Supporting Information for:

Dynamics in Flexible Pillar[n]arenes Probed by Solid-state NMR

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S1. Synthesis scheme for perethylated pillar[n]arenes (n = 5, EtP5; n = 6, EtP6)

EtP5 and EtP6 were synthesised by reaction of 1,4-diethoxybenzene with paraformaldehyde in the presence of boron trifluoride diethyl etherate followed by separation from the other pillar[n]arenes, EtPn, by column chromatography (Scheme S1).1 EtP5-α was obtained by recrystallisation from tetrahydrofuran followed by a drying step while EtP6-β was prepared by heating the as synthesis EtP6. Subsequently, both pX@EtP6 and mX@EtP6 were prepared using the solid-vapour diffusion method and oX@EtP6 via solvent evaporation as recently published.2 The PXRD patterns of all materials are given in Figure S1 and agree with the reported ones.2

Scheme S1. Synthesis of perethylated pillar[n]arenes from 1,4-diethoxybenzene and paraformaldehyde.1 The perethylated pillar[n]arenes were purified by column chromatograph to separate EtP5 and EtP6. The crystal structures of the pillar[n]arenes (5 and 6) are denoted by ‘ball and stick’ models, with carbons shown in grey, oxygens in red and protons omitted for clarity. Resulting yields obtained via this synthesis method are also given.1
2. Powder X-ray diffraction (PXRD) data

![Graphs of PXRD patterns for different samples](image)

Figure S1. Powder XRD patterns of (a) EtP5-α, (b) EtP6-β, (c) pX@EtP6, (d) mX@EtP6 and (e) oX@EtP6. Experimental and simulated data from single crystal structure data\(^2\) are given in black and grey lines, respectively. Data were collected in transmission mode on samples held on thin Mylar film in aluminium well plates on a Panalytical X’Pert PRO MPD equipped with a high throughput screening XYZ stage, X-ray focusing mirror, and PIXcel detector, using Ni-filtered Cu Kα radiation of wavelength 1.5406 Å. All PXRD patterns are consistent with those previously published in the literature.\(^2\)
S3. Differential Scanning Calorimetry (DSC) data

**Figure S2.** DSC thermogram of EtP6-β showing a phase transition from triclinic P\(\overline{1}\) to a metastable, triclinic P\(\overline{1}\) state with higher symmetry at 339 K (dashed line).\(^2\) Data were collected using a TA Instruments Discovery DSC with the following heat treatment: equilibrate to 298 K, then ramp to 303 K at 10 K per minute, then cooled back to 188 K and ramped again to 303 K.

**Figure S2** above shows a phase change of EtP6-β when being heated at 339 K. This confirms the phase change observed in the NMR data at 353 K.
S4. ThermoGravimetric Analysis (TGA) data

Figure S3. TGA data of \textit{mX@EtP6}. The data showed a 8\% weight loss that is consistent with the loss of one mole of \textit{meta}-xylene between 35 and 91 °C.\textsuperscript{2} Data were collected using a TA instrument Q5000IR analyzer with an automated vertical overhead thermobalance. \textit{mX@EtP6} was heated at a rate of 10 °C/min, under a dry nitrogen gas flow.
Figure S4. TGA data of oX@EtP6. The data showed a 9% weight loss that is consistent with the loss of one mole of ortho-xylene between 67 and 99 °C. Data were collected using a TA instrument Q5000IR analyzer with an automated vertical overhead thermobalance. oX@EtP6 was heated at a rate of 10 °C/min, under a dry nitrogen gas flow.
S5. NMR pulse programs

Figure S5. NMR pulse sequences used in this work. (a) Cross polarisation (CP) pulse sequence. (b) $^1$H saturation recovery pulse sequence to measure $^1$H $T_1$ times. $t_{sd}$ is the saturation delay between $\pi/2$ pulses and was set to 10 ms at 9.4 T or 1 ms at 14.1 T. $\tau$ is the polarisation build-up time. (c) $^{13}$C Torchia pulse sequence$^{25}$ to measure the $^{13}$C $T_1$ times. $\tau$ is the polarisation recovery delay. (d) Proton Detected Local Field (PDLF) experiment using the windowed sequence (wPDLF)$^3$ that correlates the $^{13}$C isotropic chemical shifts in $\omega_2$ with the $^{13}$C $^1$H dipolar coupling spectra in $\omega_1$. wR18$^5_2$ recouples the heteronuclear dipolar interaction during the rotor synchronised evolution period $t_1$ (while suppressing $^1$H $^1$H homonuclear dipolar couplings) to enable observation of $^{13}$C $^1$H dipolar spectra. The wR18$^1_1$ blocks also recouple the heteronuclear dipolar interaction to enable $^1$H to $^{13}$C polarisation transfer using the PRESTO sequence. SPINAL64 heteronuclear decoupling$^6$ was used during all $^{13}$C acquisition.
S6. Scaling factor determination

Recoupling sequences to reintroduce heteronuclear dipolar coupling $d_{CH}$ such as the R symmetry class\textsuperscript{5-8} used in this work results in an effective dipolar coupling constant $d^{R}_{CH}$ according to:

$$d^{R}_{CH} = \kappa_R d_{CH}$$  \hspace{1cm} (S1)

where $\kappa_R$ is the scaling factor of the recoupling sequences. Whilst this can often be determined numerically,\textsuperscript{5} this is beyond the scope of this work for the wR18\textsuperscript{5,2} block used and we have instead used a robust experimental method to determine $\kappa_R$ from a wR18\textsuperscript{5,2} PDLF experiment (Figure S5(d)) on model D-alanine as a reference. The corresponding $^{13}$C CP NMR, 2D PDLF and site specific $^{13}$C $^1$H dipolar spectra are shown in Figure S6 from which $d^{R}_{CH}$ could be determined from the outer singularities (see Experimental Section) of the $^{13}$C $\alpha$ carbon ($d^{R}_{CH} = -7.55$ kHz, Table S1). Comparison with the $d_{CH}$ value (-23.14 kHz) obtained from equation 1 in the main text and the $\alpha$–carbon proton bond length (1.093 Å) determined from neutron diffraction\textsuperscript{9} affords:

$$\kappa_R = \frac{d^{R}_{CH}}{d_{CH}} = \frac{-7550}{-23140} = 0.326$$  \hspace{1cm} (S2)

![Figure S6](image_url)

Figure S6. (a) $^{13}$C CP MAS spectrum and chemical structure, (b) PDLF spectrum and (c) site-specific $^{13}$C $^1$H dipolar spectra of D-alanine. Spectral assignments are given in the figure. Data obtained at 298 K and 9.4 T. $d^{R}_{CH}$ is measured using the outer singularities of the dipolar coupling spectra. Vertical light grey lines in the dipolar coupling spectra indicate the static limit dipolar coupling constants $d_{CH}$.

