SUPPORTING INFORMATION

for

Solid state sensing of non-polar VOCs using the bistable expansion and contraction of

helical polycarbodiimides

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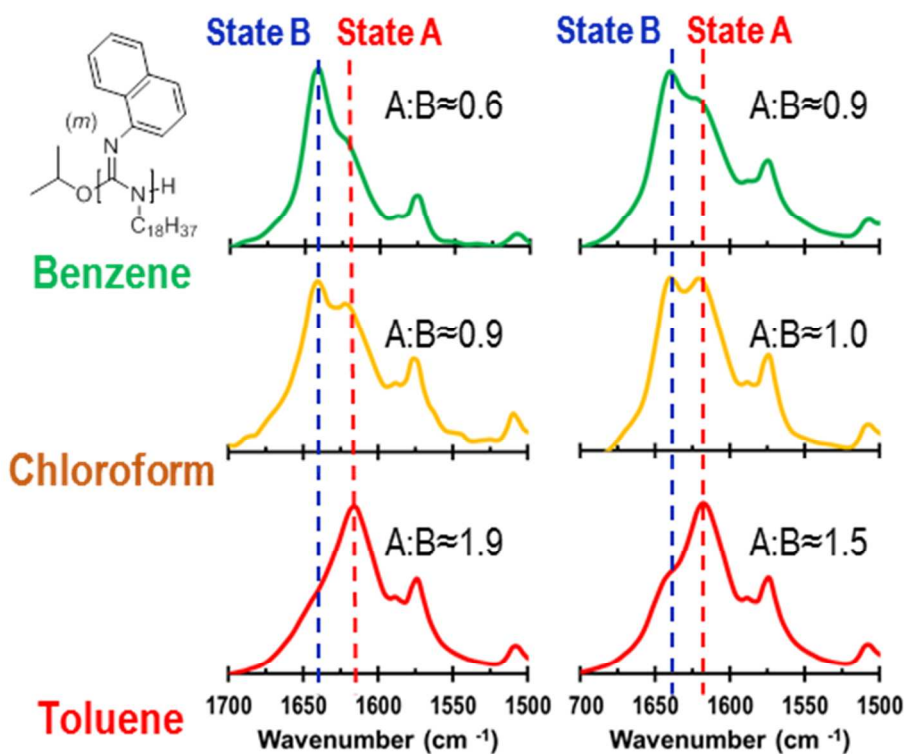

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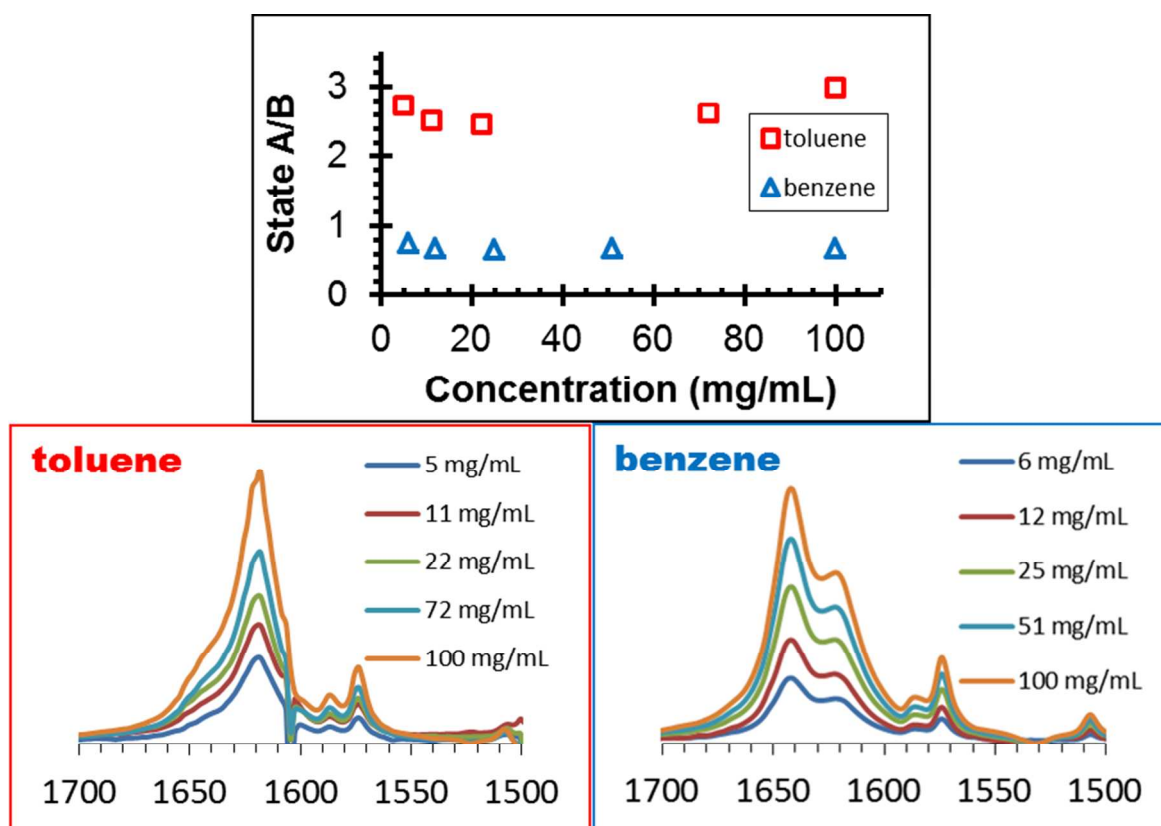
Section S1: Additional FTIR spectra of polyNOC: State A/B population independence to solution concentration and derived film thickness

