Supporting Information

Organic multishell isostructural host-guest crystals: fullerenes C_{60} inside a nitroxide open framework.

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Chemicals. bTbk was obtained as described in reference number 1.[1] Toluene (ACS reagent) and 1-chloronaphthalene (1-ClN, technical grade) were from Aldrich. One batch of C_{60} (99.9%) was from ACROS and another batch from TCI (purity >99.0%).

Crystal growth. The 1-ClN solvates were simply grown from slow cooling of hot supersaturated **bTbk** solutions in 1-ClN. For multishell crystals, the same procedures as that of the mere crystals were followed gently positioning the relevant crystals at the bottom of preliminary prepared mother liquors just prior to slow cooling to room temperature. In this case, the temperature of the mother liquor did not exceed 50°C for the 1-ClN solution and 75°C for the C_{60} saturated 1-ClN solution.

Single crystal XRD. All crystals (unit cell parameters and full experiments) were measured on a Bruker-Nonius KappaCCD diffractometer with the Mo(Kα) radiation. Data reductions were done with denzo-SMN, structures solved by direct methods and refined with Shelxl97.

Powder X ray diffraction. XRD (X-ray diffraction) patterns on powders were recorded on a Siemens D500R XRD diffractometer using Cu Kα radiation in the 5-40° 2θ range with a 0.04° step associated with a step time of 1s.

Raman spectroscopy. Raman spectra were obtained using a Horiba-Jobin-Yvon HR LabRAM apparatus (laser wavelength: λ = 514.5 nm, 100X objective, probed surface ~1 μm^2, spectral resolution ~ 1 cm^{-1}). Powders were deposited on slides. Spectra were taken on the thickest regions of the samples to have enough matter to probe. The laser power was chosen at P ~ 2 or ~ 0.2 $mW.\mu m^{-2}$ to have a good signal to noise ratio or to prevent damages. To check repeatability, spectra were recorded several times at the same spot location.

UV spectroscopy. UV-vis spectra were recorded on a Varian Cary 50 scan spectrophotometer from 200 to 800 nm with a data interval of 0.5 nm in the dual beam mode.

Channels and voids rendering. The periodically constricted channels of the **bTbk** solvates were constructed using ATOMS based on the toluene solvate crystal structure for which the solvent was artificially removed, allowing a sphere of a given diameter to slide along the channels (settings: grid spacing, 0.2 Å, unit cell values of 2, 2, 2 along a, b and c, particle radius: 1.2 Å). This process was used to provide a general view of the 1D channels consisting of aligned large pockets separated by small constrictions.

Elemental analysis. Analyses were performed using a Flash EA analyser, 1112 series Thermo Finnigan driven by the Eager 300 software (oven temperature: 970°C, gas: helium, flow rate: 140 mL/min, detector: catharometer).

Calculated assuming a **bTbk**/cavity ratio of 3/1 given by single crystal XRD. Found (Calculated):
bTbk/C_{60}/toluene (3/0.05/4.8), C 70.41 (70.46), H 9.07 (8.87), N 4.63 (4.67).
bTbk/C_{60}/1-ClN (3/0.18/3.1), C 68.00 (68.04), H 7.40 (7.30), N 4.18 (4.30).

