Electronic Supplementary Information

Obvious Vapochromic Color Changes of a Pillar[6]arene Containing One Benzoquinone Unit with a Mechanochromic Change Before Vapor Exposure

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1. Materials

All solvents and reagents were used as supplied. Pillar[6]arene containing one benzoquinone unit (**3**) was synthesized according to the previous paper.[S1]

2. Measurements

The ^{1}H NMR spectra were recorded at 500 MHz with a JEOL-ECA500 spectrometer. Powder XRD patterns were obtained on Smart Lab (Rigaku) with CuKα radiation (tube voltage, 40 kV, tube current, 20 mA). Diffuse reflectance spectra were recorded with a JASCO V-670 spectrometer. Differential scanning calorimetry (DSC) was performed using a PerkinElmer Jade DSC calorimeter equipped with an Intracooler II under a flow of dry nitrogen and with a heating rate of 10 °C/min. The FT-IR spectra were obtained using a JASCO FT-IR460 plus infrared spectrometer.

3. Activation of Solid of Pillar[6]arene 3

Pillar[6]arene **3** was dissolved in dichloromethane, and then the evaporation of dichloromethane afforded solid **3**. Drying solid **3** at 80 °C under reduced pressure for 24 h was sufficient to de-solvate all dichloromethane molecules and afforded activated solids of **3**. Removing dichloromethane was confirmed by ^{1}H NMR measurement (**Fig. S1**). No proton signals from dichloromethane indicate complete activation of solid **3**.

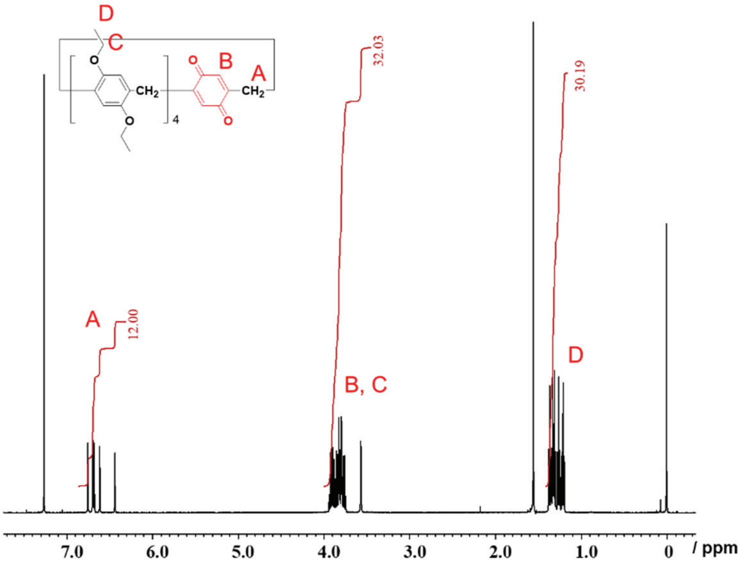


Fig. S1 ^{1}H NMR spectrum (CDCl$_3$, 25 °C) of activated solid **3**. No signals of solvents in the spectrum indicate complete activation.

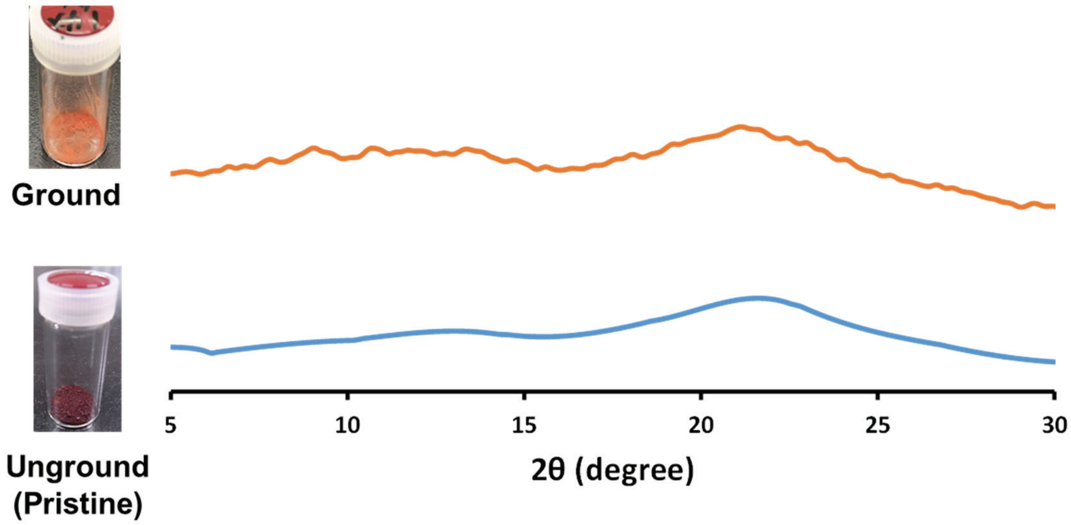


Fig. S2 PXRD patterns of activated solids **3** with and without grinding.