Figure 2 of the main text shows transmission FTIR spectra of S-polyNOC drop- or spin-cast onto KBr windows. Analogous spectra for S-polyNOC deposited onto an ATR-FTIR crystal are shown in Figure S1.

Figure S1. ATR-FTIR spectra of sling-cast (left) and drop-cast (right) films of (M)-polyNOC

Consistent with transmission FTIR spectra shown in the main text, the population of state A and state B adopted in solution can be retained in the solid state if the carrier solvent is quickly removed (i.e. spin/sling casting vs. drop casting). If the solvent is allowed to evaporate slowly, then the population bias toward state A or state B in solution will begin to be lost, approaching ~1:1 state A: state B. Although the preference toward a 1:1 mixture of state A and state B can be seen with slow evaporation in both ATR-FTIR spectra and transmission-FTIR spectra, the population of state A:state B is independent of concentration when in solution.
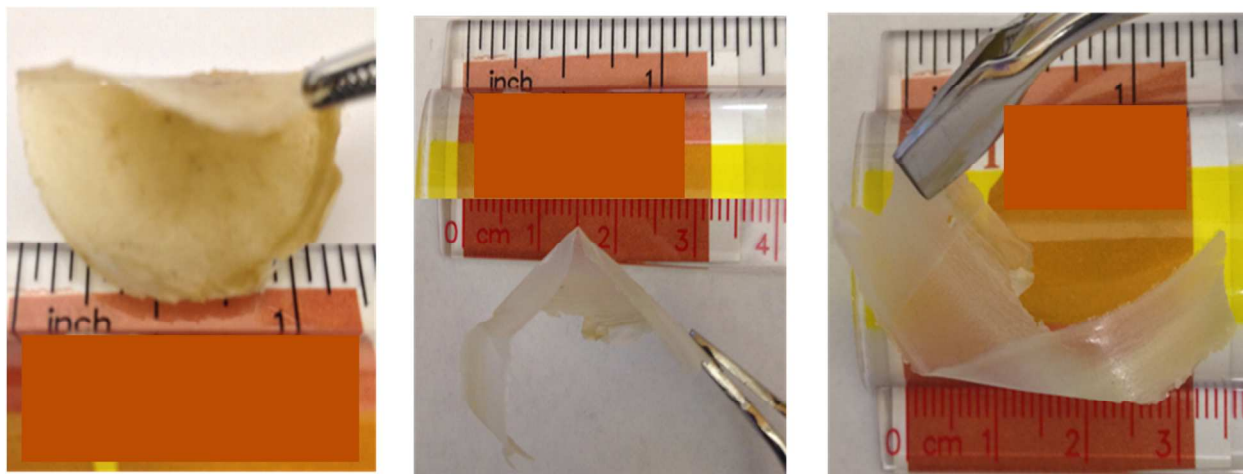

Figure S2. Concentration independence of the state A/state B population of (P)-polyNOC demonstrated from solutions of toluene and benzene ranging from 5 to 100 mg/mL. Transmission FTIR spectra of the imine stretching region is shown on the bottom and corresponding state A/state B values are shown above.