Table S1. $^{13}$C NMR spectrum assignments, $^{13}$C isotropic chemical shifts and the motional averaged dipolar coupling obtained from the 2D PDLF spectrum of D-alanine shown in Figure S6 above.

| Assignment    | $^{13}$C $\delta_{iso}$/ppm | $d^{R}_{CH}$/kHz | $d_{CH}$/kHz |
|---------------|----------------------------|-----------------|--------------|
| CH$_3$        | 20.7                       | -2.45           | -7.50        |
| HCN$_2$NH$_3$ | 51.2                       | -7.55           | -23.10       |
| C$^\text{IV}$ | 178.1                      | -0.65           | -1.99        |
Figure S7. Comparison of the $^{13}$C $^1$H dipolar spectra for each resolved CH$_3$ resonance in EtP6-$\beta$. Data were obtained at 298 K and a magnetic field of 9.4 T. The corresponding $^{13}$C isotropic chemical shift ($\delta_{iso}$) is given next to each dipolar spectrum. Dashed lines indicate the average $<d_{\text{CH}}>$ = -7.2 kHz obtained from this data which also illustrate very small change between each dipolar spectrum ($\Delta<d_{\text{CH}}>$ = 1.0 kHz); hence, in this dataset $<d_{\text{CH}}>$ = -7.1 ± 0.5 kHz. Vertical light grey lines in the spectra indicate the static limit dipolar coupling constants $d_{\text{CH}}$. 
S7. $^{13}$C NMR spectra assignments

In $pX@EtP6$, each different carbon subgroups resonances in the EtP6 host consist of multiple peaks (Figure 2(c), Table S4) which number and integration are in agreement with the number of carbons in asymmetric unit cell (e.g., 6 for CH$_2$, 12 for OC$^{IV}$ etc),$^2$ while the para-xylene resonances can be mostly assigned based on their $\delta_{iso}$. There are spectral overlaps in the 124 - 136 ppm region between the quaternary CH$_2C^{IV}$ resonances of EtP6 host and the protonated CHs of para-xylene and the spectral assignment was performed with $^{13}$C-edited CP MAS spectra. Two distinguishable CH$_3$s, CHs and quaternary carbons resonances are observed for para-xylene in $pX@EtP6$ which is in agreement with the asymmetric unit cell of this phase. Likewise, the $^{13}$C NMR spectrum of $mX@EtP6$ (Figure S9 and Table S5) reveals one meta-xylene molecule per host in the asymmetric unit cell. We point out that the $^{13}$C resonances for meta-xylene in $mX@EtP6$ and meta-xylene in solution$^{10}$ are very close (less than 1.6 ppm), which strongly supports a limited effect on the chemical shielding of meta-xylene from EtP6 resulting from size exclusion (Figure 1(d)).

The $^{13}$C NMR spectrum of $oX@EtP6$ (Figure 2(e)) allows the observation of all different types of carbon in EtP6. However, the spectrum is more poorly resolved than those of $pX@EtP6$ and $mX@EtP6$, likely due to the lower crystallinity of this material (PXRD data in Figure S1), we only provide a tentative assignment for overlapping NMR resonances between ortho-xylene and the EtP6 host (Table S6). Notably, the short contact time $^{13}$C CP spectrum (Figure S10) only enables clear identification of the CHs originating from the ortho-xylene while its CH$_3$ resonance is not directly attributable. This resonance is likely shifted to a lower frequency than in $mX@EtP6$ and $pX@EtP6$ due to the increased shielding effect of the ortho-xylene methyl groups located in the centre of the cavity (Figure 1(e)) and is therefore expected to overlap with the CH$_3$ resonances of the ethyl group around 16 ppm.

The room temperature PDLF data on the three xylene adducts revealed observable dipolar coupling for the methyl groups and CHs of the xylenes as expected (Figures S20-S22 and Section S9 below), which combined with $^{13}$C-edited CP MAS spectra (Figures S8-S10), were used to aid spectral assignments, in particular by differentiating these CHs from the CH$_2C^{IV}$ resonances of EtP6 that appear in the same spectral region (Figures 2 and S16-S18).
Table S2. $^{13}$C NMR assignments for EtP5-$\alpha$ (Figure 2(a)) with isotropic chemical shifts $\delta_{\text{iso}}$ from deconvoluted data previously published,\textsuperscript{2} spin lattice relaxation times $T_1$ obtained, motional averaged dipolar coupling constants $<d_{\text{CH}}>\text{ and order parameters } <S_{\text{CH}}>\text{. Data obtained at room temperature and 9.4 T.}$

| Assignment | $^{13}$C $\delta_{\text{iso}}$/ppm | $T_1$/s | $<d_{\text{CH}}>/kHz$ | $<S_{\text{CH}}>$ |
|------------|---------------------------------|---------|---------------------|-----------------|
| CH\textsubscript{3} | 14.42, 15.13, 15.71, 16.22, 16.83 | | 1.7 ± 0.1, -7.2 ± 0.5 | 0.31 ± 0.03 |
| CH\textsubscript{2} | 28.01, 28.67, 29.63, 35.07, 37.53 | | 166 ± 49, -23.3 ± 0.8 | 1.01 ± 0.03 |
| OCH\textsubscript{2} | 61.16, 62.50, 63.22 | 44 ± 5 | -18.4 ± 0.7 | 0.79 ± 0.03 |
| CH | 111.78, 112.49, 112.76, 113.00, 113.35 | 246 ± 27 | -23.8 ± 0.8 | 1.03 ± 0.03 |
| CH\textsubscript{3}C	extsuperscript{v} | 127.12, 127.39, 127.75, 128.49, 129.44, 130.22, 130.65, 135.36 | 262 ± 56 | N/A\textsuperscript{a} | N/A |
| OC	extsuperscript{v} | 146.51, 148.30, 149.33, 150.12, 150.31, 151.16, 151.53, 152.56, 154.12 | 217 ± 33 | N/A | N/A |

\textsuperscript{a} Not Applicable.
Table S3. $^{13}$C NMR assignments for EtP6-β (Figure 2(b)) with isotropic chemical shifts $\delta_{\text{iso}}$ from deconvoluted data previously published, spin lattice relaxation times $T_1$ obtained via area integration, motional averaged dipolar coupling constants $<d_{\text{CH}}>$ and order parameters $<S_{\text{CH}}>$. Data obtained at room temperature and 9.4 T.