Both solids **3** with and without grinding were amorphous, indicating that crystal transformation is not trigger to induce the mechanochromism.

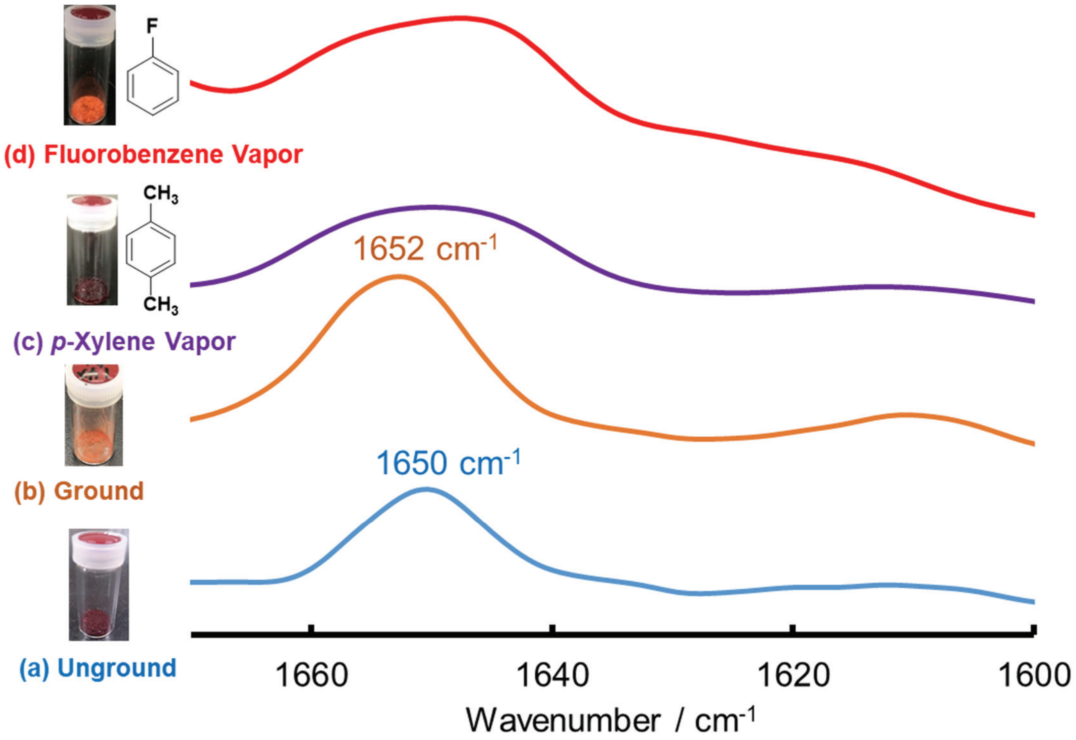


Fig. S3 FT-IR spectra, Ground (b) and unground activated solids **3** (a) before vapor exposure. Unground solids **3** after exposure to (c) p-xylene and (d) fluorobenzene vapors.

After grinding, the peak derived from C=O stretching was shifted from 1650 to 1652 cm^{-1}, indicating the CT interaction change between benzoquinone and 1,4-diethoxybenzene moieties by grinding. After uptake of these guest vapors, C=O stretching were broadening, indicating that the guest vapor uptake induced different CT interaction.