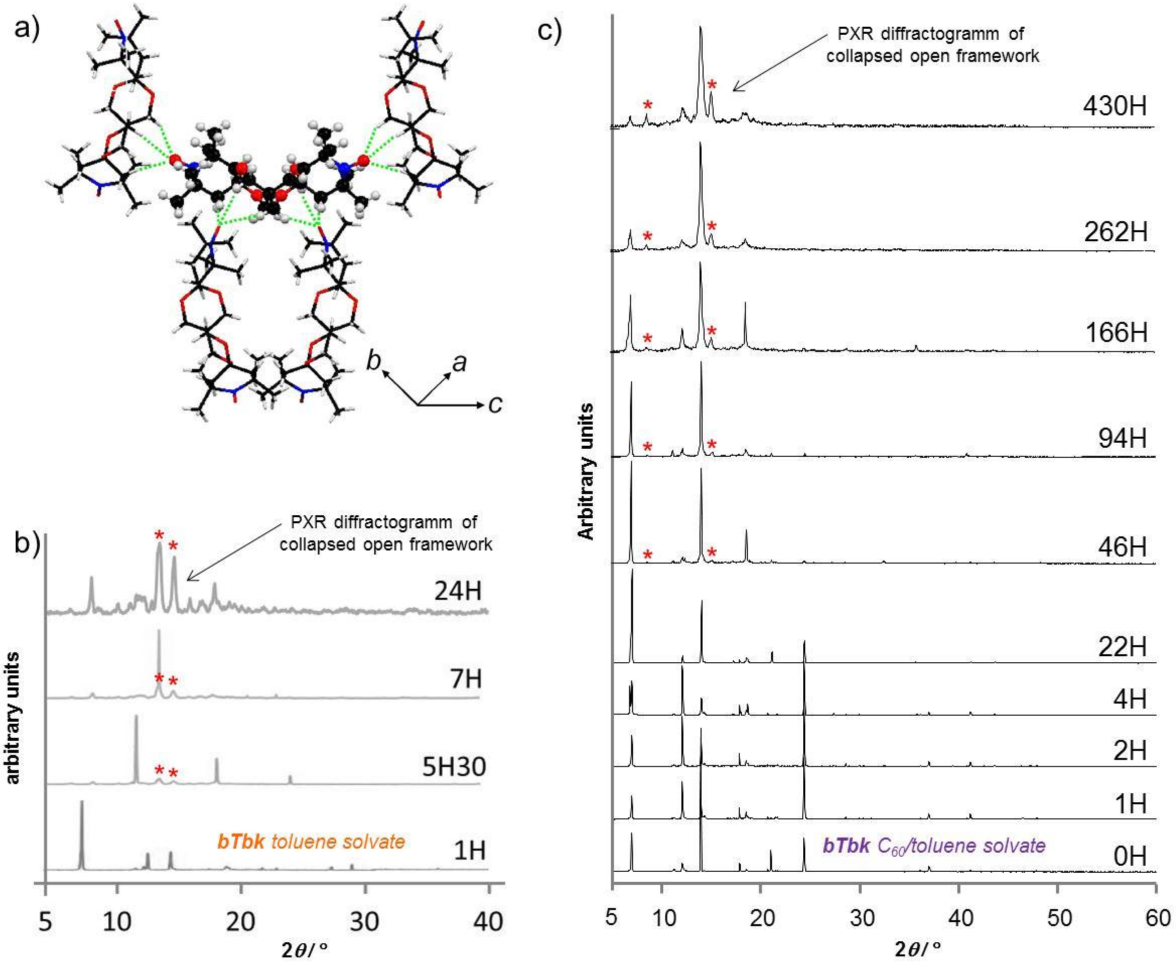

Figure S1. (a) Interplay of 12 hydrogen bonds within **bTbk** in the open framework single crystals; (b) and (c) respectively show the time evolution of the PXRD patterns of the toluene solvate of **bTbk** and the toluene solvate of **bTbk** containing C_{60} fullerenes.

There are 12 CH•••˙ON non classical H bonds per molecule of **bTbk**, four of which are considered as strong whereas the eight others are weaker.[2] In Figure S1(b), one can easily see the collapse of the open framework (red stars illustrate the main reflections of the collapsed dense phase starting to be seen around 5 hours after air exposure). Figure S1(c) shows the same trend spread over time with clear signs of dense phase occurring at only 46 hours after air exposure. One can see that all reflections are basically unaffected (except subtle intensity changes) over the first 22 hours. We assign this behavior to the C_{60} molecules that likely imped toluene escape from the channels because they tightly fit to the 1D pockets.

