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Conformational Changes in C_{methyl}-Resorcinarene Pyridine *N*-oxide Inclusion Complexes in the Solid State

Rakesh Puttreddy,[a] Ngong Kodiah Beyeh[a,b]* and Kari Rissanen[a]*

[a] *University of Jyväskylä, Department of Chemistry, P.O. Box 35, FI-40014 University of Jyväskylä, Finland.*

[b] *Aalto University School of Science, Department of Applied Physics, P.O. Box 11100, FI-00076 AALTO, Finland*

Supporting Information

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I General Information

All the solvents used for synthesis and crystal growth are reagent grade, and used as received. Pyridine *N*-oxide (**PyNO**), 2-methylpyridine *N*-oxide (**2-MePyNO**) and 3-methylpyridine *N*-oxide (**3-MePyNO**), 4-methylpyridine *N*-oxide (**4-MePyNO**), 4-methoxypyridine *N*-oxide (**4-MeOPyNO**), 4-phenylpyridine *N*-oxide (**4-PhPyNO**), quinoline *N*-oxide (**QNO**) and Isoquinoline *N*-oxide (**IsQNO**) were purchased from Sigma Aldrich while 2,6-dimethylpyridine *N*-oxide (**2,6-DiMePyNO**) and 4-nitro-2-methylpyridine *N*-oxide (**2-MeNPyNO**) were synthesized according to reported procedures.[1] C_{methyl}-Resorcinarene **1** was synthesized according to reported procedures.[2]

II Solid state analyses

X-ray experimental

Single crystal X-ray data for **2-MePyNO•1**, **4-MePyNO•1, 4-MeOPyNO•1**, **4-PhPyNO•1** and **IsQNO•1** were collected either at 120 K or 123 K on dual source Agilent SuperNova diffractometer with an Atlas detector using mirror-monochromated Cu-Kα (λ = 1.54184 Å) radiation. The data for **3-MePyNO•1**, **2-MeNPyNO•1** was measured either at 120 K or 123 K using Agilent SuperNova single-source diffractometer with an Atlas EoS CCD detector using mirror-monochromated Mo-*K*α (λ = 0.71073 Å) radiation. The data collection and reduction for all the complexes were performed using the program *CrysAlisPro*.[3] Gaussian face index absorption correction method[3] was used for all complexes, and for **IsQNO•1** multi-scan absorption correction method was used. The structures were solved with direct methods (*SHELXS*[4]) and refined by full-matrix least squares on F^2 using the *OLEX2*[5], which utilizes the *SHELXL*-2013 module.[4] Direct methods of phase determination followed by four Fourier cycles of refinement for structures **3-MePyNO•1**, **4-MePyNO•1, 4-MeOPyNO•1** and **4-PhPyNO•1** led to an electron density map from which most of the non-hydrogen atoms were found for host, guest and solvent molecules in the asymmetric unit without disorder problem. In complex **2-MePyNO•1,** one *endo* and *exo* **2-MePyNO** molecules were disordered with 25:75 and 40:60 occupancies. In complex **2-MeNPyNO•1,** the *exo* **2-MeNPyNO** molecules have shown large displacement parameter indicating disorder and no attempt was made to split these *exo* **2-MeNPyNO** molecules. In complex **IsQNO•1,** the asymmetric unit contains fractional water molecules, and no attempt was made to find hydrogen from the electron density map with prime importance given to the host and guest molecules. For all complexes, no attempt was made to locate the hydrogen atoms from Fourier difference map, and all the H-atoms were included in the refinement in the calculated positions on the riding atoms using ADD H command in Olex2. Constraints (EADP) and restraints (ISOR) commands are used where appropriate to suppress the alerts for large displacement parameter in checkcif. In few structures, the C-O distances for methanol molecules were restrained using DFIX command. Finally, continous four Fourier cycles of refinement was performed till the convergence is achieved.

Table 1. Crystal data and X-Ray experimental details for **2-MePyNO•1 - IsQNO•1**.

Complex	**2-MePyNO•1**	**3-MePyNO•1**	**4-MePyNO•1**
Empirical formula	$C_{56}H_{60}N_4O_{12}$	$C_{44}H_{46}N_2O_{10}$	$C_{45}H_{50}N_2O_{11}$
Formula weight	981.08	762.83	794.87
Temperature (K)	123.0	120.0	120.0
Crystal system	Monoclinic	Triclinic	Triclinic
Space group	*C2/c*	*P*-1	*P*-1
Unit cell dimensions: a (Å)	28.1876(12)	9.9521(7)	11.6839(4)
b (Å)	20.8706(7)	13.7594(10)	13.6838(6)
c (Å)	17.9257(7)	15.1539(12)	14.7557(6)
α (°)	90	113.562(7)	67.409(4)
β (°)	106.239(5)	94.266(6)	89.351(3)
γ (°)	90	90.364(6)	67.249(4)
Volume / Å^3	10124.8(7)	1895.3(3)	1982.39(16)
Z	8	2	2
Density (calculated) mg/m^3	1.287	1.337	1.332
Absorption Coefficient mm^{-1}	0.744	0.095	0.784
F(000)	4160	808	844
Crystal size (mm^3)	0.54 x 0.07 x 0.05	0.37 x 0.13 x 0.08	0.18 x 0.12 x 0.07
θ range for data collection (°)	3.38 to 66.75	2.94 to 25.25	3.29 to 66.74
Reflections collected [R(int)]	16567 [0.0469]	12446 [0.0399]	11197 [0.0205]
Reflections [I>2sigma(I)]	6212	4730	6037
Data completeness (%)	98.96	99.78	98.67
Data/ restraints/ parameters	8895/12/814	6848/0/541	6933/0/545
Goodness-of-fit on F^2	1.025	1.050	1.023
Final R_1 indices [I>2sigma(I)]	R_1 = 0.0651, wR_2 = 0.1663	R_1 = 0.0518, wR_2 = 0.1154	R_1 = 0.0370, wR_2 = 0.0973
Final R indices [all data]	R_1 = 0.0940, wR_2 = 0.1891	R_1 = 0.0855, wR_2 = 0.1339	R_1 = 0.0431, wR_2 = 0.1031
Largest diff. peak/hole (e.Å^{-3})	1.018/ -0.313	0.246/ -0.275	0.228/ -0.223

Complex	**2-MeNPyNO•1**	**4-MeOPyNO•1**	**4-PhPyNO•1**	**IsQNO•1**
Empirical formula	$C_{48}H_{62}N_4O_{20}$	$C_{44}H_{46}N_2O_{12}$	$C_{54}H_{50}N_2O_{10}$	$C_{53}H_{58}N_2O_{16}$
Formula weight	1017.03	794.83	886.96	979.01
Temperature (K)	120.0	123.0	120.0	123.0
Crystal system	Monoclinic	Monoclinic	Monoclinic	Orthorhombic
Space group	$P2_1$	*C2/c*	$P2_1/c$	*Pnma*
Unit cell dimensions: a (Å)	10.8492(6)	18.6065(3)	13.3203(4)	16.5611(4)
b (Å)	20.9713(8)	14.6623(3)	16.1527(4)	20.8203(8)
c (Å)	11.4872(6)	14.2271(3)	20.8931(4)	14.9973(4)
α (°)	90	90	90	90
β (°)	107.111(6)	102.641(2)	100.307(2)	90
γ (°)	90	90	90	90
Volume / Å^3	2497.9(2)	3787.28(13)	4422.80(19)	5171.2(3)
Z	2	4	4	4
Density (calculated) mg/m^3	1.349	1.394	1.332	1.257
Absorption Coefficient mm^{-1}	0.106	0.843	0.748	0.775
F(000)	1080	1680	1872	2072
Crystal size (mm^3)	0.18 x 0.14 x 0.08	0.13 x 0.08 x 0.06	0.23 x 0.06 x 0.04	0.24 x 0.09 x 0.09
θ range for data collection (°)	2.98 to 25.25	3.87 to 66.75	3.37 to 66.75	3.63 to 66.72
Reflections collected [R(int)]	16891 [0.0300]	16391 [0.0289]	12192	13761 [0.0295]
Reflections [I>2sigma(I)]	7249	3081	7976	3758
Data completeness (%)	99.66	99.86	98.71	97.86
Data/ restraints/ parameters	8754/10/666	3356/0/269	12192/0/608	4622/7/373
Goodness-of-fit on F^2	1.024	1.050	0.871	1.058
Final R_1 indices [I>2sigma(I)]	R_1 = 0.0668, wR_2 = 0.1763	R_1 = 0.0324, wR_2 = 0.0816	R_1 = 0.0390, wR_2 = 0.0943	R_1 = 0.0542, wR_2 = 0.1490
Final R indices [all data]	R_1 = 0.0814, wR_2 = 0.1896	R_1 = 0.0352, wR_2 = 0.0839	R_1 = 0.0633, wR_2 = 0.1011	R_1 = 0.0670, wR_2 = 0.1590
Largest diff. peak/hole (e.Å^{-3})	0.621/ -0.366	0.194/ -0.244	0.241/ -0.247	0.633/ -0.256