The state A:state B population of polyNOC was found to be independent of concentration in the range that could be measured by transmission FTIR spectroscopy. An overlay of transmission FTIR spectra for (P)-polyNOC dissolved in toluene and benzene ranging from 25-100 mg/mL can be seen in Figure S2. The state A/B population of (P)-polyNOC in the range measured was 0.68 ± 0.04 when dissolved in benzene and 2.66 ± 0.21 when dissolved in toluene. The higher standard deviation for toluene solutions is attributed to less than ideal subtraction of the overlapping C-C stretching mode of toluene at approximately 1605 cm^{-1} (neat toluene typically absorbs at 1614 cm^{-1}). Benzene does not absorb in the imine stretching region producing a more reliable measure of the state A/B population of polyNOC at different concentrations.

Section S2: Qualitative physical properties of polyNOC films with different State A/B populations

Samples of R- and S-polyNOC (200:1 catalyst: monomer, M_n~80 kDa) drop cast from different solvents yielded free-standing films with significantly different physical properties that could be seen with the eye and felt by touch. S-polyNOC dissolved in host solvents that afforded mostly state A, mostly state B, and approximately 50:50 state A:state B displayed the clearest differences in physical properties.
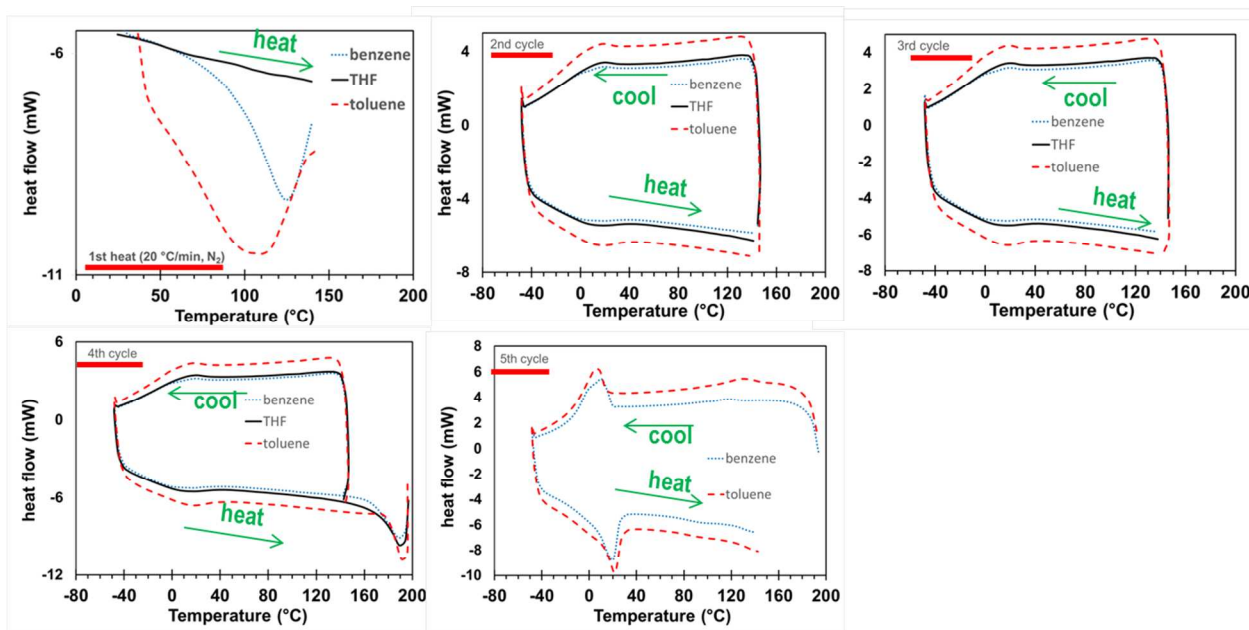
Figure S3. P-polyNOC films drop-cast from 25 mg/mL solutions of toluene (left), THF (middle), and benzene (right)

Toluene (A/B~1.4) yielded spongey polyNOC films that would break when folded and creased. Benzene (A/B~0.7) yielded films with the most robust physical properties qualitatively similar to a traditional thermoplastic (e.g. polyethylene); films could be repeatedly folded and creased. Tetrahydrofuran (A/B~0.9) yielded polyNOC films with a soft, slightly tacky feel that could be easily handled and folded but that would rip very easily.