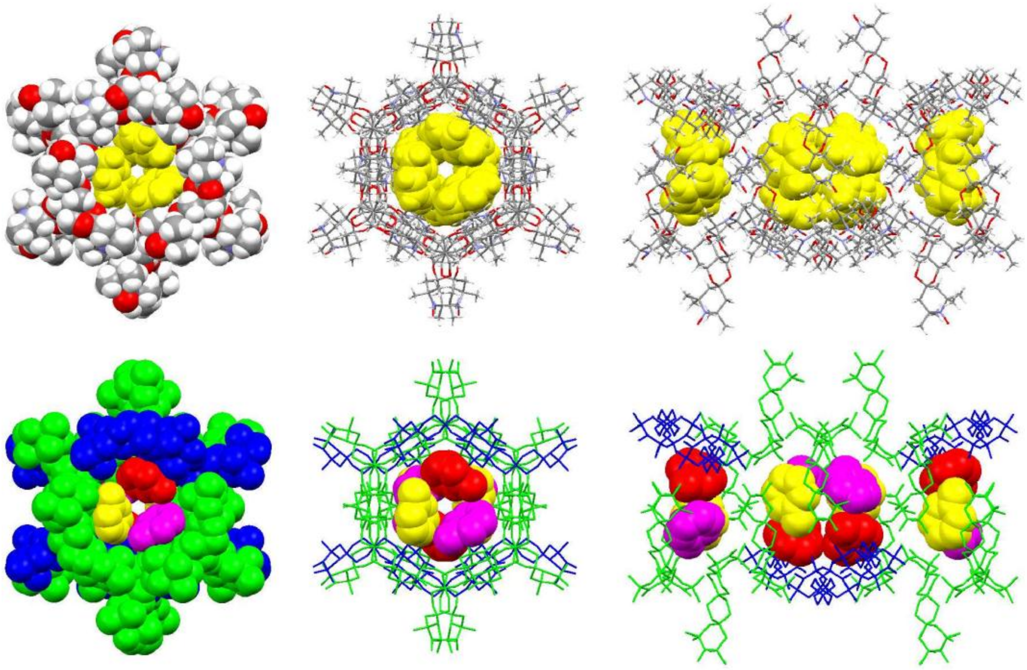

Figure S2. Additional views of the channel structure of the toluene solvate of **bTbk**.

Symmetry expansion of the asymmetric unit shows the hexagonal symmetry of the structure with pockets along the 1D channels that are filled with molecules of solvent (toluene). Concerning guest positioning, none of the 16 determined structures allowed to precisely locate molecules in the channels except the one with toluene. Moreover, a finest description of their orientation within the channels was tentatively explored by recording X ray data on a single crystal at 100K. This shows some molecule ordering causing the unit cell to double in size as compared to the one recorded at 293 K (present work). These results will be reported in a future full article.

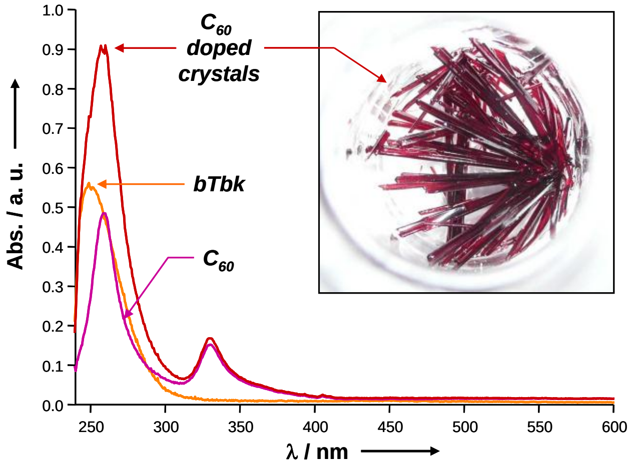

Figure S3. UV-vis spectra of the dissolved red C_{60} doped crystals, **bTbk** and C_{60} in $CHCl_3$. The inset shows a batch of wet C_{60} doped crystals grown from toluene.