| Assignment | $^{13}$C $\delta_{\text{iso}}$/ppm | $T_1$/s | $<d_{\text{CH}}>$/kHz | $<S_{\text{CH}}>$ |
|------------|-----------------------------------|---------|----------------------|----------------|
| CH<sub>3</sub> | 14.25 14.52 15.00 15.36 15.75 15.99 16.30 17.03 | 2.4 ± 0.1 | -7.2 ± 0.5 | 0.31 ± 0.03 |
| CH<sub>2</sub> | 27.83 28.58 29.43 29.88 33.27 34.09 | 182 ± 34 | -22.4 ± 0.8 | 0.97 ± 0.03 |
| OCH<sub>2</sub> | 62.15 62.80 63.47 63.75 64.78 65.30 65.48 66.15 | 25 ± 2 | -18.1 ± 0.7 | 0.78 ± 0.03 |
| CH | 111.68 112.01 112.98 113.95 115.20 116.11 116.55 117.28 | 262 ± 27 | -23.9 ± 0.8 | 1.03 ± 0.03 |
| CH<sub>2</sub>C<sup>IV</sup> | 123.86 124.30 125.83 126.72 127.77 128.45 129.05 131.38 131.76 | 236 ± 26 | N/A<sup>a</sup> | N/A |
| OC<sup>IV</sup> | 150.08 151.13 150.40 150.67 151.38 153.00 153.92 | 227 ± 14 | N/A | N/A |

<sup>a</sup> Not Applicable.
Figure S8. $^{13}$C edited experiments of $pX@EtP6$ obtained by comparing the $^{13}$C CP MAS NMR spectra acquired with contact times of (a) 50 µs and (b) 2000 µs. Data were obtained at a magnetic field of 9.4 T. Spectral assignments are given in the figure (see Figure 1). The red daggers ($\dagger$) (also shown in red in the spectral deconvolution in Figure S11) denote signals arising from the para-xylene guest. The CH resonances of para-xylene are apparent in the spectrum obtained at a short contact time of 50 µs where the signal intensities of the quaternary carbons are largely reduced. Spinning sidebands are marked with asterisks (*).
Table S4. $^{13}$C NMR assignments for $pX@EtP6$ (Figure 2(c)) with isotropic chemical shifts $\delta_{\text{iso}}$ from spectral deconvolution in Figure S11, spin lattice relaxation times $T_1$ obtained via area integration, motional averaged dipolar coupling constants $<d_{\text{CH}}>$ and order parameters $<S_{\text{CH}}>$. Data obtained at room temperature and 9.4 T. Red daggers (†) denote signals arising from para-xylene guest.

| Assignment | $^{13}$C $\delta_{\text{iso}}$/ppm | $T_1$/s | $<d_{\text{CH}}>/kHz$ | $<S_{\text{CH}}>$ |
|------------|----------------------------------|---------|----------------|----------------|
| CH$_3$     | 14.0 14.4 14.9 15.2 15.5 16.0 18.7 (†) 20.5 (†) | 15.9 ± 0.1 6.9 ± 0.5 | 0.30 ± 0.03 |
| CH$_2$     | 27.9 29.4 30.8 31.2 32.8 37.8 | 86 ± 32 21.6 ± 0.8 | 0.94 ± 0.03 |
| OCH$_2$    | 61.8 62.4 62.9 | 63.3 63.9 64.1 64.8 65.0 | 39 ± 3 18.4 ± 0.7 | 0.81 ± 0.03 |
| CH          | 111.0 111.5 112.1 113.6 114.2 114.6 115.4 115.8 117.2 | 140 ± 10 22.4 ± 0.8 | 0.94 ± 0.03 |
| CH$_2$C$^\text{IV}$ | 125.8 126.3 126.6 127.4 127.6 | 128.7 129.4 (†) 129.8 (†) 130.3 132.8 (†) 133.4 (†) | 140 ± 15 | N/A$^a$ N/A |
| OC$^\text{IV}$ | 148.6 149.0 149.5 149.7 | 150.6 150.9 151.5 152.1 152.5 | 127 ± 11 | N/A N/A |

$^a$ Not Applicable.
Figure S9. $^{13}$C edited experiments of $m$X@EtP6 obtained by comparing the $^{13}$C CP MAS NMR spectra acquired with contact times of (a) 50 $\mu$s and (b) 2000 $\mu$s. Data were obtained at a magnetic field of 9.4 T. Spectral assignments are given in the figure (see Figure 1). The red daggers (†) (also shown in red in the spectral deconvolution in Figure S12) denote signals arising from the meta-xylene guest. The CH resonances of meta-xylene are apparent in the spectrum obtained at a short contact time of 50 $\mu$s where the signal intensities of the quaternary carbons are largely reduced. Spinning sidebands are marked with asterisks (*).
Table S5. $^{13}$C NMR assignments for $mX@$EtP6 (Figure 2(d)) with isotropic chemical shifts $\delta_{iso}$ from spectral deconvolution in Figure S12, spin lattice relaxation times $T_1$ obtained via area integration, motional averaged dipolar coupling constants $<d_{CH}>$ and order parameters $<S_{CH}>$. Data obtained at room temperature and 9.4 T. Red daggers (†) denote signals arising from meta-xylene guest.

| Assignment | $^{13}$C $\delta_{iso}$/ppm | $T_1$/s | $<d_{CH}>$/kHz | $<S_{CH}>$ |
|------------|----------------------------|---------|----------------|-----------|
| CH$_3$     | 14.4                       |         | -6.9 ± 0.5     | 0.30 ± 0.03 |
|            | 15.2                       |         |                |           |
|            | 15.3                       |         |                |           |
|            | 15.8                       | 2.8 ± 0.1|                |           |
|            | 16.2                       |         |                |           |
|            | 16.4                       |         |                |           |
|            | 21.6 (†)                   |         |                |           |
| CH$_2$     | 31.2                       |         | -22.2 ± 0.8    | 0.97 ± 0.03 |
|            | 31.5                       |         |                |           |
|            | 33.2                       | 168 ± 17|                |           |
| OCH$_2$    | 62.2                       |         | -19.2 ± 0.7    | 0.84 ± 0.03 |
|            | 63.3                       |         |                |           |
|            | 64.2                       | 45 ± 3  |                |           |
|            | 64.5                       |         |                |           |
|            | 65.4                       |         |                |           |
| CH         | 111.4                      |         | -23.5 ± 0.8    | 0.99 ± 0.03 |
|            | 111.9                      |         |                |           |
|            | 114.9                      |         |                |           |
|            | 116.4                      | 158 ± 11|                |           |
| CH$_3$C$^{IV}$ | 126.6 (†)                  |         | N/A$^a$        | N/A       |
|            | 126.8                      |         |                |           |
|            | 127.6                      |         |                |           |
|            | 128.4 (†)                  | 136 ± 9 |                |           |
|            | 129.0                      |         |                |           |
|            | 130.1 (†)                  | 130.6   |                |           |
|            | 137.2 (†)                  |         |                |           |
| O$^{IV}$   | 149.3                      |         | N/A            | N/A       |
|            | 149.9                      |         |                |           |
|            | 151.1                      | 189 ± 11|                |           |
|            | 151.6                      |         |                |           |
|            | 152.5                      |         |                |           |