Analogous qualitative behavior was also observed for films cast from dichloromethane (majority state A) and chloroform (majority state B) suggesting that the state A/B population is mainly responsible for differences in crystallinity and not solvent volatility. In addition, all films were drop cast in an environment saturated with the casting solvent to mitigate differences in crystallinity associated with evaporation rate. This was accomplished by placing a small beaker (e.g. 50 mL) half full of casting solvent, and with a wick (piece of weigh paper) along its side, underneath a larger beaker (e.g. 500 mL) placed upside down. Solutions of polyNOC (25 mg/mL) were then drop-cast on a silicon wafer, glass slide, or KBr plate placed alongside the smaller beaker. The coated substrate was then removed from the solvent vapor chamber after ca. 17 hours and dried under full dynamic vacuum (5-200 mTorr) for 2-3 hours at room temperature.

The qualitative physical properties of polyNOC films drop-cast from different solvents are consistent with the core-dual shell model introduced in the main text. The expanded state A conformation of segments of single polymer chains is attributed to intramolecular crystallization of n-octadecyl substituents in-between 1-naphthyl substituents (i.e. within the inner shell of the polyNOC core-dual shell tertiary structure). The additional crystalline phases associated with the inner shell crystallization were observed in DSC measurements and resulted in a measured increase of intermolecular spacing between polyNOC chains via GI-XRD. The increased distance between polyNOC chains in a predominantly state A conformation is consistent with less entanglement between n-octadecyl chains.

Section S3: Differential scanning calorimetry of (M)-polyNOC drop-cast from toluene, benzene, and THF
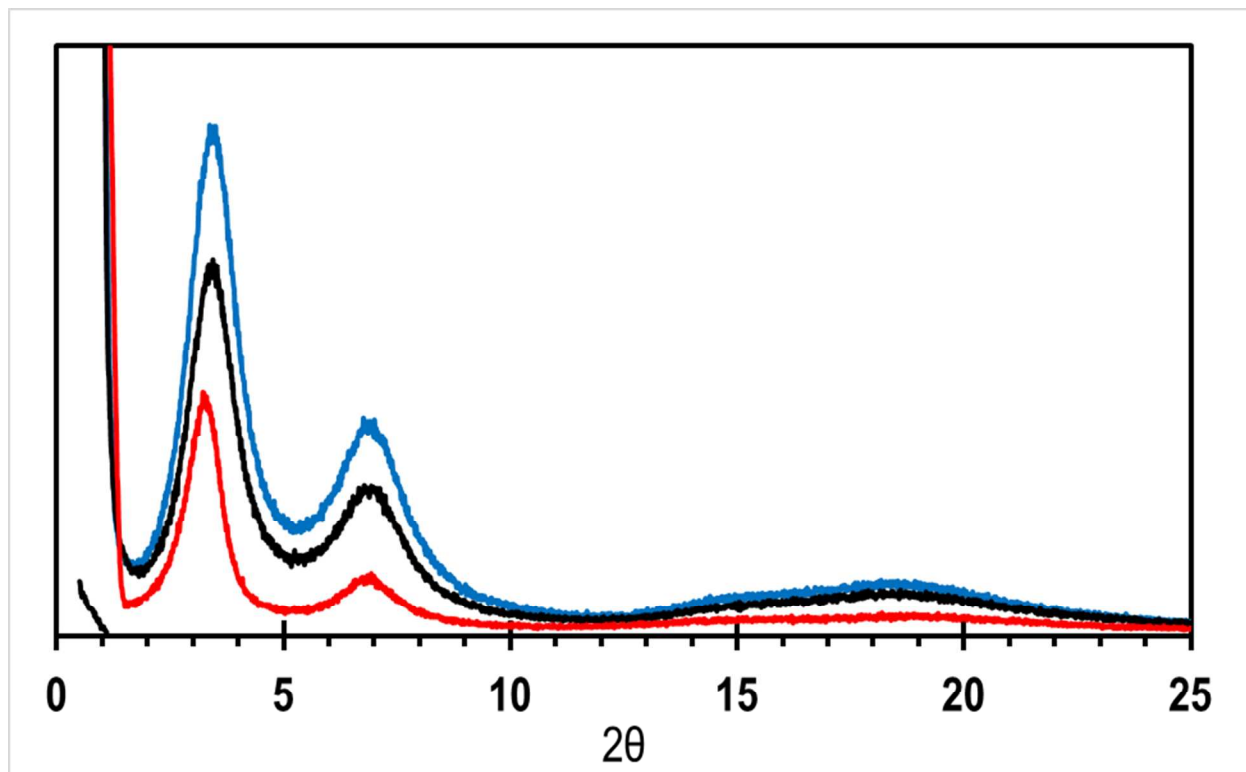