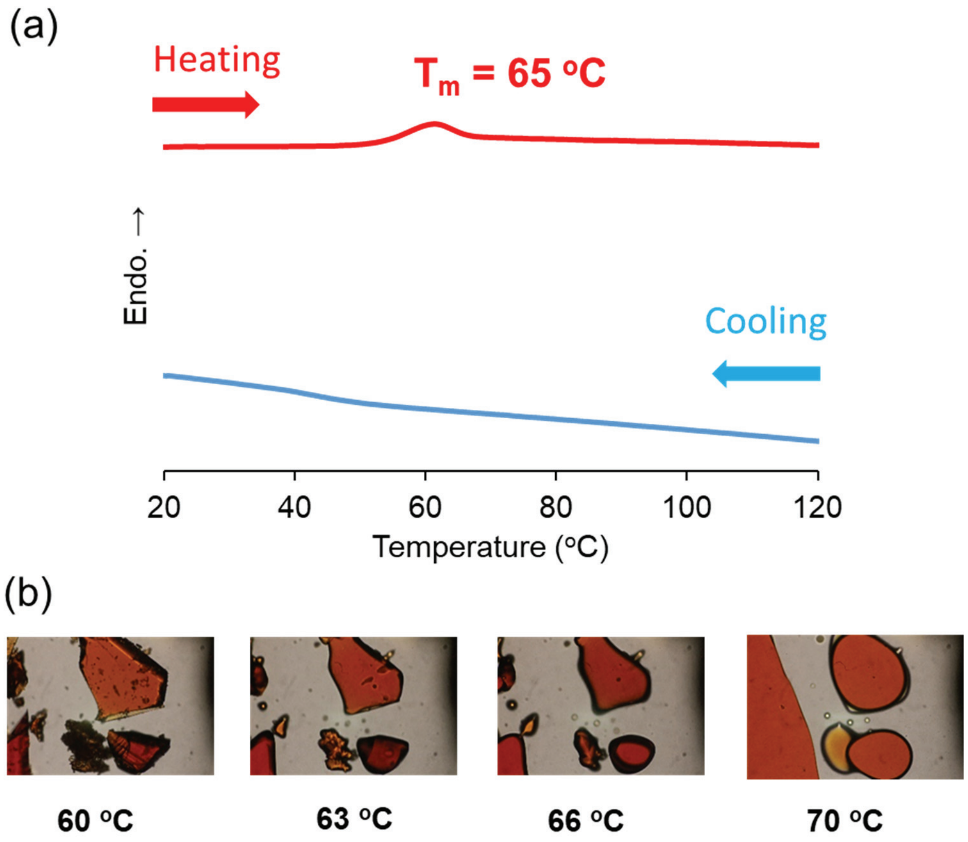
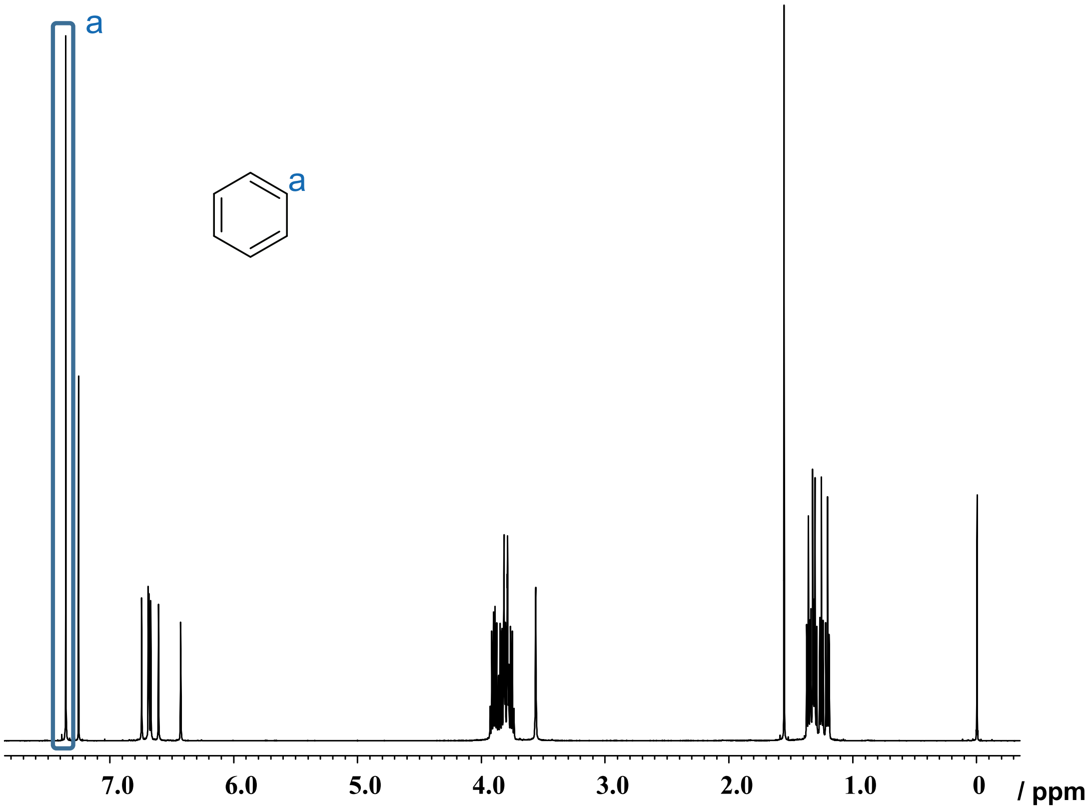
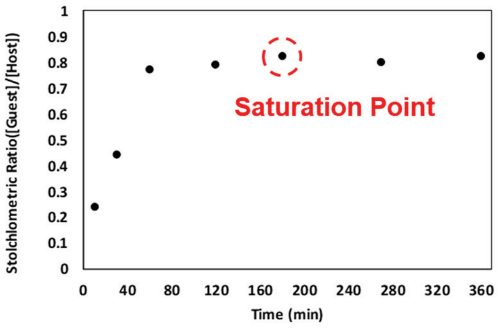


Fig. S4 (a) DSC curves and of activated solid **3**. (b) Photographs of optical microscope of solid **3** at 60, 63, 66 and 70 °C.

4. Aromatic Vapor Uptake Experiments

An open 5 mL vial containing 20 mg of activated solids of **3** with and without grinding was placed in a sealed 50 mL vial containing 5 mL of each Aromatic guest solution. Activated solids of **3** were exposed under saturated vapor pressure in the closed vessel at 25 °C. Uptake of aromatic vapor by solid **3** was monitored by ^{1}H NMR by completely dissolving the solids in $CDCl_3$ (**Figs. S5-S10**). Color change was investigated by diffuse reflectance spectroscopy (**Fig. S11**). The assembled structures were investigated by PXRD measurements (**Fig. S12**).