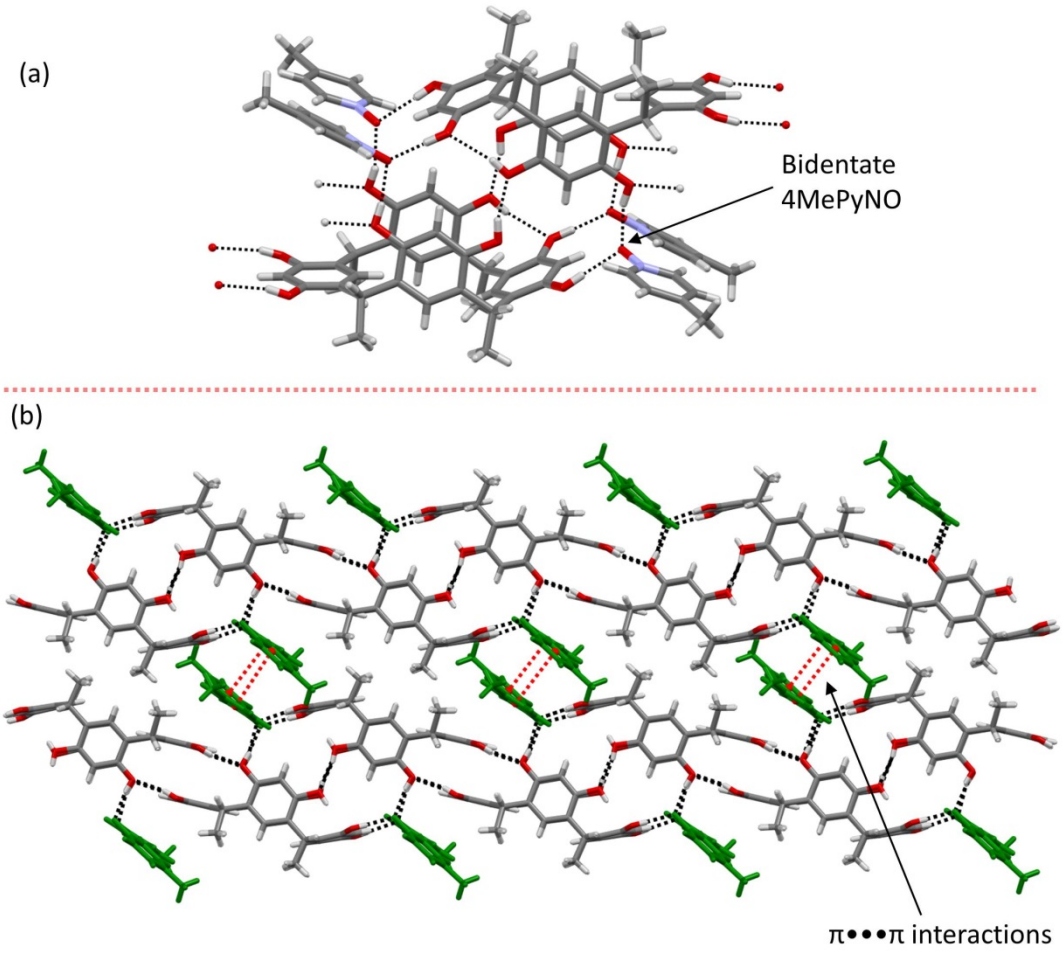

Fig. S1 (a) Section of 1-D tubular assembly to show bidentate nature of **4-MePyNO** in **4-MePyNO•1** (b) Section of crystal packing to shown the π•••π interactions between **4-MePyNO** molecules. Guest **4-MePyNO** molecules are coloured in green for clarity. Black broken lines represent hydrogen bonding and red broken lines represent centroid-to-centroid distances between **4-MePyNO** molecules.

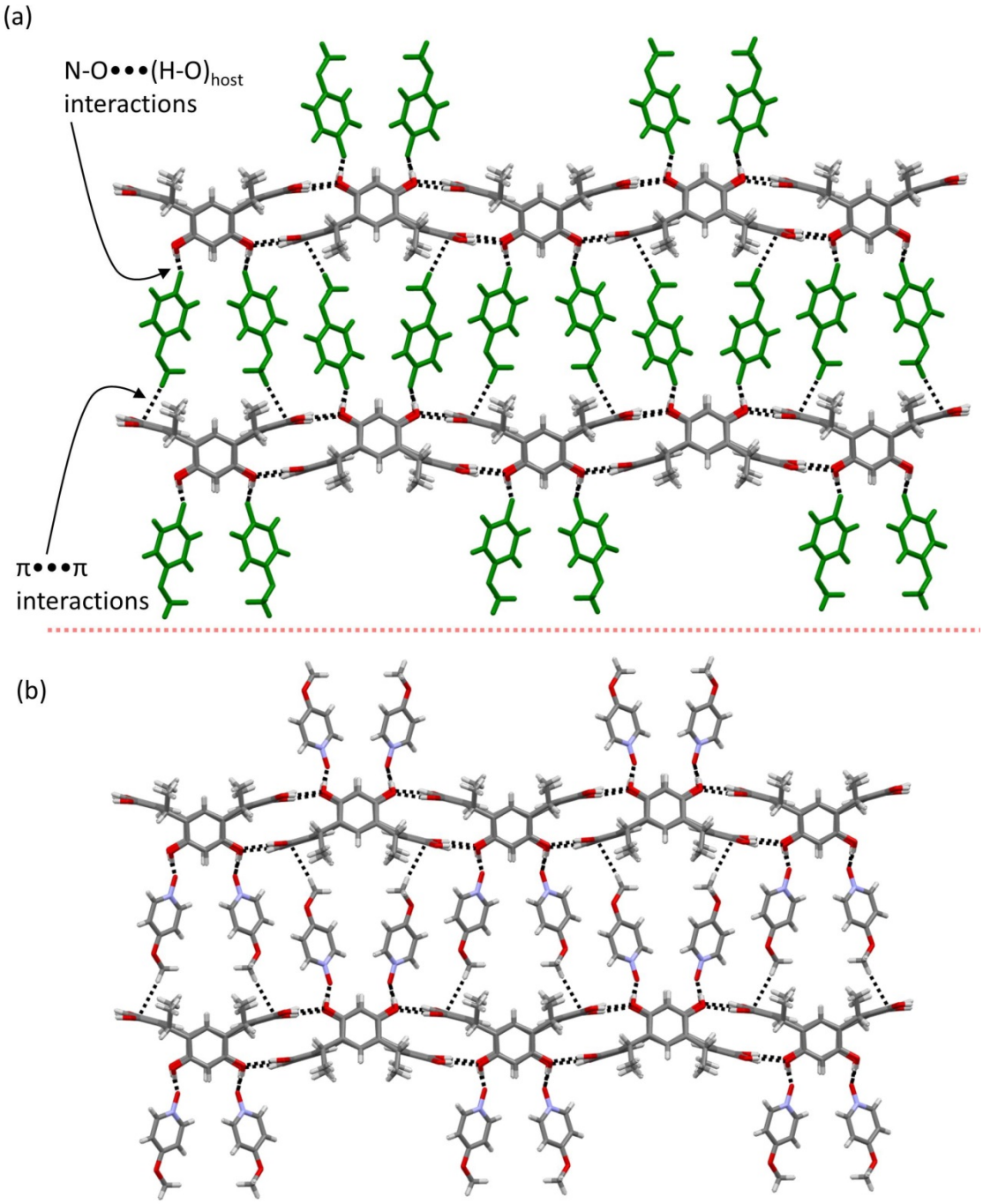

Fig. S2 Section of crystal packing of **4-MeOPyNO•1** to show interdigitation of 1-D polymers stabilized by C-H•••π interactions. In (a), the guest **4-MeOPyNO** molecules are shown in green colour to differentiate from (b).