Figure S4. Overlaid DSC thermograms for 5 mg samples of (m)-polyNOC drop-cast from benzene (blue traces), tetrahydrofuran (black traces; THF), and toluene (red traces) heated from room temperature to 150 °C (top left), then cooled to -50 °C and heated to 150 °C two times (top middle and top right, respectively), cooled to -50 °C and heated to 200 °C (bottom left), and

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finally cooling to -50 °C and heated to 150 °C (bottom middle). All experiments were conducted in a nitrogen environment and with a heating/cooling rate of 20 °C/min.
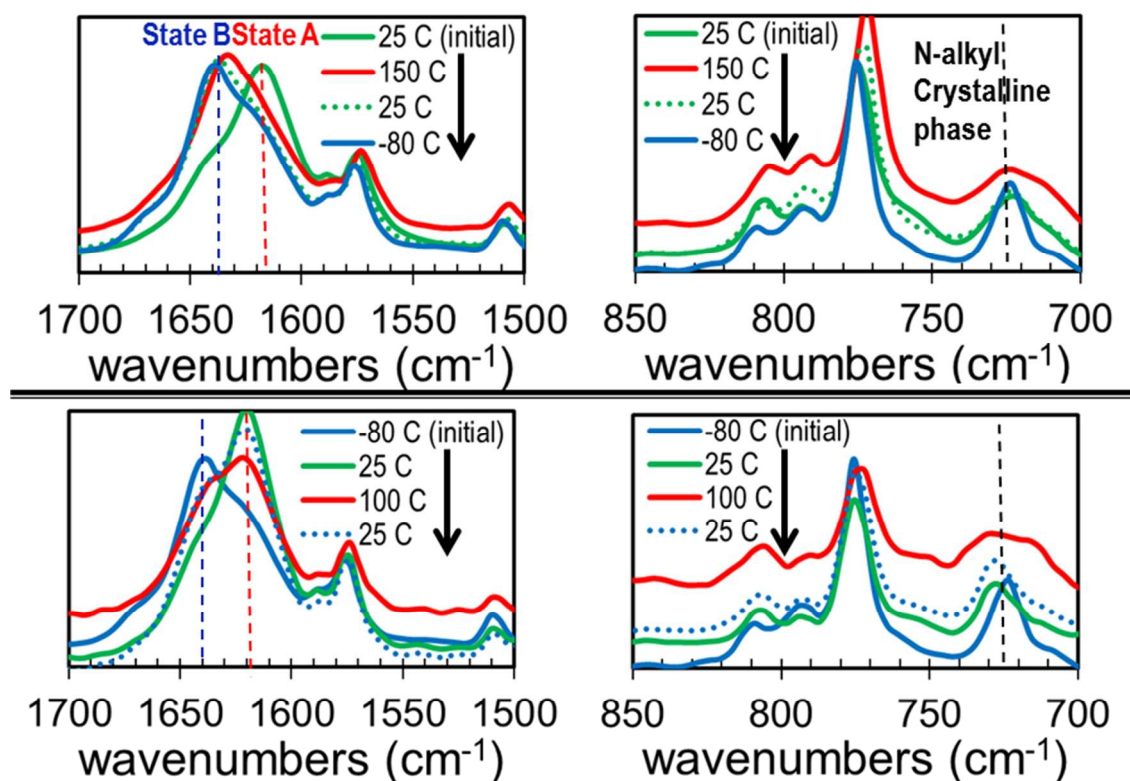
As mentioned in the main text, crystallinity of polyNOC films was influenced by the state A/B population adopted in solution before casting. Additional DSC traces after the processing history had been removed for (M)-polyNOC films cast from benzene, THF, or toluene are shown in figure S4. After fully melting n-octadecyl crystalline phases by heating to 150 °C at 20 °C/min all three polyNOC films exhibited identical crystallization endotherms centered at ca. 20 °C while cooling and corresponding melting exotherms centered at ca. 10 °C when re-heating (Figure S4, upper middle set of DSC traces). The transitions were reproducible when heating/cooling between -50 °C and 150 °C (Figure S4, upper right set of DSC traces). Heating further to 200 °C on a subsequent heating/cooling cycle revealed an additional, sharp endotherm centered at 190 °C for all polyNOC films which is associated with de-polymerization (Figure S4, lower left set of DSC traces). A final heating/cooling cycle displayed sharp endotherms and exotherms for each film centered at ca. 10 °C and 20 °C, respectively (Figure S4, lower middle set of DSC traces). The sharp transitions are nearly identical to the crystallization and melting of *N*-1-naphthyl-*N'*-(n-octadecyl)carbodiimide monomer.