$^a$ Not Applicable.
Figure S10. $^{13}$C edited experiments of oX@EtP6 obtained by comparing the $^{13}$C CP MAS NMR spectra acquired with contact times of (a) 50 $\mu$s and (b) 2000 $\mu$s. Data were obtained at a magnetic field of 9.4 T. Spectral assignments are given in the figure (see Figure 1). The red daggers ($\dagger$) (also shown in red in the spectral deconvolution (Figure S13) denote signals arising from the ortho-xylene guest. The CH resonances of ortho-xylene are apparent in the spectrum obtained at a short contact time of 50 $\mu$s where the signal intensities of the quaternary carbons are largely reduced. Spinning sidebands and signals arising from unknown minor phase(s) are marked with asterisks (*) and dashes (#), respectively.
Table S6. $^{13}$C NMR assignments for ox@EtP6 (Figure 2(e)) with isotropic chemical shifts $\delta_{iso}$ from spectral deconvolution shown in Figure S13, spin lattice relaxation times $T_1$ obtained via area integration, motional averaged dipolar coupling constants $<d_{CH}>$ and order parameters $<S_{CH}>$. Data obtained at room temperature and 9.4 T. Red daggers (†) denote signals arising from the aromatic carbons in ortho-xylene guest (the CH$_3$ is not resolved) and (#) denote amorphous signals. Overlapping resonances between the guest and the host in the in the 15-17 ppm and 123-137 ppm region of the $^{13}$C CP MAS NMR spectrum prevents spectral assignment of the CH$_3$ and only allow tentative assignment of the CH$_2$C$^{IV}$ carbons.

| Assignment | $^{13}$C $\delta_{iso}$/ppm | $T_1$/s | $<d_{CH}>$/kHz | $<S_{CH}>$ |
|------------|-----------------------------|---------|----------------|-----------|
| **CH$_3$** | 15.1 15.9 16.3              | 2.0 ± 0.1 | -7.1 ± 0.5     | 0.31 ± 0.03 |
| **CH$_2$** | 28.6 29.8 30.6 33.0 37.6   |         |                 |            |
| **OCH$_2$** | 62.1 62.7 63.1 63.8 65.4 (#) | 26 ± 2 | -18.3 ± 0.7     | 0.81 ± 0.03 |
| **CH**     | 111.4 111.9 114.9 116.4    | 89 ± 4  | -23.8 ± 0.8     | 1.00 ± 0.03 |
| **CH$_3$C$^{IV}$** | 124.0 (#) 125.4 126.3 126.7 | 52 ± 5 | N/A$^a$         | N/A       |
| **OC$^{IV}$** | 149.2 149.6 150.2 151.8 151.5 152.1 | 88 ± 4 | N/A            | N/A       |

$^a$ Not Applicable.
Figure S11. Experimental $^{13}$C CP MAS NMR spectrum of $pX@EtP6$ (full line) with the total fit and spectrum deconvolutions shown with dotted and dashed lines, respectively. Integration values for each carbon subgroup are given. Data obtained at 298 K and 9.4 T. Each panel shows chemically distinct carbons environments of the EtP6 host. Spectral assignments are given in the figure (see Figure 1) and are obtained from known isotropic chemical shifts, $^{13}$C-edited experiments and 2D PDLF data (see manuscript). Note that the low resolution of some of the resonances results in uncertainty in the estimated integration. Red daggers (†) denote signals arising from the para-xylene guest.
Figure S12. Experimental $^{13}$C CP MAS NMR spectrum of $mX@EtP6$ (full line) with the total fit and spectrum deconvolutions shown with dotted and dashed lines, respectively. Integration values for each carbon subgroup are given. Data obtained at 298 K and 9.4 T. Each panel shows chemically distinct carbons environments of the EtP6 host. Spectral assignments are given in the figure (see Figure 1) and are obtained from known isotropic chemical shifts, $^{13}$C-edited experiments and 2D PDLF data (see manuscript). Red daggers (†) denote signals arising from the meta-xylene guest.
Figure S13. Experimental $^{13}$C CP MAS NMR spectrum of oX@EtP6 (full line) with the total fit and spectrum deconvolutions shown with dotted and dashed lines, respectively. Integration values for each carbon subgroup are given. Data obtained at 298 K and 9.4 T. Each panel shows chemically distinct carbons environments of the EtP6 host. Spectral assignments are given in the figure (see Figure 1) and are obtained from known isotropic chemical shifts, $^{13}$C-edited experiments and 2D PDLF data (see manuscript). Note that the low resolution of some of the resonances results in uncertainty in the estimated integration. The overlapping peaks in the CH$_3$ region do not allow for the CH$_3$ of the ortho-xylene guest to be accurately identified. Broad signals tentatively assigned to some unknown amorphous phase(s) are marked with dashes (#). Red daggers (†) denote signals arising from the ortho-xylene guest.
Variable temperature $^{13}$C NMR spectra

Figure S14. Variable temperature $^{13}$C CP NMR spectra of guest-free EtP5-$\alpha$ collected at the temperatures given in the figure. Data was obtained at 9.4 T. Spectral assignments are given in the figure (see Figure 1) and correspond to those previously published. Asterisks (*) denote spinning sidebands.
Figure S15. Variable temperature $^{13}$C CP NMR spectra of guest-free EtP6-β collected at the temperatures given in the figure. Data shown in black and blue were obtained at 9.4 and 14.1 T, respectively. Spectral assignments are given in the figure (see Figure 1) and correspond to those previously published. The dotted line indicates a polymorphic transition in EtP6-β (see DSC data in Figure S2). Asterisks (*) denote spinning sidebands.
Figure S16. Variable temperature $^{13}$C CP NMR spectra of pX@EtP6 collected at the temperatures given in the figure. Data shown in black and blue were obtained at 9.4 T and 14.1 T, respectively. Spectral assignments are given in the figure (see Figure 1) and are derived from known isotropic chemical shifts, $^{13}$C-edited experiments (Figure S8) and PDLF data (see manuscript). Red daggers (†) and asterisks (*) denote signals arising from the para-xylene guest and spinning sidebands, respectively.
Figure S17. Variable temperature $^{13}$C CP NMR spectra of MX@EtP6 collected at the temperatures given in the figure. Data shown in black and blue were obtained at 9.4 T and 14.1 T, respectively. Spectral assignments are given in the figure (see Figure 1) and are derived from the known isotropic chemical shifts, $^{10}$ $^{13}$C-edited experiments (Figure S9) and PDLF data (see manuscript). The dashed line indicates that meta-xylene signals are mostly lost between room temperature and 323 K, this temperature being in the range of the weight loss in the TGA data (Figure S3). It is likely that the meta-xylene remains in the rotor as a liquid phase that would not be detectable under the CP conditions used. Red daggers (†) and asterisks (*) denote signals arising from the meta-xylene guest and spinning sidebands, respectively.
Figure S18. Variable temperature $^{13}$C CP NMR spectra of oX@EtP6 collected at the temperatures given in the figure. Data shown in black and blue were obtained at 9.4 T and 14.1 T respectively. Spectral assignments are given in the figure (see Figure 1) and are derived from known isotropic chemical shifts, $^{13}$C-edited experiments (Figure S10) and PDLF data (see manuscript). Ortho-xylene is not lost at 330 K as this process occurs above 340 K (see TGA data in Figure S4). Broad signals tentatively assigned to some unknown amorphous phase(s) are marked with dashes (#). Red daggers ($^\dagger$) and asterisks (*) denote signals arising from the ortho-xylene guest and spinning sidebands, respectively.
Figure S19. Experimental $^{13}$C CP MAS NMR spectrum of EtP6 (full line) obtained at 383 K and 9.4 T with the total fit and spectrum deconvolutions shown with dotted and dashed lines, respectively. Integration values for each carbon subgroup are given. Each panel shows chemically distinct carbon environments of EtP6. Spectral assignments are given in the figure (see Figure 1). Integrations match with half the number of non-equivalent carbon atoms in the asymmetric unit cell of EtP6-β.
S9. Additional proton detected local field NMR spectra