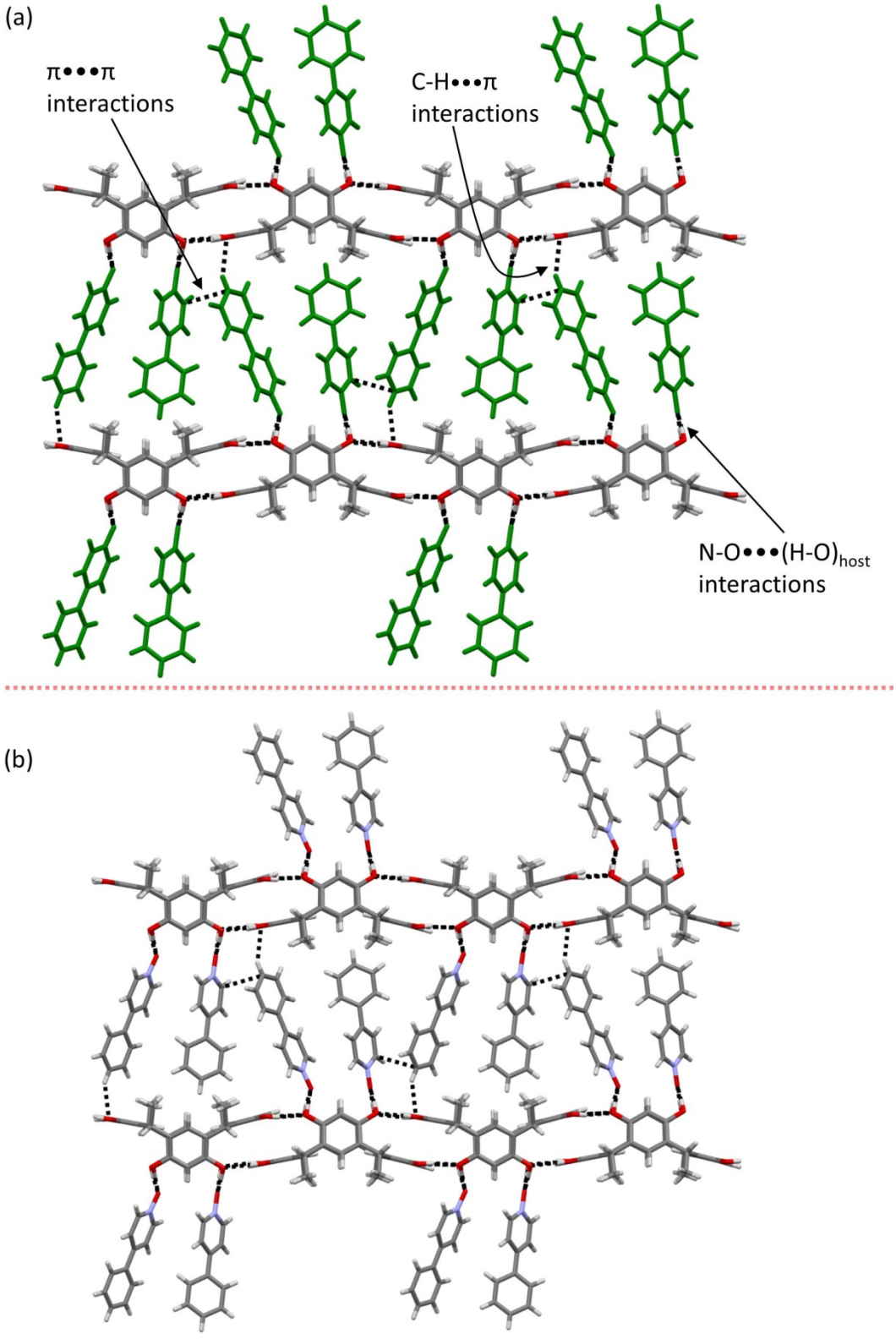

Fig. S3 Section of crystal packing of **4-PhPyNO•1** to show interdigitation of 1-D polymers stabilized by C-H•••π and π•••π interactions. In (a), the guest **4-PhPyNO** molecules are shown in green colour to differentiate from (b).

In complex **2-MeNPyNO•1,** the guest **2-MeNPyNO** resides close to host **1** aromatic ring and exhibits π•••π stacking at centroid-to-centroid distances of *ca.* 3.7 Å. Guests **2-MeNPyNO** and solvent molecules together decorates 1-D polymeric chain of host **1** molecules to give 3-D crystal packing as shown in Figure S4b. Also, a closer layer-by-layer look of 3-D crystal packing of **2-MeNPyNO•1** revealed that the 1-D host tubular assemblies are connected by two methanol molecules generating 2-D supramolecular sheet motifs as shown in Figure S4c.

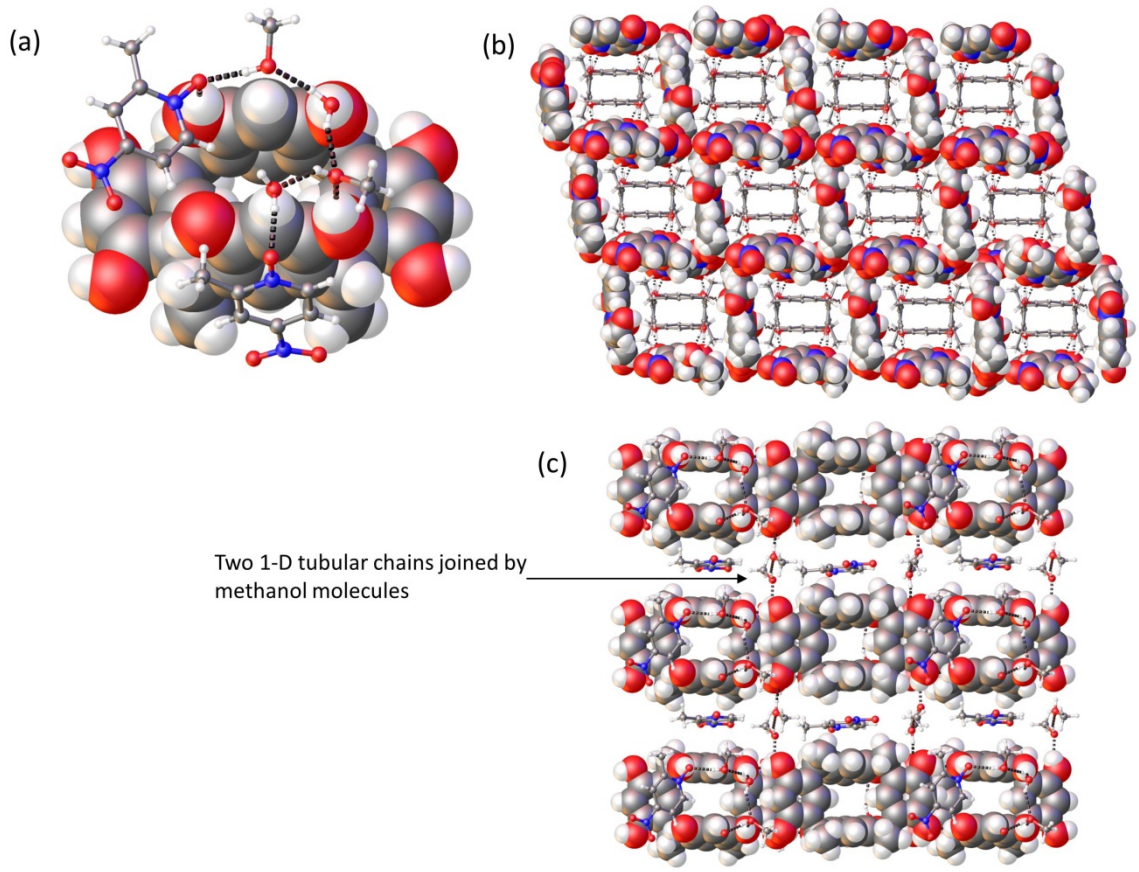

Fig. S4 (a) Asymmetric unit of **2-MeNPyNO•1**. b) Boat conformation of host **1** embedded with guests and solvent molecules (shown in CPK model). (c) Section of 3-D crystal packing of **2-MeNPyNO•1** viewed down the *a*-axis to show the H-bond templated 2-D sheet formation.