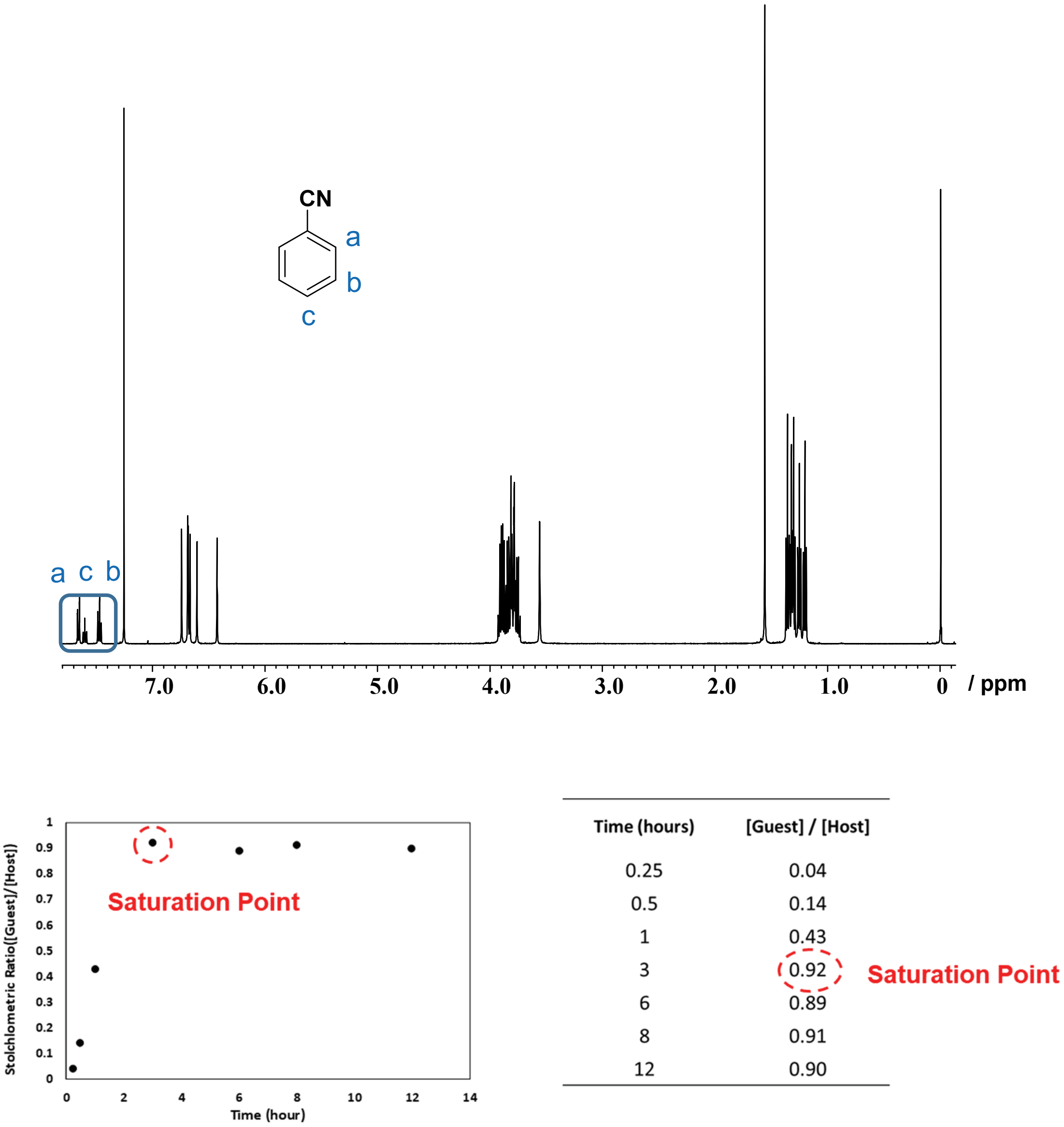




Time (minutes)	[Guest] / [Host]
10	0.24
30	0.44
60	0.77
120	0.79
180	0.82
270	0.8
360	0.82