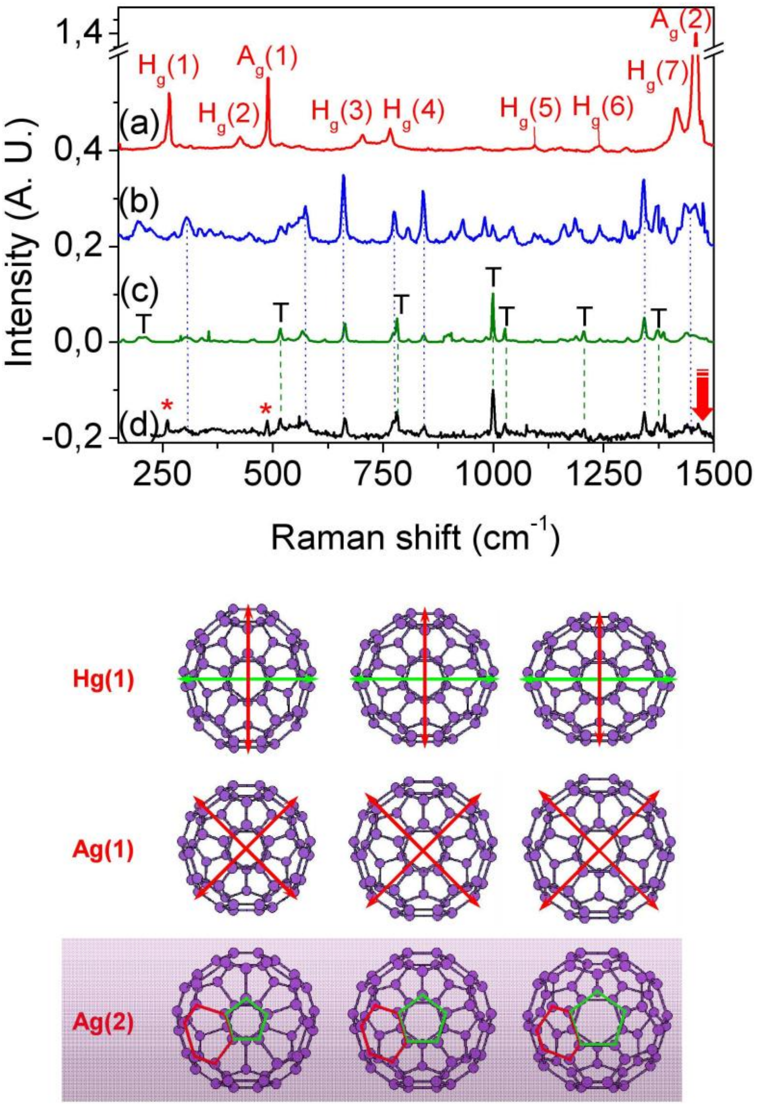

Figure S4. Raman spectra recorded with λ=514.5 nm for (a) C_{60}, (b) **bTbk**, (c) **bTbk** crystals filled by toluene, (d) **bTbk** crystal filled by toluene and C_{60}.

Figure S4 shows Raman spectra of respectively (a) C_{60}, (b) **bTbk** crystals unfilled, (c) **bTbk** crystals filled by toluene and (d) **bTbk** crystals filled by toluene and C_{60} in the spectral range 250-1500 cm^{-1}. The vibrational spectrum of a free C_{60} contains 46 degenerated modes. From these, only two A_g and eight H_g modes are Raman active.[3] Spectrum (a) of Figure S4 displays them. The band related to the $A_g(2)$ mode at 1460 cm^{-1}, called the tangential mode, is the more intense. This is due to an electronic resonance effect using a laser with λ=514.5 nm.[4] The band related to the $A_g(1)$ mode at 489 cm^{-1}, called the radial mode, and the $H_g(1)$ mode at 266 cm^{-1}, called the squashing mode, are less intense by a factor of ≈ 10. Other bands are weaker by nearly another order of magnitude. Figure S4 (b) displays the Raman spectrum of **bTbk**. More than 30 bands are evidenced in the spectral region studied. Hopefully three bands are more intense and are situated at 1342, 840 and 660 cm^{-1}. Slightly weaker bands are situated at 1447, 777, 572 and 306 cm^{-1}. In the spectral range of Figure S4, the Raman spectrum of toluene is dominated by two bands at 1004 and 786 cm^{-1}. Other intense bands are situated at 1379, 1208, 1030, 521 and 216 cm^{-1}.[5] These frequencies have been marked by a "T" in Figure S4. The Raman spectrum of **bTbk** crystals filled by toluene is the superposition of the toluene and **bTbk** spectra. Finally the Raman spectrum of **bTbk** crystals filled by toluene and C_{60} looks like the spectrum of Figure S4 (c) with two additional bands, marked by stars, which are related to the $A_g(1)$ and $H_g(1)$ vibrational modes of C_{60}. One has to note that the band related to the $A_g(2)$ vibrational mode of C_{60} is not visible.