Figure S20. (a) $^{13}$C CP MAS spectrum, (b) PDLF spectrum and (c) selected site-specific $^{13}$C $^1$H dipolar spectra for $\text{pX@EtP6}$. Spectral assignments are given in the figure and correspond to those previously published. The data presented above was obtained at 298 K and 9.4 T. $\langle d_{CH} \rangle$ is measured using the outer singularities of the dipolar coupling spectra as highlighted in the experimental section. Vertical light grey lines indicate the static limit dipolar coupling constants $d_{CH}$ calculated from equation 1 and the computed CH distances obtained at the DFT level on the various conformers identified by CSP. Red daggers ($^\dagger$) and asterisks (*) denote signals arising from the para-xylene guest and spinning sidebands, respectively.
Figure S21. (a) $^{13}$C CP MAS spectrum, (b) PDLF spectrum and (c) selected site-specific $^{13}$C $^1$H dipolar spectra for $mX@EtP6$. Spectral assignments are given in the figure and correspond to those previously published. The data presented above was obtained at 298 K and 9.4 T. $\langle d_{CH} \rangle$ is measured using the outer singularities of the dipolar coupling spectra as highlighted in the experimental section. Vertical light grey lines indicate the static limit dipolar coupling constants $d_{CH}$ calculated from equation 1 and the computed CH distances obtained at the DFT level on the various conformers identified by CSP. Red daggers (†) and asterisks (*) denote signals arising from the meta-xylene guest and spinning sidebands, respectively.
Figure S22. (a) $^{13}$C CP MAS spectrum, (b) PDLF spectrum and (c) selected site-specific $^{13}$C $^1$H dipolar spectra for oX@EtP6. Spectral assignments are given in the figure and correspond to those previously published. The data presented above was obtained at 298 K and 9.4 T. $<d_{CH}>$ is measured using the outer singularities of the dipolar coupling spectra as highlighted in the experimental section. Vertical light grey lines indicate the static limit dipolar coupling constants $d_{CH}$ calculated from equation 1 and the computed CH distances obtained at the DFT level on the various conformers identified by CSP. Broad signals tentatively assigned to some unknown amorphous phase(s) are marked with dashes (#). Red daggers (†) and asterisks (*) denote signals arising from the ortho-xylene guest and spinning sidebands, respectively.
Figure S23. (a) $^{13}$C CP MAS spectrum, (b) PDLF spectrum and (c) selected site-specific $^{13}$C $^1$H dipolar spectra for guest-free EtP6-$\beta$. Spectral assignments are given in the figure and correspond to those previously published.$^1$ The data presented above was obtained at 100 K and 9.4 T. $\langle d_{\text{CH}} \rangle$ is measured using the outer singularities of the dipolar coupling spectra as highlighted in the experimental section. Vertical light grey lines indicate the static limit dipolar coupling constants $d_{\text{CH}}$ calculated from equation 1 and the computed CH distances obtained at the DFT level on the various conformers identified by CSP. Asterisks (*) denote spinning sidebands.
Figure S24. (a) $^{13}$C CP MAS spectrum at 100 K, (b) PDLF spectrum at 100 K and (c) comparison of selected site-specific $^{13}$C $^1$H dipolar spectra for the host CH$_2$IV quaternary carbon in pX@EtP6 obtained at 298 K and 100 K. Data presented above were obtained at 14.1 T. Spectral assignments are given in the figure. Signals arising from the adsorbed para-xylene guest are assigned with red daggers (†). Vertical light grey lines in the spectra indicate the static limit dipolar coupling constants $d_{CH}$. Asterisks (*) denote spinning sidebands.
Figure S25. (a) $^{13}$C CP MAS spectrum at 100 K, (b) PDLF spectrum at 100 K and (c) comparison of selected site-specific $^{13}$C $^1$H dipolar spectra for the host CH$_2$CIV quaternary carbon in $mX@EtP6$ obtained at 298 and 100 K. Data presented above were obtained at 14.1 T. Spectral assignments are given in the figure. Signals arising from the adsorbed meta-xylene guest are assigned with red daggers (†). No 2D PDLF signal is observed for the quaternary carbon of the meta-xylene due to poor signal to noise. Vertical light grey lines in the spectra indicate the static limit dipolar coupling constants $d_{CH}$. Asterisks (*) denote spinning sidebands.
Figure S26. (a) $^{13}$C CP MAS spectrum at 100 K, (b) PDLF spectrum at 100 K and (c) comparison of selected site-specific $^{13}$C $^1$H dipolar spectra for the host CH$_2$CIV's quaternary carbon in oX@EtP6. Data presented above were obtained at 14.1 T. Spectral assignments are given in the figure. Signals arising from the adsorbed ortho-xylene guest are assigned with red daggers ($\dagger$), except the corresponding methyl resonance which is not directly attributable (see text). Broad signals tentatively assigned to some unknown amorphous phase(s) are marked with dashes (#). Vertical light grey lines in the spectra indicate the static limit dipolar coupling constants $d_{CH}$. Asterisks (*) denote spinning sidebands.
S10. Additional $^1\text{H}$ and $^{13}\text{C}$ spin lattice relaxation rates $T_1^{-1}$ vs. temperatures