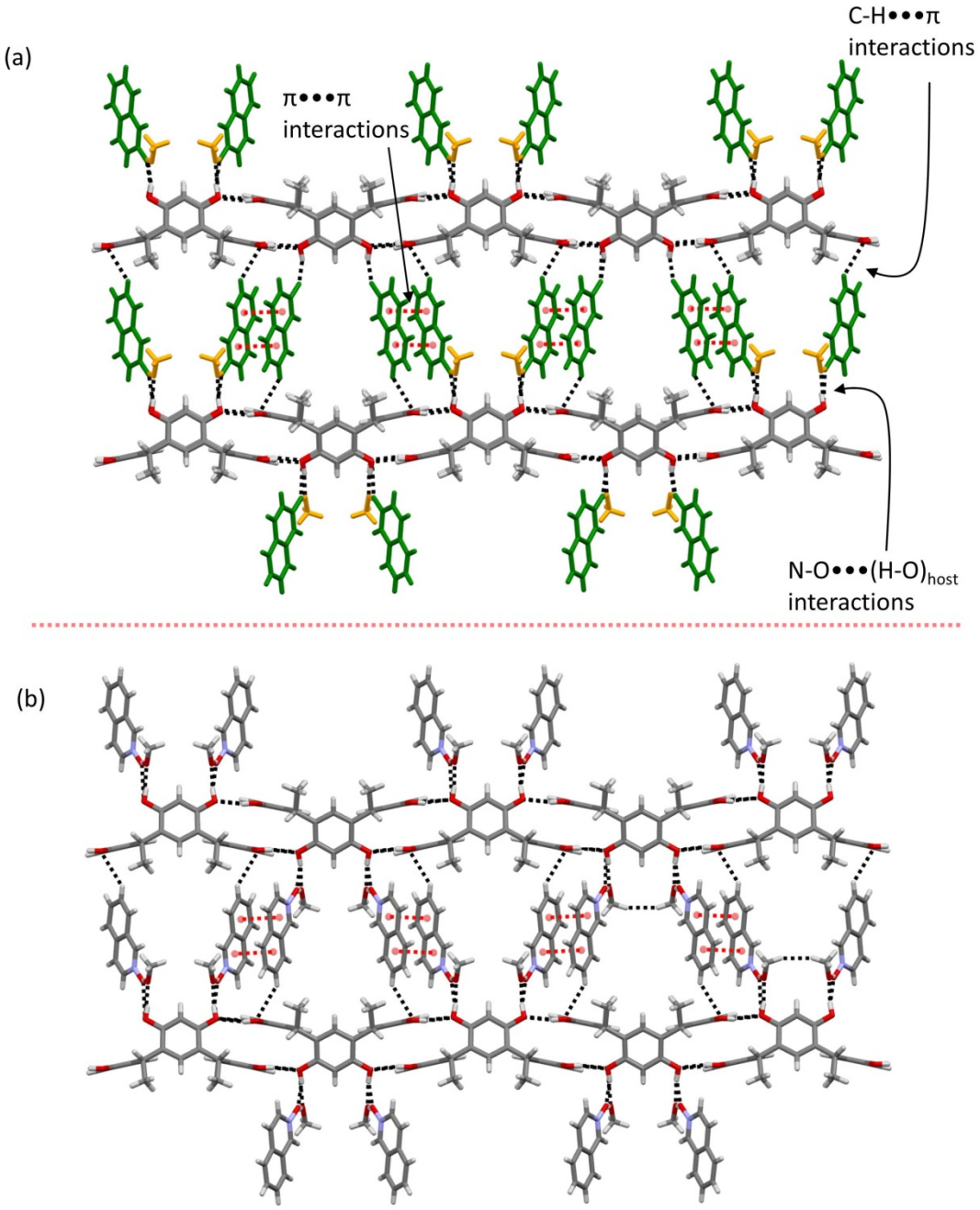

Fig. S5 Section of crystal packing of **IsQNO•1** to show interdigitation of 1-D polymers stabilized by C-H•••π and π•••π interactions. In (a), the guest **IsQNO** molecules are shown in green colour to differentiate from (b). Methanol molecules are shown in organge colour. Black broken lines represent hydrogen bonding and red broken lines represent centroid-to-centroid distances between **IsQNO** molecules.

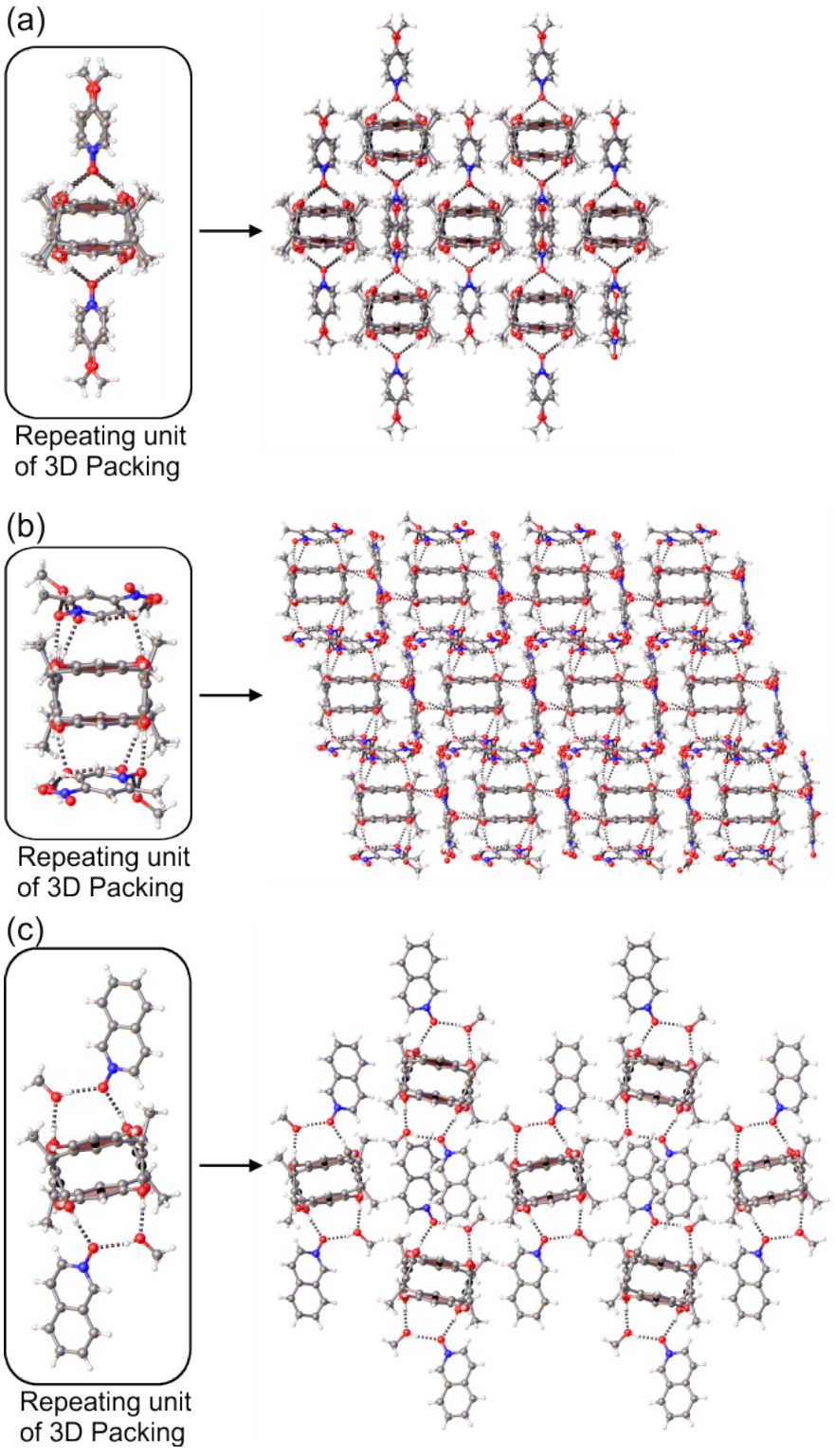

Fig. S6 (a) Repeating unit of 3-D crystal packing in **4-MeOPyNO•1** (left-side) and section of 3-D crystal packing of complex **4-MeOPyNO•1** (right-side). (b) Repeating unit of 3-D crystal packing in **2-MeNPyNO•1** (left-side) and section of 3-D crystal packing of complex **2-MeNPyNO•1** (right-side). (c) Repeating unit of 3-D crystal packing in **IsQNO•1** (left-side) and section of 3-D crystal packing of complex **IsQNO•1** (right-side).