Section S4: X-ray diffraction patterns of (M)-polyNOC

Figure S5. Out-of-plane GI-XRD patterns of (M)-polyNOC drop cast onto silicon wafers from 35 mg/mL solutions of chloroform (blue, top), THF (black, middle), or toluene (red, bottom).

Section S5: Data and additional discussion for the temperature-dependence of the state A/B population in polyNOC films.

Figure S6. Temperature-dependence of polyNOC state A/B population in thin films. ATR-FTIR spectra of (M)-polyNOC film at selected temperatures while heating from 25-150 °C, cooling to -80 °C (top), heating from -80 to 100 °C, and then cooling to 25 °C (bottom); the imine stretching region used to monitor the state A/B population is shown on the left and the fingerprint region used to monitor octadecyl crystallization is shown on the right.

Variable-temperature IR experiments were conducted on polyNOC films deposited on a probe-type ATR-FTIR crystal. The influence of n-octadecyl crystallization on the state A/B population

was probed by monitoring the State A/B population of a polyNOC film while heating/cooling above and below the melting point of n-octadecyl substituents (100-120 °C). For example, thin films of (M)-polyNOC heated to either 100 or 150 °C are shown in Figure S6.

The State A/B population of (M)-polyNOC steadily decreased from ~1.6 at room temperature until leveling off between 135-140 °C to ~0.8. The State A/B population remained constant when heated to 150 °C, dropping slightly to 0.7 when cooled past room temperature and down to -80 °C. In contrast, the State A/B population could be reversibly biased if only heated up to 100 °C before being cooled. Complete melting of n-octadecyl substituents locks in a state A/B of 0.8 until being cooled passed the recrystallization temperature, at which point the state A/B can be again modulated by heating and cooling.

The fingerprint region of high-resolution FTIR spectra has been used to identify and monitor the crystalline phases of n-alkyl grafted bottle-brush polymers during heating and cooling, corroborated with analogous X-ray diffraction studies.[1] The number and type of crystalline phases could not be determined from FTIR spectra collected with 4 cm^{-1} resolution, but obvious changes in the fingerprint region were observed both with and without changes in the State A/B ratio. For example, spectra overlays in Figure S6 (right side) display a broadening of the C-H stretch absorbance centered at ca. 724 cm^{-1} when heated to 100 °C, appearing to split into two overlapping absorbance bands centered at 715 and 735 cm^{-1}, which eventually turns into a single broad hump when heated to 150 °C. A single peak reappears, sharpening and slightly red-shifting when cooled to -80 °C.

Although the GI-XRD and DSC suggest that different crystalline phases are associated with State A and State B, unique changes associated with State A and State B could not be seen in the C-H stretching region, but changes that were seen suggest that crystalline phase changes of

n-octadecyl substituents can occur with and without changes in the State A/B population. This behavior is consistent with two types of n-octadecyl crystallization – intermolecular crystallization between the outer shell of polyNOC chains and intramolecular crystallization within the inner shell of polyNOC chains (in-between 1-naphthyl substituents).

References

1. Shi, H.; Wang, H.; Xin, J. H.; Zhang, X.; Wang, D. *Chem. Commun.* **2011**, *47*, 3825.