It is known that interaction between C_{60} and a solvent is revealed by the presence in the Raman spectrum of induced bands resulting from a lowering of the symmetry.[6] In the case of C_{60} in toluene, it is known that a band is situated at 1140 cm^{-1}, and is as high as the band related to the $A_g(1)$ mode. In the spectrum (c) of Figure S4, this band has not been detected, meaning that the coupling between C_{60} and toluene filling **bTbk** crystal is weak or absent.

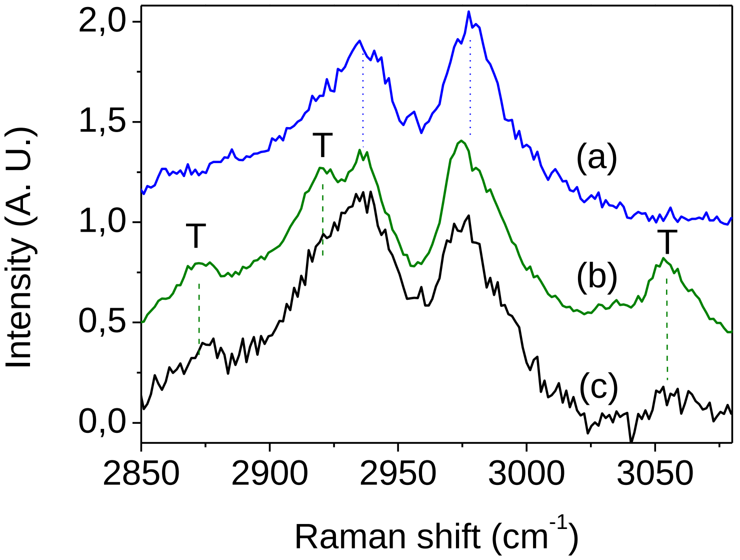

Figure S5. Raman spectra recorded with λ=514.5 nm for (a) **bTbk**, (b) **bTbk** crystal filled by toluene (T letter), (c) **bTbk** crystal filled by toluene and C_{60}.

Figure S5 displays three Raman spectra in the spectral range 2850-3080 cm^{-1} involving respectively (a) **bTbk** alone, (b) **bTbk** crystals filled by toluene and (c) **bTbk** crystals filled by both toluene and C_{60}. The Raman spectrum of **bTbk** crystal displays two strong bands at 2978 and 2936 cm^{-1}. The Raman spectrum of **bTbk** crystals filled by toluene is composed by these two bands plus 3 other bands situated at 3050, 2930 and 2870 cm^{-1} which are attributed to toluene, according to ref[5] (marked by a “T” on Figure S5). The Raman spectrum of **bTbk** crystals filled by toluene and C_{60} also displays these bands. Then the introduction of C_{60} does not modify the bondings involved.

As concerning the Raman spectra in the regions 250-1500 cm^{-1} and 2850-3080 cm^{-1}, we conclude that filling **bTbk** crystals with toluene does not modify the bondings of these two molecules. When adding C_{60}, this is still true for **btbk** and toluene.

***Table S1_a.* Crystal data and structure refinement parameters for the bTbk C$_{60}$ toluene solvate.**

Before and after Squeeze (very high guest disordering)

Identification name	**bTbk toluene C$_{60}$**	**bTbk toluene C$_{60}$_sqz**
CCDC number	927969	927970
Empirical formula	$C_{11.5} H_{20} N_1 O_3$	
Formula weight	220.29	
Temperature	293(2) K	
Wavelength	0.71073 Å	
Crystal system	trigonal	
Space group	R-3c	
Unit cell dimensions	a = 25.1752(7) Å	
	c = 30.0006(5) Å	
Volume	16466.7(7) Å^3	
Z	36	
Density (calculated)	0.800 Mg/m^3	
Absorption coefficient	0.057 mm^{-1}	
F(000)	4320	
Crystal size	0.3 × 0.3 × 0.25 mm^3	
Theta range for data	1.62 to 28.24°	
Index ranges	0<h<33, -28<k<0, -38<l<37	
Reflections collected	8536	
Independent reflections	4431	
Completeness to theta =	97.6%	
Refinement method	Full-matrix least-squares on	
Data / restraints / parameters	4431 / 0 / 141	
Goodness-of-fit on F2	1.532	1.037
Final R indices [I>2sigma(I)]	R1 = 0.1355, wR2 = 0.3915	R1 = 0.0742, wR2 = 0.2537
R indices (all data)	R1 = 0.2020, wR2 = 0.4360	R1 = 0.1172, wR2 = 0.2886
Largest diff. peak and hole	1.036 and -0.379 e.Å^{-3}	0.28 and -0.219 e.Å^{-3}