The $^1\text{H}$ spin lattice relaxation rates $T_1^{-1}$s have been obtained versus temperatures in the 383 - 243 K and 298 - 100 K temperature range at 9.4 T (Figures S27(a), $\nu_0(^1\text{H}) = 400 \text{ MHz}$, $\nu_0(^{13}\text{C}) = 100 \text{ MHz}$) and 14.1 T (Figures S28(a), $\nu_0(^1\text{H}) = 600 \text{ MHz}$, $\nu_0(^{13}\text{C}) = 150 \text{ MHz}$), respectively, for EtP6-$\beta$ all xylene-adsorbed EtP6 adducts and EtP5-$\alpha$ (data only available at 9.4 T for this phase). The corresponding $^1\text{H}$ MAS NMR spectra of all materials are broadened by $^1\text{H}$ $^1\text{H}$ homonuclear dipolar coupling and are poorly resolved as discussed in Section S11 ($^1\text{H}$ MAS spectra under various experimental conditions are given in Figures S32-S36) hence $^1\text{H}$ $T_1$ values are obtained from spectral integration of the entire spectra. Additionally, the $^1\text{H}$ $T_1$'s are fairly long (3 s for EtP6-$\beta$ at 298 K and 9.4 T) and $^1\text{H}$ $^1\text{H}$ spin diffusion results in an equilibration of the $T_1$ values for all resonances so that it is likely that the $^1\text{H}$ $T_1$'s detect the same motional processes. At 14.1 T and for all materials, the $^1\text{H}$ $T_1$'s values increase with increasing temperatures, reaching a maximum around 160 K for $pX@EtP6$, 170 K for $mX@EtP6$ and 190 K for both EtP6-$\beta$ and $oX@EtP6$, and then decreasing above these temperatures (Figure S28(a)). At these $T_1^{-1}$ maxima, the motion is near the $^1\text{H}$ Larmor frequency $\omega_{0,H}$ (in rad.s$^{-1}$) with the following expression being satisfied:\textsuperscript{11}

$$\omega_{0,H}T_c \approx 0.62 \tag{S3}$$

from which a $T_c$ value of 2.5 x10$^{-10}$ s at the aforementioned temperatures for the named materials could be obtained for $^1\text{H}$ at 14.1 T. The $^1\text{H}$ $T_1$'s maxima are not observed in the 383 - 243 K temperature range accessible on the MAS probe at 9.4 T which is in agreement with the largely magnetic field independence of dipolar coupling driven $T_1$ values as illustrated in Figures S28(a) and S29(a), and equation S4 (see below).

Importantly, there is a marked dependency of the $T_1^{-1}$ maxima temperature with the materials under consideration which decrease from $\sim$190 K for EtP6-$\beta$ and $oX@EtP6$ to $\sim$170 K for $mX@EtP6$ and $\sim$160 K for $pX@EtP6$. It is well known that the position of the $T_1^{-1}$ maximum depends on $T_c$ with colder temperatures required to satisfy equation S3 for larger molecular size resulting in slower tumbling.\textsuperscript{11} The temperature dependency of the $T_1^{-1}$ maximum therefore indicates decreasing tumbling rates for EtP6-$\beta$ and $oX@EtP6$ to $mX@EtP6$ and to $pX@EtP6$ that are associated with larger molecular assemblies. These suggest that ortho-xylene has little effect on the relaxation rates of the host due to its larger spatial freedom as observed above from xylene CH dipolar coupling experiments, whereas both meta-xylene and para-xylene shift this maximum towards lower temperatures (170 K and 160 K, respectively) suggesting that the filling of the pillar[6]arene void upon loading of meta-xylene and the adaptive adsorption of para-xylene results in an overall smaller conformation.

It is assumed that the $^1\text{H}$ relaxation is driven by $^1\text{H}^{-1}\text{H}$ homonuclear dipole-dipole coupling and the longitudinal relaxation rates $T_1^{-1}$ can be related to $T_c$ with the following equation (in the approximation of isotropic motion):\textsuperscript{11,12}

$$\frac{1}{T_1} = \frac{3}{10} \left(\frac{\mu_0}{4\pi}\right)^2 \gamma_0^2 \hbar^2 \left(\sum_i \frac{1}{r_i^6}\right)^2 \left[\frac{T_c}{1 + \omega_{0,H}^2 T_c^2} + \frac{4T_c}{1 + 4\omega_{0,H}^2 T_c^2}\right] \tag{S4}$$

by summing over all the effective $^1\text{H}^{-1}\text{H}$ internuclear distances $r$. The local magnetic fields fluctuation term of this expression is proportional to the square of the dipole-dipole coupling constant while the terms in squared bracket are the spectral density functions. All other possible relaxation mechanisms for a spin 1/2 nucleus such as those driven by CSA, spin-rotation or scalar coupling are likely quite small for $^1\text{H}$ to satisfy the frequencies for relaxation and have therefore been neglected.
Figure S27. (a) $^1$H and (b) $^{13}$C spin–lattice relaxation rates ($T_1^{-1}$) Arrhenius plots. Data were obtained at 9.4 T for guest-free EtP$_5$-$\alpha$ (stars), guest-free EtP$_6$-$\beta$ (circles), $pX$@EtP$_6$ (squares), $mX$@EtP$_6$ (diamonds) and $oX$@EtP$_6$ (triangles). The data were fitted to a stretch exponential function in the form of $1 - \exp\left(-\left(\tau/T_1\right)^{\alpha}\right)$ and the errors associated are given to a 95% confidence level and are smaller than the symbol sizes.
Figure S28. (a) $^1$H and (b) $^{13}$C spin–lattice relaxation rates ($T_1^{-1}$) Arrhenius plots. Data were obtained at 14.1 T for EtP6-$\beta$ (circles), $pX@EtP6$ (squares), $mX@EtP6$ (diamonds) and $oX@EtP6$ (triangles). The data were fitted to a stretch exponential function in the form of $1 - \exp\left[-\left(\tau/T_1\right)^\alpha\right]$ and the errors associated are given to a 95% confidence level and are smaller than the symbol sizes.
Figure S29. (Left) $^1$H spin–lattice relaxation rates $T_1^{-1}$ against correlation times $\tau_c$ and (right) corresponding $^1$H correlation frequencies $\tau_c^{-1}$ Arrhenius plots. Data shown in black and blue were obtained at 9.4 T and 14.1 T, respectively, for (a) guest-free EtP5-α (stars), (b) guest-free EtP6-β (circles), (c) pX@EtP6 (squares), (d) mX@EtP6 (diamonds) and (e) oX@EtP6 (triangles). The associated errors are smaller than the symbol sizes. The solid (-) lines in the left panels are those obtained from a dipolar coupling relaxation mechanism (equation S4) at both fields using experimentally determined local field fluctuations terms of $2 \times 10^9$, $5 \times 10^9$, $3 \times 10^9$ and $2 \times 10^9$ s$^{-2}$ for EtP6-β, pX@EtP6, mX@EtP6 and oX@EtP6, respectively (A calculated value of $5 \times 10^9$ s$^{-2}$ from the $^1$H–$^1$H distances computed by CSP was used for EtP5-α as no $T_1$ minimum was found in the temperature range studied) and in the right panels are fit to the Arrhenius equation.
Combining equations S3 and S4 above at the temperatures of the $^1$H $T_1$ minimum allows the determination of the local dipolar magnetic fields fluctuation term to be determined. Experimental values of $2 \times 10^3$ s$^{-2}$ for EtP6-$\beta$ and $aX@EtP6$, $3 \times 10^3$ s$^{-2}$ for $mX@EtP6$ and $5 \times 10^3$ s$^{-2}$ for $pX@EtP6$ were obtained which compares extremely well with the value of $5 \times 10^3$ s$^{-2}$ calculated for all materials from the explicit expression of the local fields and using the shortest $^1$H-$^1$H distances in the known CSP data of these phases. No $T_1$ minimum is observed for EtP5-$\alpha$ in the temperature range studied preventing the local field term to be determined so this later calculated value was used.