Saturation Point

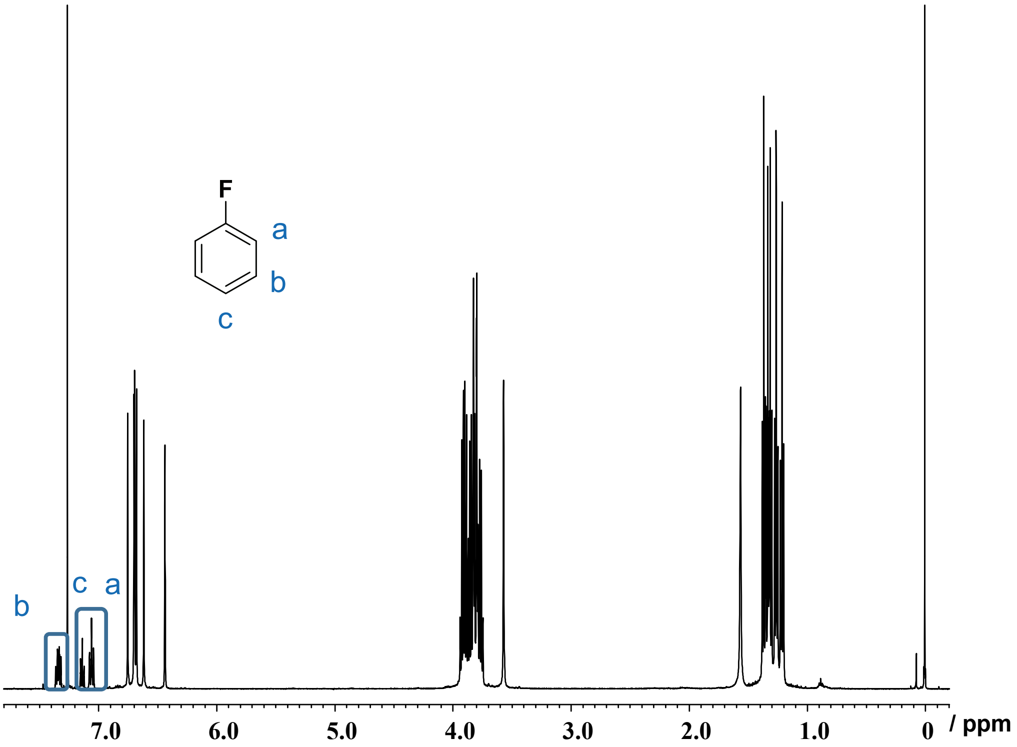
Fig. S5 ^{1}H NMR spectrum (25 °C, $CDCl_3$) of crystals of **3** after exposing to benzene vapor for 3 h. The stoichiometry was determined by monitoring integration ratio between proton signals from phenyl proton of benzene and phenyl moiety of **3**.

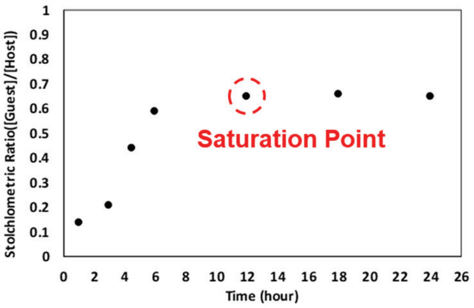


Time (hours)	[Guest] / [Host]
0.25	0.04
0.5	0.14
1	0.43
3	0.92
6	0.89
8	0.91
12	0.90

Saturation Point

Fig. S6 ^{1}H NMR spectrum (25 °C, $CDCl_3$) or crystals of **3** after exposing to cyanobenzene vapor for 3 h. The stoichiometry was determined by monitoring integration ratio between proton signals from phenyl proton of cyanobenzene and phenyl moiety of **3**.

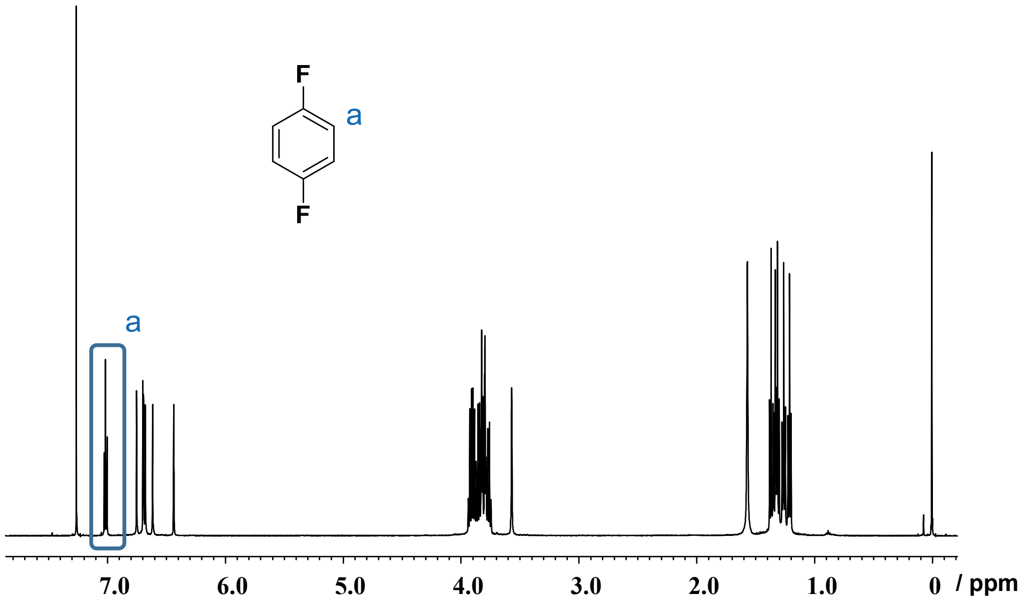


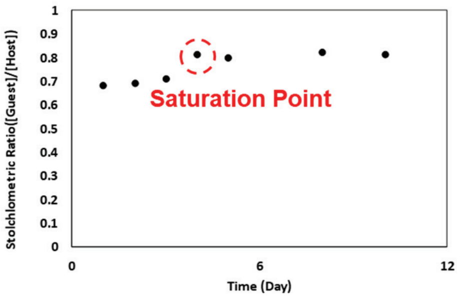


Time (hours)	[Guest] / [Host]
1	0.14
3	0.21
4.5	0.44
6	0.59
12	0.65
18	0.66
24	0.65