III Solution Studies

^{1}H NMR spectra were recorded on a Bruker Avance DRX 500 MHz spectrometer. All signals are given as δ values in ppm using residual solvent signals as the internal standard. For sample preparation, a 10 mM stock solution of C_{methyl}-resorcinarene and 20 mM stock solution of the guests (**PyNO**, **2-MePyNO**, **3-MePyNO**, **4-MePyNO**, **4-MeOPyNO**, **2-MeNPyNO**, **4-PhPyNO**, **2,6-DiMePyNO**, **QNO**, and **IsQNO**) were prepared in CD_3OD. For the pure host, 300 µL of the stock solution was measured to NMR tube and diluted with 150 µL of pure CD_3OD to give a 6.6 mM sample concentration. For the pure guests, 150 µL of the stock solution was measured to NMR tube and diluted with 300 µL of pure CD_3OD to give a 6.6 mM sample concentration. For a 1:1 host-guest mixture, 300 µL of the host and 150 µL of the guests were measured to give a 6.6 mM concentration of both the host and the guests. The spectra were calibrated using the CD_3OD signal (δ_{CD3} = 3.31 ppm) as internal standard.

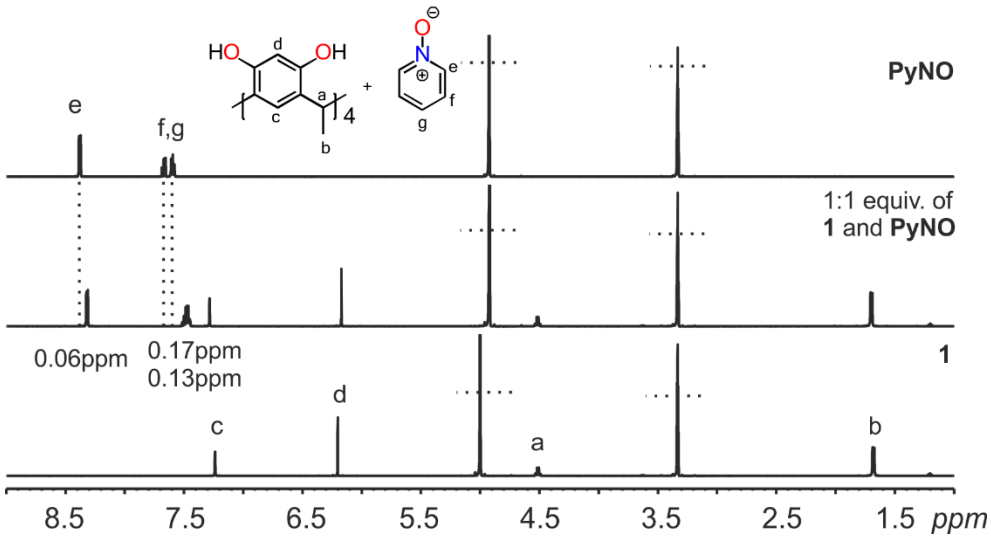

Fig. S7. ^{1}H NMR (CD_3OD, 293 K) of host **1** and **PyNO** guest. The shift changes of the guest signals in ppm are highlighted.

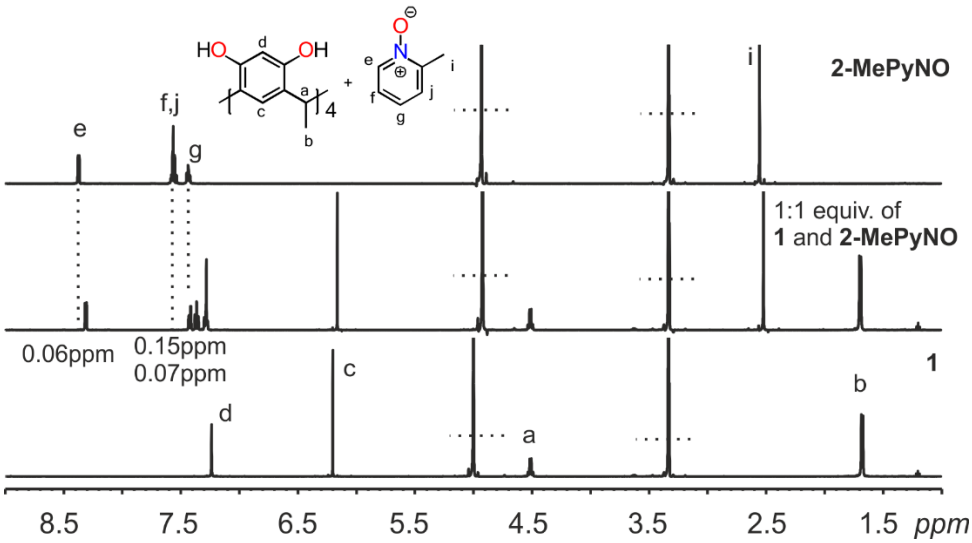

Fig. S8. ^{1}H NMR (CD_3OD, 293 K) of host **1** and **2-MePyNO** guest. The shift changes of the guest signals in ppm are highlighted.

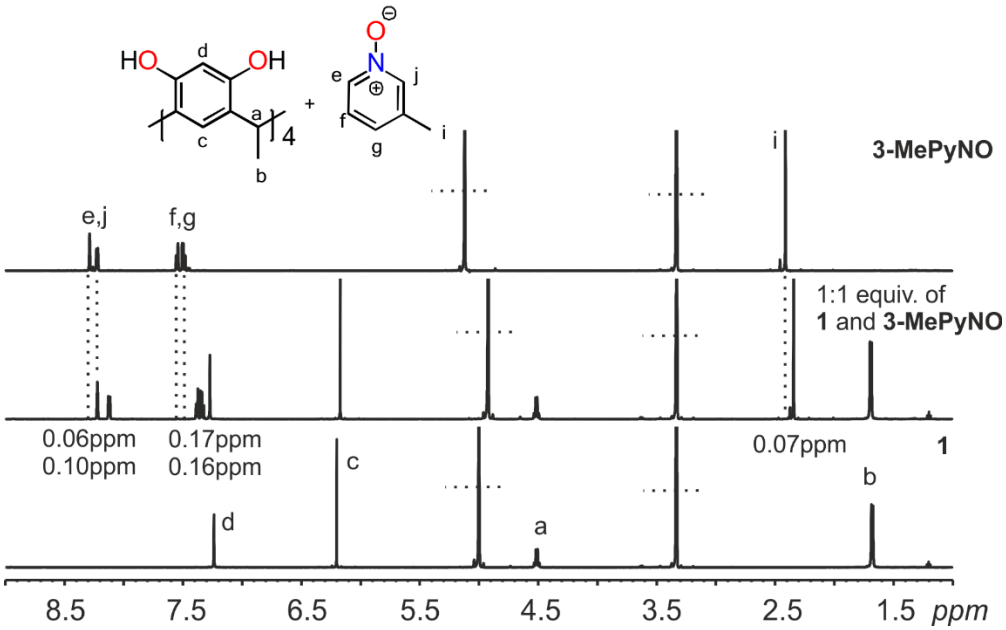

Fig. S9. ^{1}H NMR (CD_3OD, 293 K) of host **1** and **3-MePyNO** guest. The shift changes of the guest signals in ppm are highlighted.

