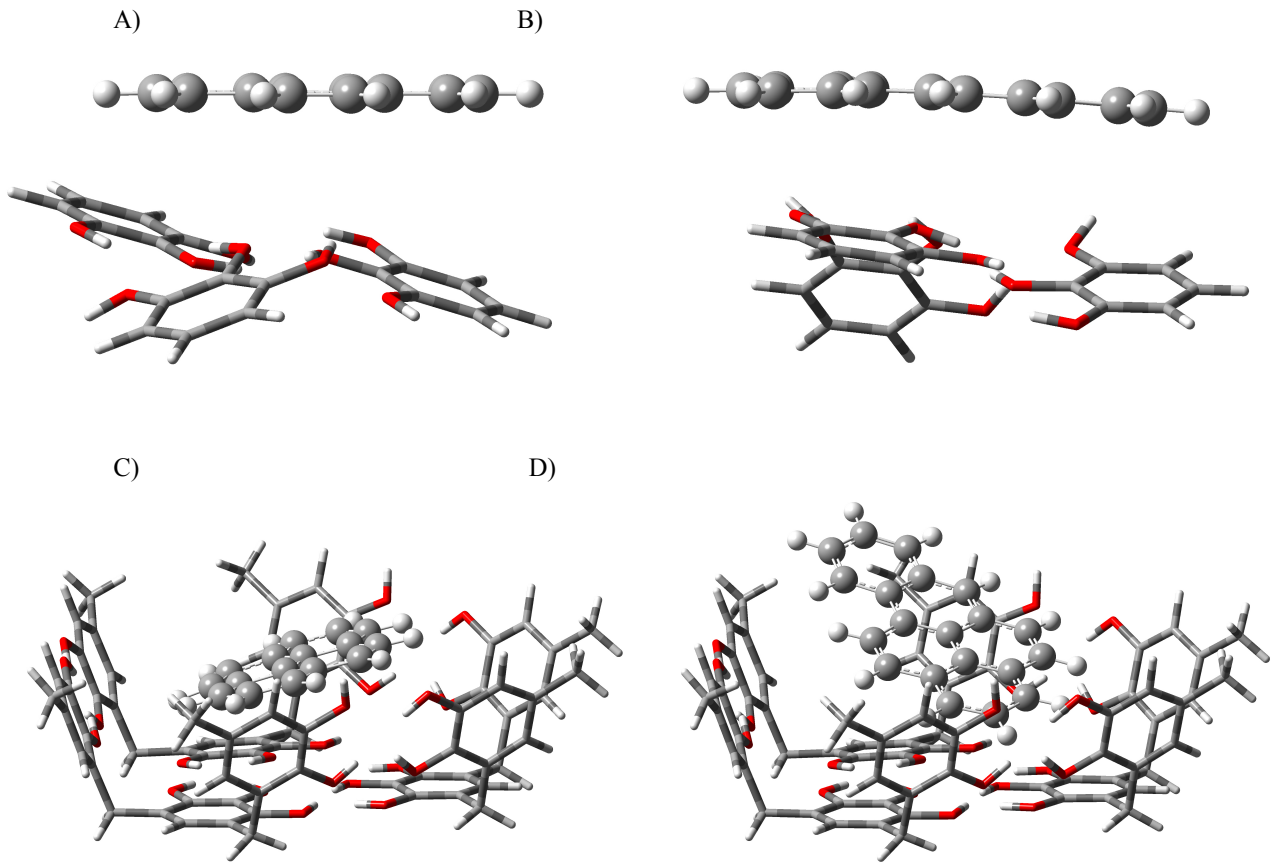

Figure S1. Views of a) the pyrene - wall segment; b) the benzo[α]pyrene - wall segment; c) the pyrene – half nano-capsule; d) the benzo[α]pyrene – half nano-capsule.