Saturation Point

Fig. S7 ^{1}H NMR spectrum (25 °C, $CDCl_3$) of crystals of **3** after exposing to fluorobenzene vapor for 12 h. The stoichiometry was determined by monitoring integration ratio between proton signals from phenyl proton of fluorobenzene and phenyl moiety of **3**.

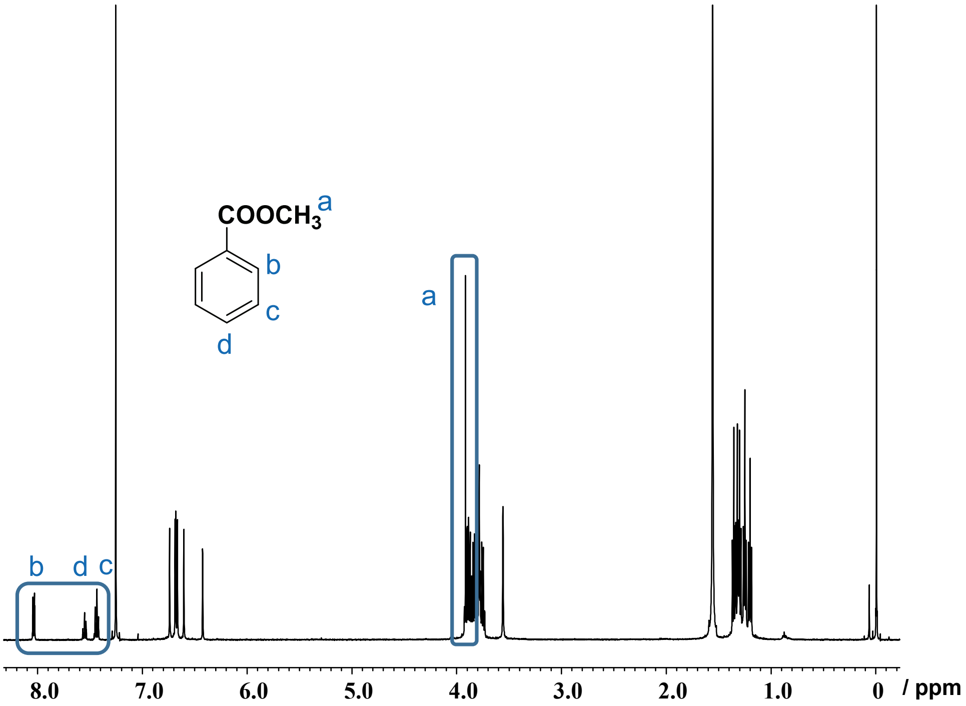


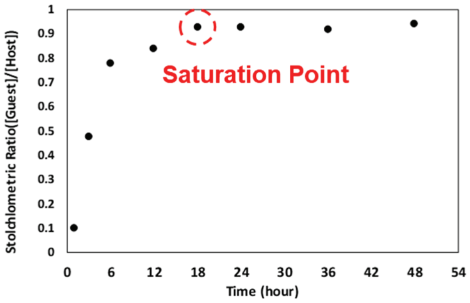


Time (days)	[Guest] / [Host]
1	0.68
2	0.69
3	0.71
4	0.81
5	0.80
8	0.82
10	0.81

Saturation Point

Fig. S8 ^{1}H NMR spectrum (25 °C, CDCl$_3$) of crystals of **3** after exposing to *p*-difluorobenzene vapor for 4 days. The stoichiometry was determined by monitoring integration ratio between proton signals from phenyl proton of *p*-difluorobenzene and phenyl moiety of **3**.