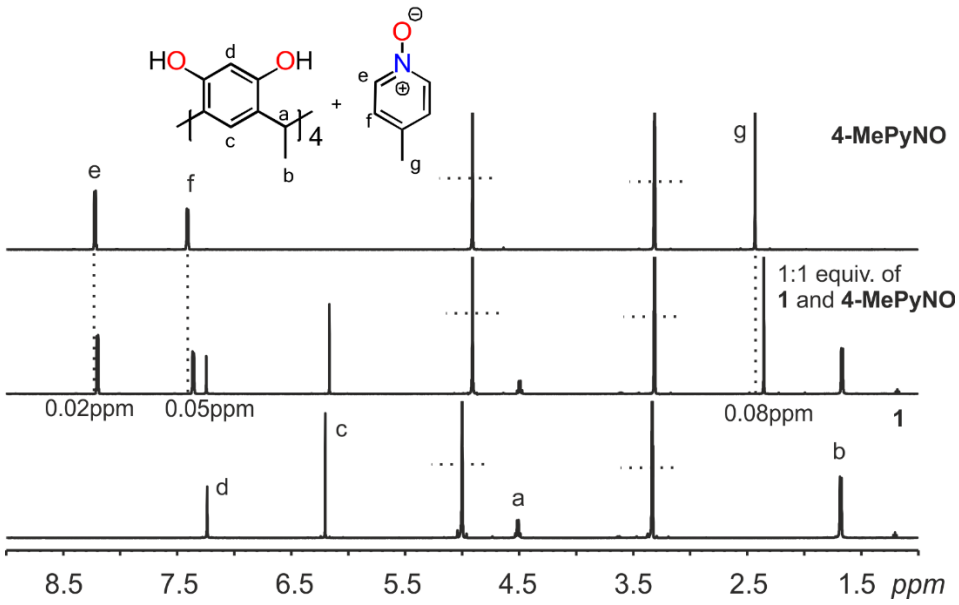

Fig. S10. ^{1}H NMR (CD_3OD, 293 K) of host **1** and **4-MePyNO** guest. The shift changes of the guest signals in ppm are highlighted.

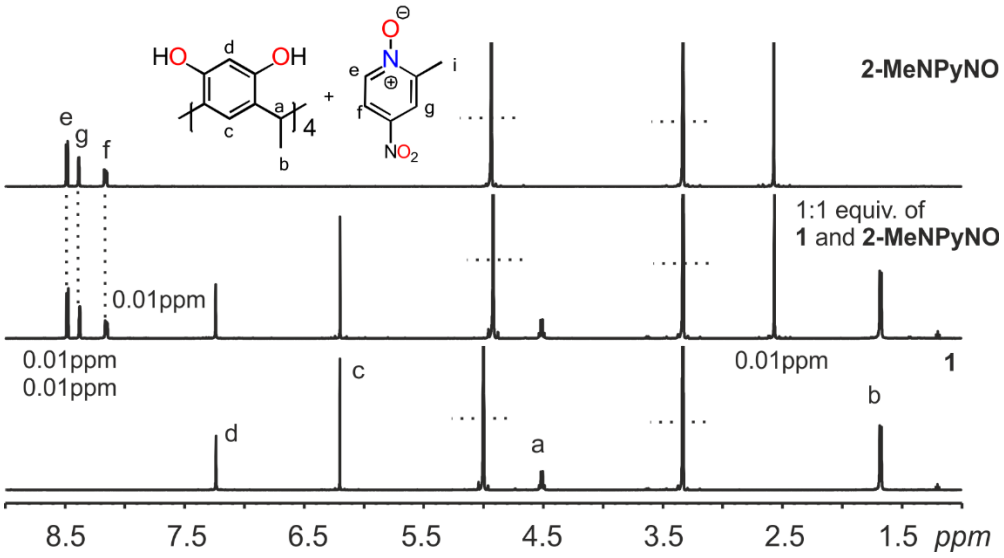

Fig. S11. ^{1}H NMR (CD_3OD, 293 K) of host **1** and **2-MeNPyNO** guest. The shift changes of the guest signals in ppm are highlighted.

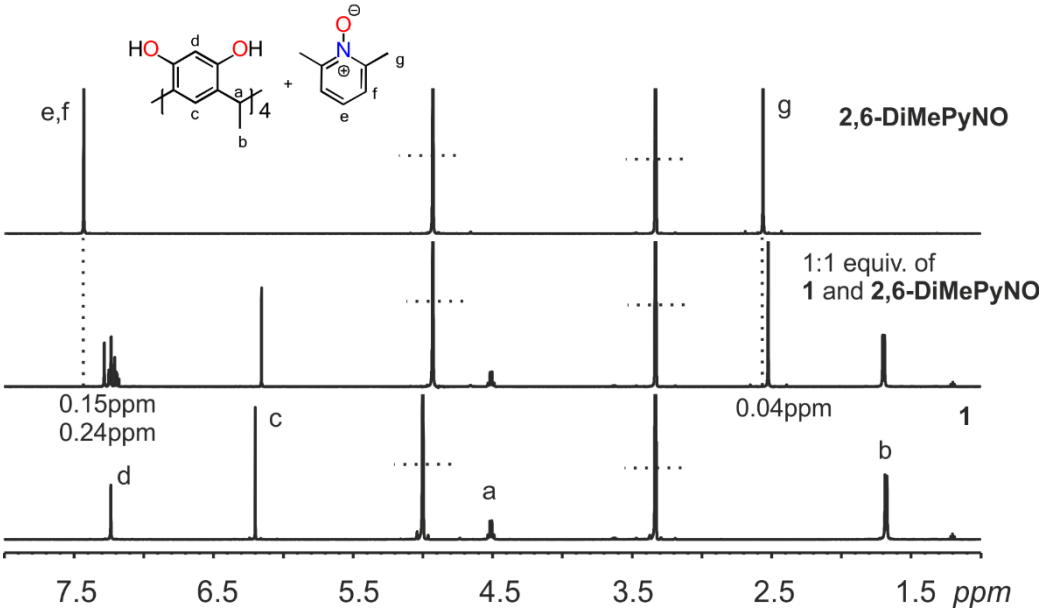

Fig. S12. ^{1}H NMR (CD_3OD, 293 K) of host **1** and **2,6-DiMePyNO** guest. The shift changes of the guest signals in ppm are highlighted.

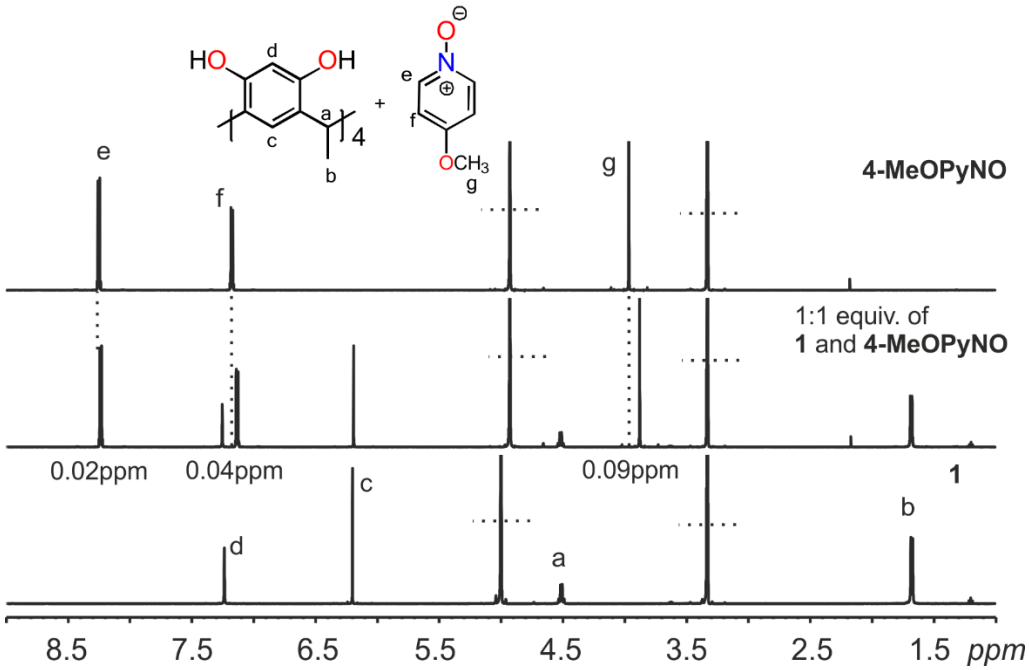

Fig. S13. ^{1}H NMR (CD_3OD, 293 K) of host **1** and **4-MeOPyNO** guest. The shift changes of the guest signals in ppm are highlighted.