Table S1_b. **Crystal data and structure refinement parameters for the bTbk C_{60}-1-ClN solvate. Before and after Squeeze** (very high guest disordering)

Identification name	**bTbk C_{60}-1-ClN**	**bTbk C_{60}-1-ClN_sqz**
CCDC number	927971	927972
Empirical formula	$C_{11.5} H_{20} N_1 O_3$	
Formula weight	220.29	
Temperature	293(2) K	
Wavelength	0.71073 Å	
Crystal system	trigonal	
Space group	R-3c	
Unit cell dimensions	a = 25.1890(8) Å	
	c = 30.1466(6) Å	
Volume	16565.0(8) Å^3	
Z	36	
Density (calculated)	0.795 Mg/m^3	
Absorption coefficient	0.057 mm^{-1}	
F(000)	4320	
Crystal size	0.7 × 0.5 × 0.3 mm^3	
Theta range for data	1.62 to 28.23°	
Index ranges	0<h<33, -28<k<0, -38<l<37	
Reflections collected	8470	
Independent reflections	4419	
Completeness to theta =	97.1%	
Refinement method	Full-matrix least-squares on	
Data / restraints / parameters	4419 / 0 / 141	
Goodness-of-fit on F2	1.763	1.142
Final R indices [I>2sigma(I)]	R1 = 0.1572, wR2 = 0.4459	R1 = 0.0915, wR2 = 0.3019
R indices (all data)	R1 = 0.2195, wR2 = 0.4854	R1 = 0.1353, wR2 = 0.337
Largest diff. peak and hole	1.085 and -0.448 e.Å^{-3}	0.312 and -0.25 e.Å^{-3}

Squeeze calculations and estimation of the guests disorder. The Squeeze procedure[7] can be applied to crystal structures in some cases in order to artificially correct the data from unobserved disordered molecules. It estimates the voids within the crystals in terms of volume and residual unassigned electron densities. The SQUEEZE output for the **bTbk**/C_{60}-toluene and **bTbk**/C_{60}-1-ClN host/guest complexes are reported in Table S2.

Table S2. **SQUEEZE outputs for crystals of bTbk/C_{60}-toluene (left) and bTbk/C_{60}-1-ClN (right).**

```
loop_
  _platon_squeeze_void_nr
_platon_squeeze_void_average_x
_platon_squeeze_void_average_y
_platon_squeeze_void_average_z
_platon_squeeze_void_volume
_platon_squeeze_void_count_electrons
_platon_squeeze_void_content
1  0.000  0.000 -0.001      2312      723 ' '
2  0.333  0.667  0.261      2297      722 ' '
3  0.667  0.333  0.427      2297      722 ' '
```

```
loop_
  _platon_squeeze_void_nr
_platon_squeeze_void_average_x
_platon_squeeze_void_average_y
_platon_squeeze_void_average_z
_platon_squeeze_void_volume
_platon_squeeze_void_count_electrons
_platon_squeeze_void_content
1  0.000  0.000 -0.001      2363      957 ' '
2  0.333  0.667  0.263      2344      955 ' '
3  0.667  0.333  0.427      2344      955 ' '
```

The estimation of the contents of the cavities in each crystal was performed as follow. Regardless of the crystal, a first look at the shape of the three voids calculated by SQUEEZE revealed that they form channels along the c-axis (Figure S6). Each of these channels is itself constituted of two cavities - the ones containing the guests molecules - connected by two smaller spaces probably expandable in order to facilitate the diffusion of solvent molecules in the open framework.