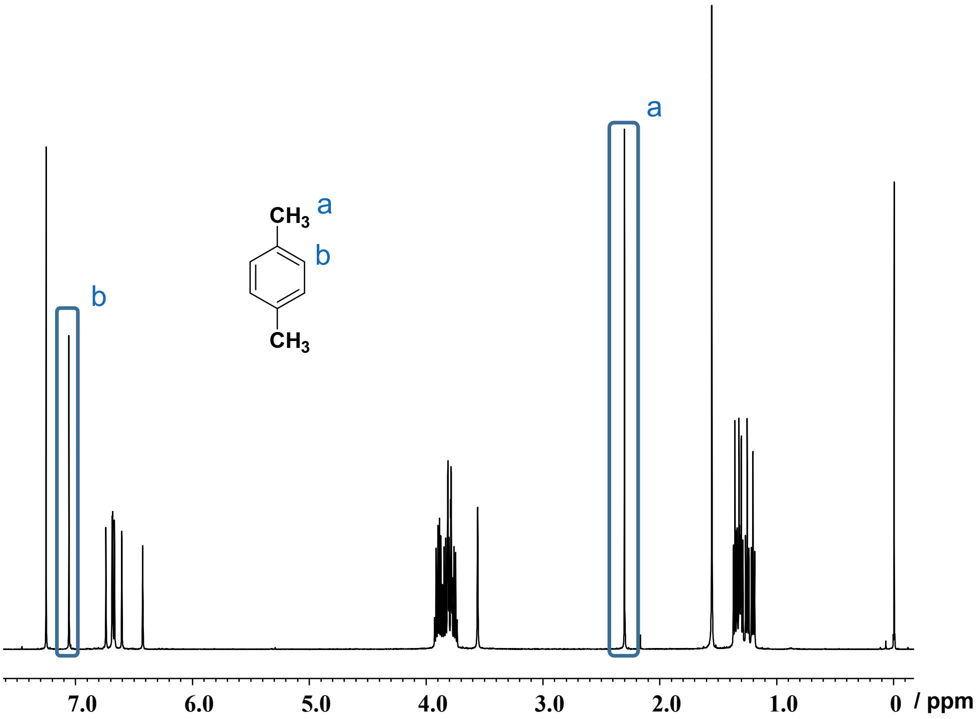


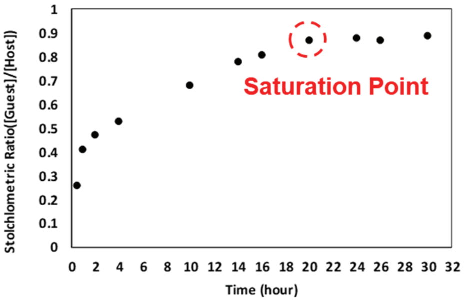


Time (hours)	[Guest] / [Host]
1	0.10
3	0.48
6	0.78
12	0.84
18	0.93
24	0.93
36	0.92
48	0.94

Saturation Point

Fig. S9 ^{1}H NMR spectrum (25 °C, $CDCl_3$) of crystals of **3** after exposing to methyl benzoate vapor for 18 h. The stoichiometry was determined by monitoring integration ratio between proton signals from phenyl proton of methyl benzoate and phenyl moiety of **3**.





Time (hours)	[Guest] / [Host]
0.5	0.26
1	0.41
2	0.47
4	0.53
10	0.68
14	0.78
16	0.81
20	0.87
24	0.88
26	0.87
30	0.89

Saturation Point

Fig. S10 ^{1}H NMR spectrum (25 °C, $CDCl_3$) of crystals of **3** after exposing to *p*-xylene vapor for 20 h. The stoichiometry was determined by monitoring integration ratio between proton signals from phenyl proton of *p*-xylene and phenyl moiety of **3**.