Figure S29 displays the corresponding $^1$H $T_1^{-1}$ versus $\tau_c$ logarithmic plots for all samples at 9.4 T (black data) and 14.1 T (blue data). The $T_1^{-1}$ and $\tau_c$ values extracted from this approach show no field dependence in the fast motion limit where $\tau_c$ are much shorter than the Larmor frequency i.e. $\omega_0, \alpha, \tau_c \ll 1$ (left hand side of the $T_1^{-1}$ maxima) as expected from equation S4. The $\tau_c$’s extracted from this approach do not vary significantly between the materials and suggest the same similar motional process. The temperature dependence of the correlation frequencies $\tau_c^{-1}$ was subsequently modelled with the Arrhenius equation (equation 3 in the main text). Assuming a single activation energy, fit to $\tau_c^{-1}$ versus reciprocal temperatures (Figure S29) is satisfactory and the extracted $E_s$ (Table S7) are small, suggesting similar facile motion of the pillar[n]arene assemblies. Upon adsorption of para-xylene and ortho-xylene into EtP6-$\beta$, the activation barriers very slightly increase by ca. 0.5-0.8 kJ mol$^{-1}$ while it decreases by 0.6 kJ mol$^{-1}$ in the case of $mX@EtP6$ material. The assumed isotropic motion and associated errors with these values imply that these $E_s$ should simply be taken as an indication of possible motional effects of xylens into EtP6-$\beta$. In the case of $pX@EtP6$ and $oX@EtP6$, it is postulated that their larger $E_s$ vs. the one for EtP6-$\beta$ capture increase in the steric hindrance of the assemblies upon adsorption of para-xylene and ortho-xylene (Figures 1(c) and 1(e)), resulting in overall larger conformation of these materials and therefore slower overall dynamics when xylens occupy ($pX@EtP6$) or partially occupy ($oX@EtP6$) the pillar[6]arene void. In contrast, the smaller $E_s$ obtained for $mX@EtP6$ could be potentially due to folding of the pillar[6]arene void upon meta-xylene adsorption (Figure 1(d)) and associated with the position of the meta-xylene on top of the pillar[6]arene core.

**Table S7.** Comparison of the attempt frequencies $\tau_c^{-1}$ and activation energy barriers $E_s$ of guest-free EtP5-$\alpha$, guest-free EtP6-$\beta$, $pX@EtP6$, $mX@EtP6$ and $oX@EtP6$ obtained from the Arrhenius plots of the $^1$H correlation frequencies $\tau_c^{-1}$.

| Pillar[n]arenes | $\tau_{c,0}^{-1}/s^{-1}$ | $E_s$/kJ mol$^{-1}$ | $^a$ |
|-----------------|--------------------------|---------------------|-----|
| EtP5-$\alpha$   | $9 \times 10^{11}$       | 7                   |     |
| EtP6-$\beta$    | $2 \times 10^{11}$       | 6                   |     |
| $pX@EtP6$       | $6 \times 10^{11}$       | 6                   |     |
| $mX@EtP6$       | $2 \times 10^{11}$       | 5                   |     |
| $oX@EtP6$       | $4 \times 10^{11}$       | 6                   |     |

$^a$ Errors are in the order of 1 kJ mol$^{-1}$. $^b$ Data in the 383 - 243 K temperature range only available.
Figure S30. (Left) $^{13}$C spin–lattice relaxation rates $T_1^{-1}$ against correlation times $\tau_c$ and (right) corresponding $^{13}$C correlation frequencies $\tau_c^{-1}$ Arrhenius plots. Data shown in black and blue outlines were obtained at 9.4 T and 14.1 T, respectively, for (a) guest-free EtP5-$\alpha$ (stars), (b) guest-free EtP6-$\beta$ (circles), (c) pX@EtP6 (squares), (d) mX@EtP6 (diamonds) and (e) oX@EtP6 (triangles). Selected carbon subgroups have been plotted here with the following colour coding for CH$_2$ (light blue), CH (pink) and CH$_2$CIV (yellow) (Figure 1) whilst plot giving the three other carbons are given in Figure 7. The associated errors are smaller than the symbol sizes. In the left panels, the dashed (·-) lines are those obtained from dipolar coupling and CSA relaxation mechanisms (equation 4) for CH (pink), the solid lines (-) from a dipolar coupling relaxation mechanism (equation 5) for CH$_2$ (light blue) and the dotted (··) lines from a CSA relaxation mechanism (equation 6) for CH$_2$CIV (yellow) at both fields, using the experimentally determined local magnetic fields terms (values from EtP6-$\beta$ were used for EtP5-$\alpha$ as no $T_1$ minimum was found in the temperature range studied). A $T_1$ minima was found for OC$^{IV}$ in oX@EtP6 in the temperature range studied at 9.4 T, therefore this data was used to extract correlation times and is plotted for this series. In the right panels, the lines are fit to the experimental data using the Arrhenius equation.
Figure S31. (Left) $^{13}$C spin–lattice relaxation rates $T_1^{-1}$ against correlation times $\tau_c$ and (right) corresponding $^{13}$C correlation frequencies $\tau_c^{-1}$ Arrhenius plots. Data shown in black and blue outlines were obtained at 9.4 T and 14.1 T, respectively, for the xylene methyl groups in (a) $pX@EtP6$ (squares) and (b) $mX@EtP6$ (diamonds). Overlaps of the ortho-xylene methyl group with the host $\text{CH}_3$ in $oX@EtP6$ (Figure S18) prevent there $T_1$ to be measured. The associated errors are smaller than the symbol sizes. In the left panels, the solid (-) lines are those obtained from a dipolar coupling relaxation mechanism (equation 5) for $\text{CH}_3$ at both fields, using the calculated local magnetic fields term and distances available in literature from diffraction data. In the right panels, the lines are fit to the experimental data using the Arrhenius equation.
Very high field and variable temperature $^1$H NMR spectra