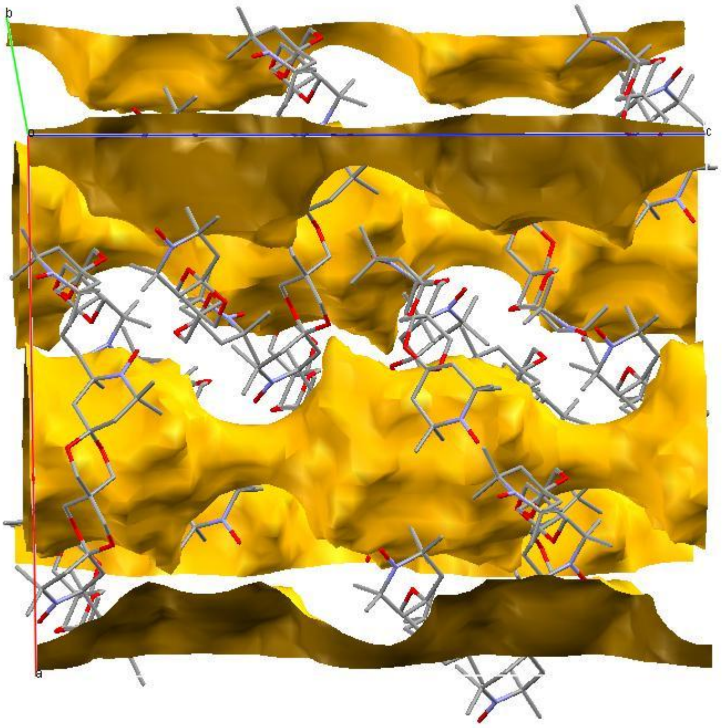

Figure S6. Representation of the voids forming channels along the the c-axis for **bTbk**/C_{60}-toluene.

The volume and electrons content of one cavity (the guest part of the host/guest complex we were interested in) could therefore be crudely estimated from SQUEEZE by subtracting from one void (e.g. one channel at x=0, x=0.333 or x=0.667) the volume and count electrons of the two connecting spaces and then halving the remaining volume and count electrons. The challenge was then to estimate the connecting space volume and electrons content. For that purpose we went back to the structure of our **bTbk**/toluene crystal published earlier[8] in which the solvent fills the cavities. The SQUEEZE calculations revealed that despite the presence of solvent, some voids remained in the crystal structure, and more particularly the spaces connecting the guests cavities as for **bTbk**/C_{60}/toluene or **bTbk**/C_{60}/1-ClN (see the SQUEEZE output below and Fig. S7). Hereafter we call that remaining voids "background".

```
loop_
_platon_squeeze_void_nr
_platon_squeeze_void_average_x
_platon_squeeze_void_average_y
_platon_squeeze_void_average_z
_platon_squeeze_void_volume
_platon_squeeze_void_count_electrons
_platon_squeeze_void_content
1  0.000  0.000  0.000      79      12 ' '
2  0.000  0.000  0.250      67      28 ' '
3  0.000  0.000  0.500      79      12 ' '
4  0.000  0.000  0.750      67      28 ' '
5  0.333  0.667  0.167      78      12 ' '
6  0.333  0.667  0.417      65      28 ' '
7  0.333  0.667  0.667      78      12 ' '
8  0.333  0.667  0.917      65      28 ' '
9  0.667  0.333  0.083      65      28 ' '
10  0.667  0.333  0.333      78      12 ' '
11  0.667  0.333  0.583      65      28 ' '
12  0.667  0.333  0.833      78      12 ' '
```