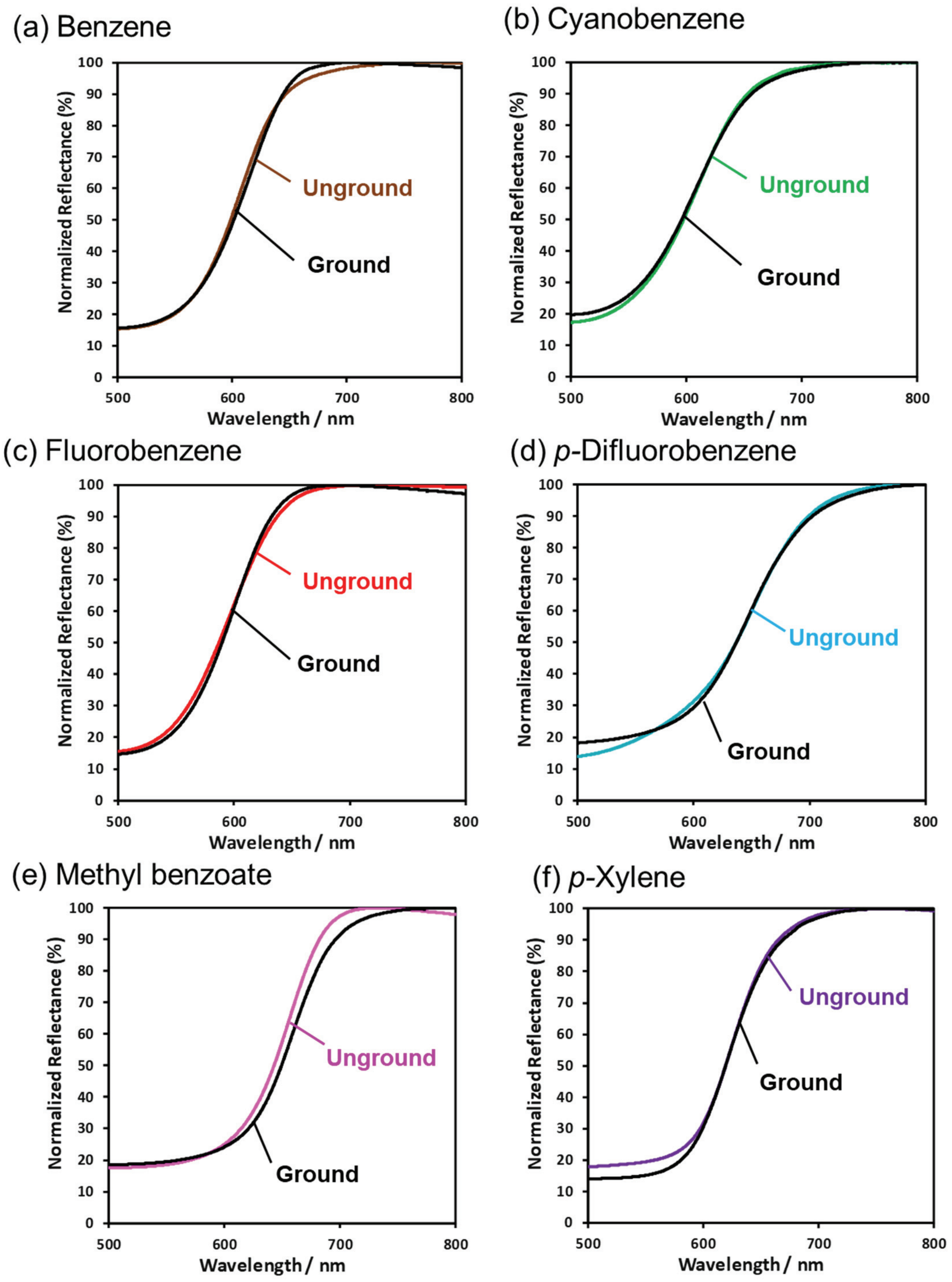
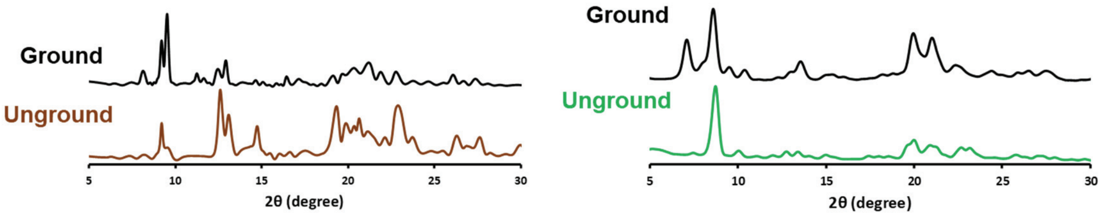
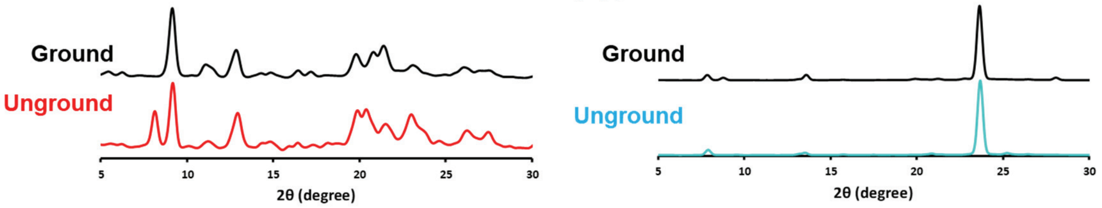


Fig. S11 Diffuse reflection spectra of solids **3** with and without grinding after exposing to (a) benzene, (b) cyanobenzene, (c) fluorobenzene, (d) *p*-difluorobenzene, (e) methyl benzoate and (f) *p*-xylene vapors.


(a) Benzene (b) Cyanobenzene


(c) Fluorobenzene (d) *p*-Difluorobenzene

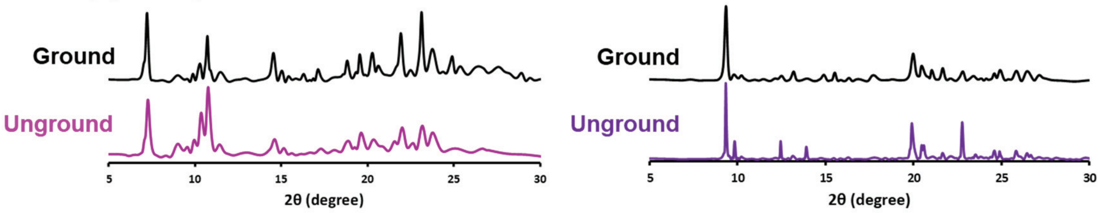

(e) Methyl benzoate (f) *p*-Xylene

Fig. S12 PXRD patterns of solids **3** with and without grinding after exposing to (a) benzene, (b) cyanobenzene, (c) fluorobenzene, (d) *p*-difluorobenzene, (e) methyl benzoate and (f) *p*-xylene vapors.

5. Reference

S1) T. Ogoshi, D. Yamafuji, D. Kotera, T. Aoki, S. Fujinami and T. Yamagishi, *J. Org. Chem.,* 2012, **77**, 11146.