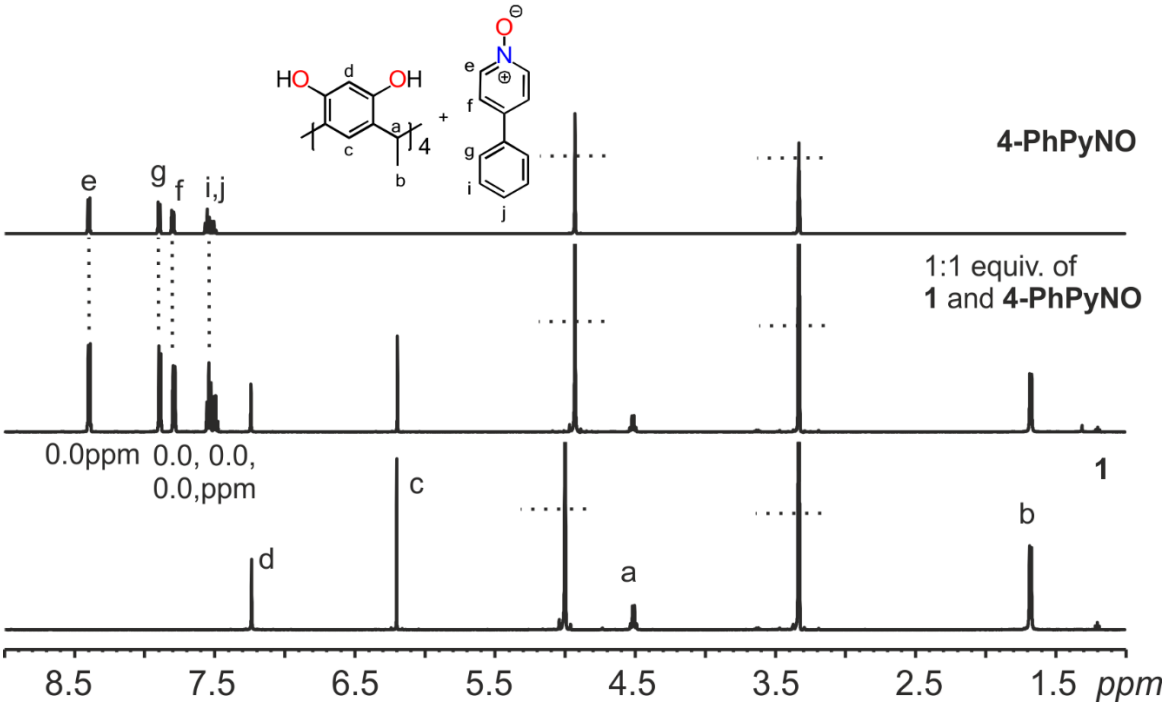

Fig. S14. ^{1}H NMR (CD_3OD, 293 K) of host **1** and **4-PhPyNO** guest. The shift changes of the guest signals in ppm are highlighted.

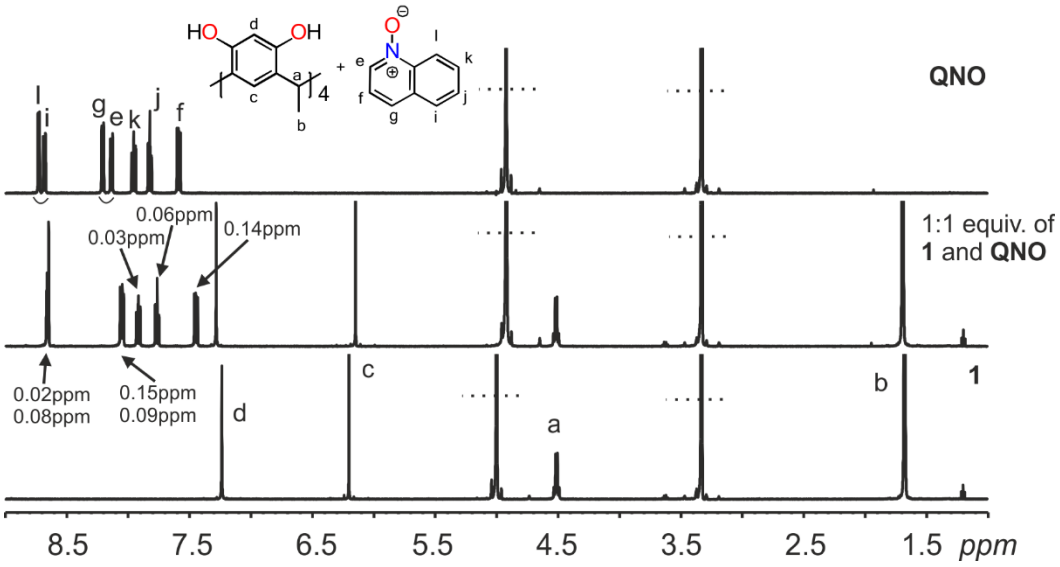

Fig. S15. ^{1}H NMR (CD_3OD, 293 K) of host **1** and **QNO** guest. The shift changes of the guest signals in ppm are highlighted.

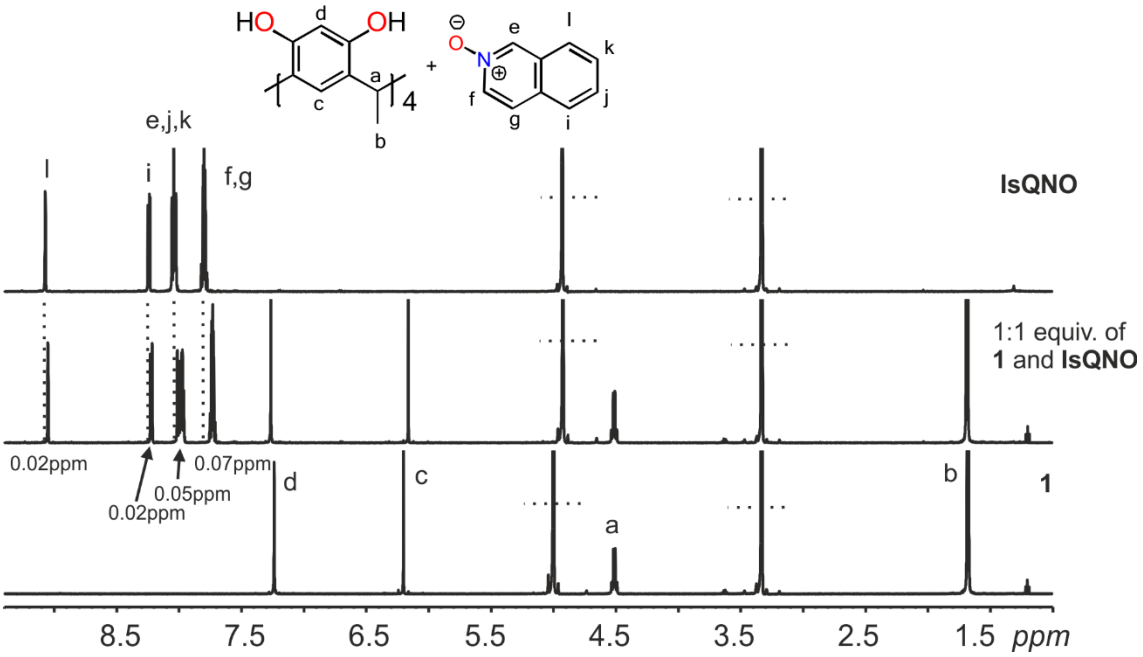

Fig. S16. ^{1}H NMR (CD_3OD, 293 K) of host **1** and **IsQNO** guest. The shift changes of the guest signals in ppm are highlighted.