$^1$H one pulse spectra were obtained at 9.4 T for EtP5-$\alpha$, EtP6-$\beta$, $pX$@EtP6, $mX$@EtP6 and $oX$@EtP6 as shown in panel (a) in Figures S32-S36 respectively. Limited resolution allows for identification of very chemical distinct sites. Upon increasing the field to 20 T and increasing the MAS rate to 60 kHz, resolution of the $^1$H one pulse spectra increases, to allow further sites to be identified (panel (b) in Figures S32-S36) however, due to the significant broadening due to $^1$H $^1$H dipolar coupling within $^1$H spectra within the solid state, only limited information can be obtained. The $^1$H one pulse spectra obtained upon variable temperature at 14.1 T are shown in panel (c) of Figures S32-S36. The T$_1$ values extracted from the corresponding variable temperature saturation recovery experiments are shown in Figure S28(a) and used to extract corresponding correlation times $\tau_c$ as discussed in the manuscript.
Figure S32. $^1$H one pulse MAS NMR spectra of EtP$\alpha$ obtained (a) under MAS at $v_r = 12.5$ kHz and 9.4 T, (b) under variable temperature conditions at $v_r = 12.5$ kHz and 9.4 T and (c) at $v_r = 60$ kHz at 20 T. Spectral assignments are given in the figure.
Figure S33. $^1$H one pulse NMR spectra of EtP6-$\beta$ (a) obtained at $\nu_r = 12.5$ kHz and 9.4 T (b) obtained under variable temperature conditions at $\nu_r = 12.5$ kHz and 9.4 T and (c) obtained at $\nu_r = 60$ kHz at 20 T. Spectral assignments are given in the figure.
Figure S34. $^1$H one pulse NMR spectra of $\text{pX@EtP6}$ (a) obtained at $\nu_r = 12.5$ kHz and 9.4 T (b) obtained under variable temperature conditions at $\nu_r = 12.5$ kHz and 9.4 T and (c) obtained at $\nu_r = 60$ kHz at 20 T. Spectral assignments are given in the figure.
Figure S35. $^1$H one pulse NMR spectra of mX@EtP6 (a) obtained at $\nu_r = 12.5$ kHz and 9.4 T (b) obtained under variable temperature conditions at $\nu_r = 12.5$ kHz and 9.4 T and (c) obtained at $\nu_r = 60$ kHz at 20 T. Spectral assignments are given in the figure.
Figure S36. $^1$H one pulse NMR spectra of oX@EtP6 (a) obtained at $\nu_r = 12.5$ kHz and 9.4 T (b) obtained under variable temperature conditions at $\nu_r = 12.5$ kHz and 9.4 T and (c) obtained at $\nu_r = 60$ kHz at 20 T. Spectral assignments are given in the figure.
S12. Expression of the $^{13}\text{C}$ chemical shift tensors

Using the Haeberlen convention, these are defined as:

$$\Delta \delta_C = \delta_{33} - \frac{\delta_{11} + \delta_{22}}{2}$$  \hspace{1cm} (S5)

and

$$\eta_C = \frac{\delta_{22} - \delta_{11}}{\delta_{33} - \delta_{\text{iso}}}$$  \hspace{1cm} (S6)

with $\delta_{\text{iso}}$ the isotropic chemical shift (trace of the tensor):

$$\Delta \delta_C = \delta_{33} - \frac{\delta_{11} + \delta_{22}}{2}$$  \hspace{1cm} (S7)
S13. References

(S1) Hu, X.-B.; Chen, Z.; Chen, L.; Zhang, L.; Hou, J.-L.; Li, Z.-T. Pillar\[n\]Arenes (n = 8–10) with Two Cavities: Synthesis, Structures and Complexing Properties. *Chem. Commun.* 2012, 48, 10999–11001.

(S2) Jie, K.; Liu, M.; Zhou, Y.; Little, M. A.; Pulido, A.; Chong, S. Y.; Stephenson, A.; Hughes, A. R.; Sakakibara, F.; Ogoshi, T. et al. Near-Ideal Xylene Selectivity in Adaptive Molecular Pillar\[n\]Arene Crystals. *J. Am. Chem. Soc.* 2018, 140, 6921–6930.

(S3) Perras, F. A.; Wang, Z.; Naik, P.; Slowing, I. I.; Pruski, M. Natural Abundance $^{17}$O DNP NMR Provides Precise O–H Distances and Insights into the Brønsted Acidity of Heterogeneous Catalysts. *Angew. Chemie - Int. Ed.* 2017, 56, 9165–9169.

(S4) Fung, B. M.; Khitrin, A. K.; Ermolaev, K. An Improved Broadband Decoupling Sequence for Liquid Crystals and Solids. *J. Magn. Reson.* 2000, 142, 97–101.

(S5) Brinkmann, A.; Levitt, M. H. Symmetry Principles in the Nuclear Magnetic Resonance of Spinning Solids: Heteronuclear Recoupling by Generalized Hartmann-Hahn Sequences. *J. Chem. Phys.* 2001, 115, 357–384.

(S6) Carravetta, M.; Edén, M.; Zhao, X.; Brinkmann, A.; Levitt, M. H. Symmetry Principles for the Design of Radiofrequency Pulse Sequences in the Nuclear Magnetic Resonance of Rotating Solids. *Chem. Phys. Lett.* 2000, 321, 205–215.

(S7) Edén, M. Enhanced Symmetry-Based Dipolar Recoupling in Solid-State NMR. *Chem. Phys. Lett.* 2003, 378, 55–64.

(S8) Zhao, X.; Edén, M.; Levitt, M. H. Recoupling of Heteronuclear Dipolar Interactions in Solid-State NMR Using Symmetry-Based Pulse Sequences. *Chem. Phys. Lett.* 2001, 342, 353–361.

(S9) Lehmann, M. S.; Koetzle, T. F.; Hamilton, W. C. Precision Neutron Diffraction Structure Determination of Protein and Nucleic Acid Components. I. The Crystal and Molecular Structure of the Amino Acid L-Alanine. *J. Am. Chem. Soc.* 1972, 94, 2657–2660.

(S10) Krüger, T.; Vorndran, K.; Linker, T. Regioselective Arene Functionalization: Simple Substitution of Carboxylate by Alkyl Groups. *Chem. - A Eur. J.* 2009, 15, 12082–12091.

(S11) Abragam, A. *Principles of Nuclear Magnetism*; Oxford University Press: New York, 1963.

(S12) Steigel, A.; Spiess, H. W. *Dynamic NMR Spectroscopy*, 1st ed.; Springer-Verlag: Berlin Heidelberg, 1978.

(S13) Ibberson, R. M.; David, W. I. F.; Parsons, S.; Prager, M.; Shankland, K. The Crystal Structure of M-Xylene and p-Xylene, C$_8$D$_{10}$, at 4.5 K. *J. Mol. Struct.* 2000, 524, 121–128.

(S14) Haeberlen, U. *High Resolution NMR in Solids. Selective Averaging*; Academic Press: New York, 1968.