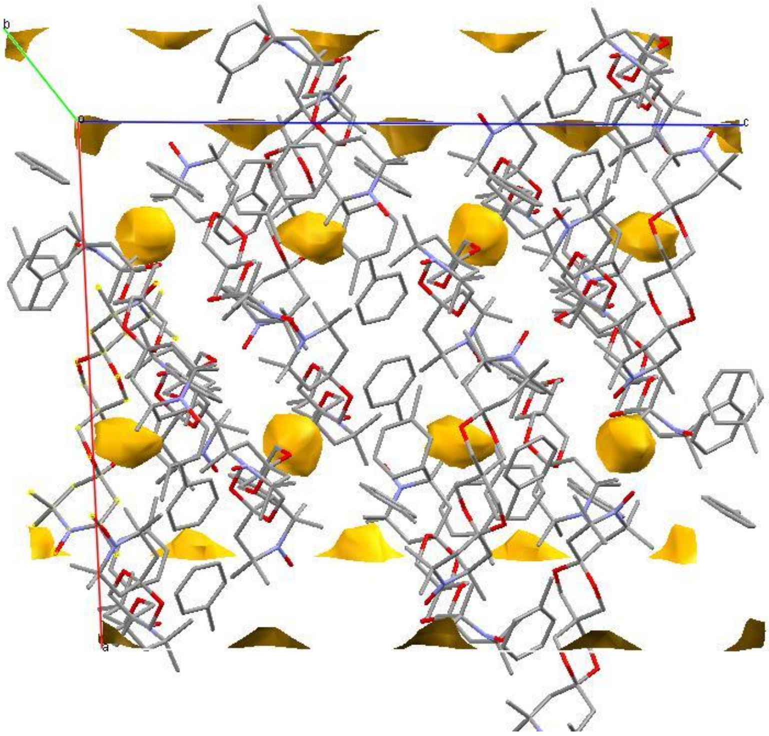

***Figure S7*.** Representation of the small voids in the host/guest complex **bTbk**/toluene.

This background could therefore be used as a crude estimation of the values to subtract from the voids calculated by SQUEEZE for our two other compounds of interest. The background for the volume is then equal to 2*79 Å^3 + 2*67 Å^3 = 292 Å^3 (calculated for the channel at coordinate x=0, the values being more or less the same for the two other channels). The background for the electrons content is equal to 2*12 + 2*28 = 80 electrons.

To summarize the concept we can write the following equation used to estimate the properties of one empty cavity (e.g. estimation of its volume in the case of the **bTbk**/C_{60}/toluene crystal) considering one of the 3 channels (x=0, x=0.333 or x=0.667): cavity$_{vol}$(**bTbk**/C_{60}-toluene) = [void$_{vol}$(**bTbk**/C_{60}-toluene) – void$_{vol}$(**bTbk**/toluene)]/2.
From that equation the volume of the cavity for our host/guest complexes was calculated and rounded to 1000 Å^3 for both cavities, and the electrons count rounded to 320 and 435 electrons for **bTbk**/C_{60}/toluene and **bTbk**/C_{60}/1-ClN respectively.

On that basis we then tried to estimate the nature and the number of solvent molecules able to fit within such a cavity in terms of total volume and electron counts, in correlation with the experimental data from the elemental analysis and the number of unassigned electrons found by SQUEEZE.
The van der Waals volume for C_{60}, toluene and 1-ClN can be approximate to 570 Å^3, 160 Å^3 and 180 Å^3 respectively and the number of electrons is equal to 360, 50 and 87 for C_{60}, toluene and 1-ClN respectively.
For **bTbk**/C_{60}/toluene : one cavity (1000 Å^3) can contain one C_{60} (570 Å^3) + 2 toluenes (320 Å^3) or 6 toluenes (960 Å^3) as in the case of the crystal **bTbk**/toluene (which 6 toluenes have been localized experimentally). The elemental analysis revealed a ratio C_{60}/toluene equal to 0.05/4.8. That composition can only be achieved if we consider a disorder of packing within the crystal where the cavity of one unit cell among 10 contains 1 C_{60} + 2 toluenes and the cavities of the remaining 9 unit cells contain 6 toluenes each. Indeed the mean ratio C_{60}/toluene among 10 unit cell is 1/56, (which correspond to 0.08/4.8) that is compatible with the elemental analysis, but also compatible with the volume of the cavity deduced from our

calculations ([(570 + 2*160) + 9*(6*160)]/10 = 953 Å^3) and also the number of electrons estimated ([(360 + 2*50) + 9*(6*50)]/10 = 316 electrons).

Following the same procedure for our host/guest complex **bTbk**/C_{60}/1-ClN we estimated that the composition of the cavities could be modelled by a disorder of packing among four unit cells: the cavity in one unit cell contains one C_{60} and two 1-ClN, the remaining three unit cells contain five 1-ClN each. The mean C_{60}/1-ClN ratio is then 1/16 or 0.18/3 which is compatible with the elemental analysis and the estimated volume of the cavity ([(570 + 2*180) + 3*(5*180)]/4 = 907 Å^3) and the number of electrons ([(360 + 2*87) + 3*(5*87)]/4 = 459 electrons).

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