Variable Temperature 1H NMR

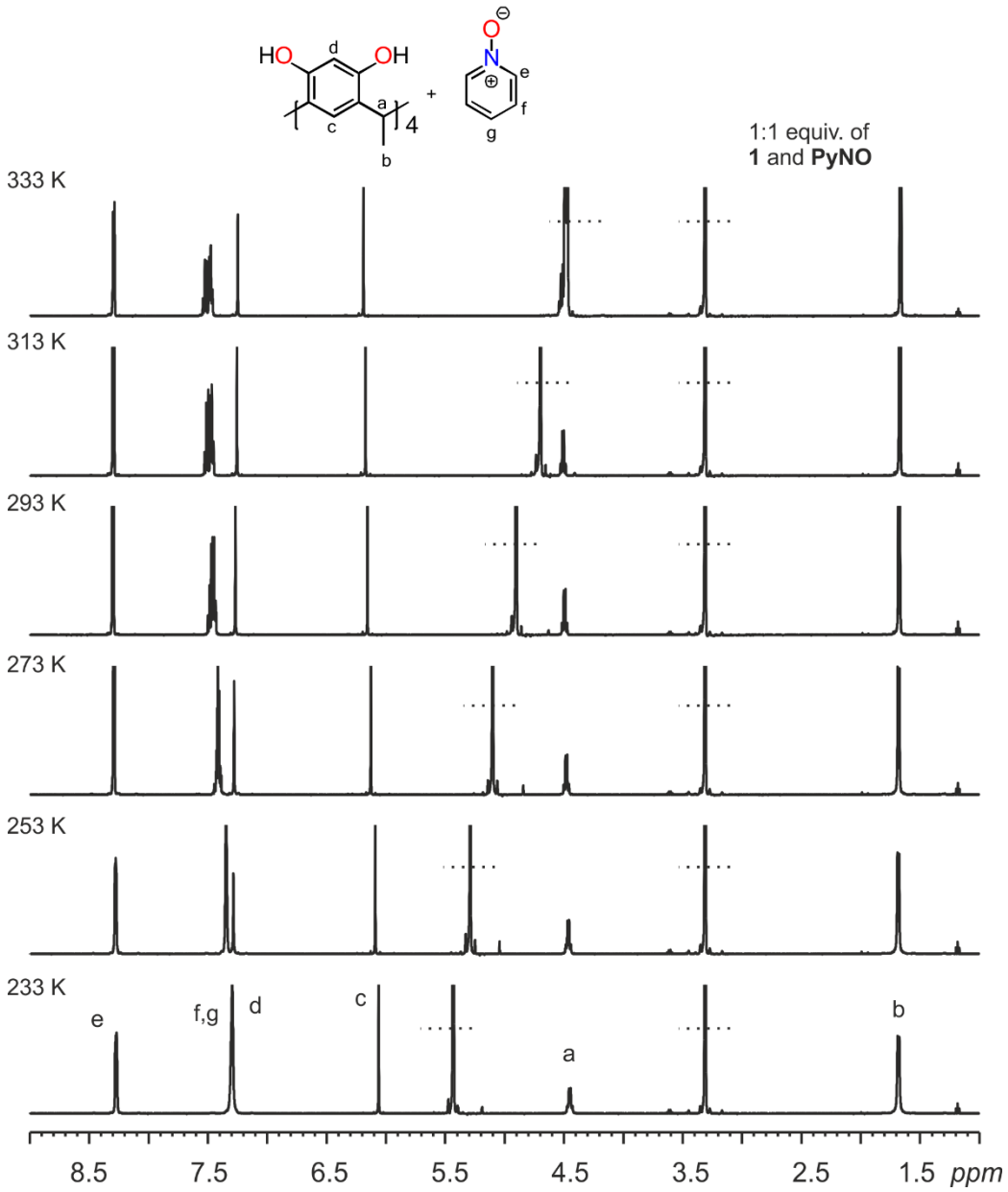

Fig. S17. Variable temperature ^{1}H NMR (CD_3OD) of host **1** and **PyNO** guest. No conformational change of the host was observed.

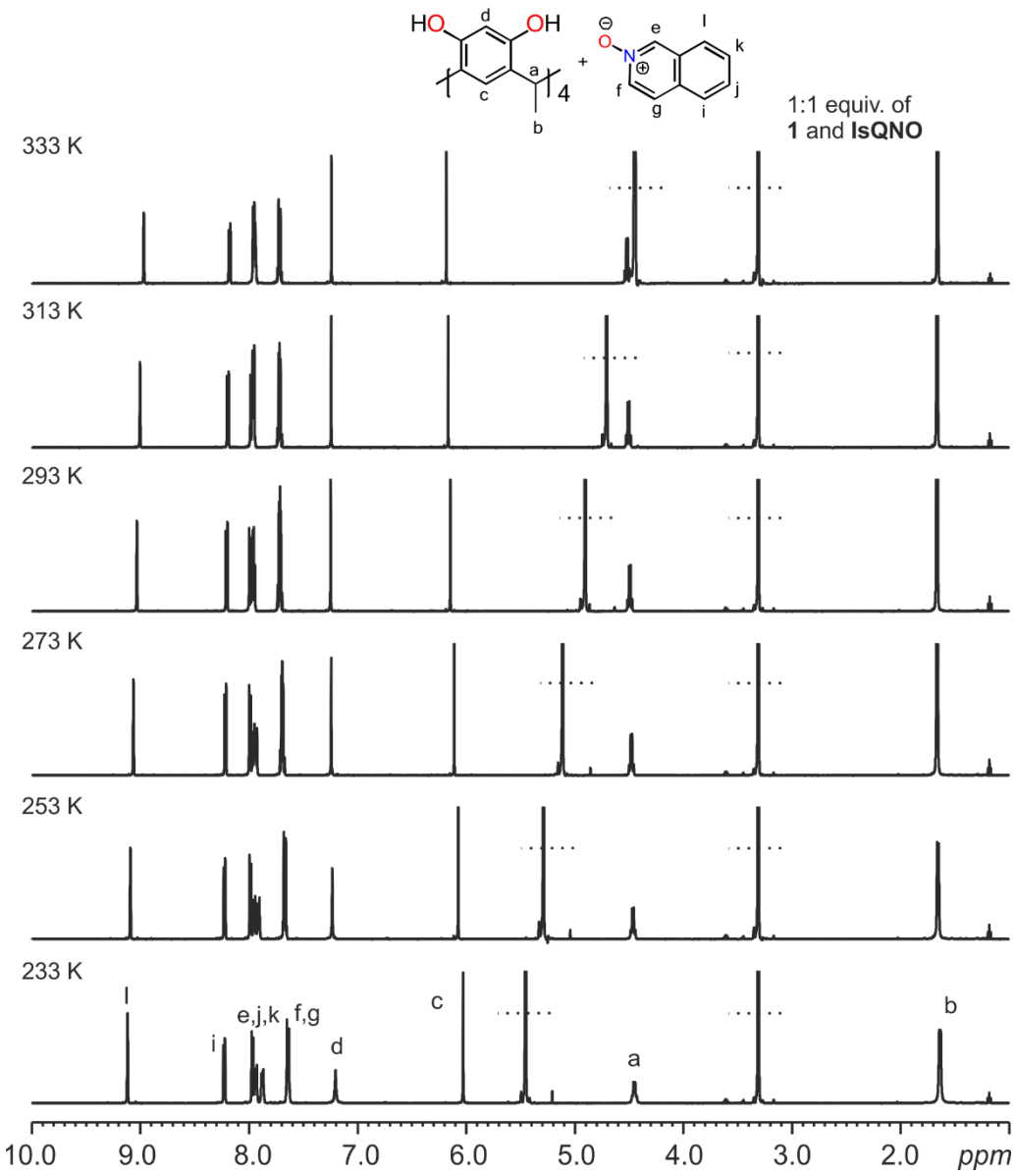

Fig. S18. Variable temperature ^{1}H NMR (CD_3OD) of host **1** and **IsQNO** guest. No conformational change of the host was observed.

VI References

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