Supporting Information

Pyridyl-phenylethynylene *Bis*-Urea Macrocycles: Self-Assembly and Utility as a Nanoreactor for the Selective Photoreaction of Isoprene

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1. Synthesis and characterization of *bis*-urea macrocycle 1.



Scheme S1. Synthesis of the macrocycle. (a) $Pd(PPh_3)_2Cl_2$, TBAF•3H₂O, 80 °C (b) NBS/ PPh₃, THF, -10 °C to rt (c) Triazinanone, NaH, THF, reflux (d) 1:1 of 20% [NH(CH₂CH₂OH)₂/H₂O, adjusted with HCl to pH~2] : MeOH, reflux.

1.1 Synthesis of the diol compound.¹



Scheme S2. Synthesis of the diol compound.



Figure S1. ¹H-NMR (DMSO-d₆, 400 MHz) of the diol compound.



Figure S2. ¹³C-NMR (DMSO-d₆, 100 MHz) of the diol compound.

1.2 Synthesis of the dibromide compound:







Figure S3. ¹H-NMR (CDCl₃, 400 MHz) of the dibromo compound.



Figure S4. ¹³C-NMR (CDCl₃, 100 MHz) of the dibromo compound.

1.3 Synthesis of the protected macrocycle:



Scheme S4. Synthesis of the protected macrocycle.



Figure S5. ¹H-NMR (CDCl₃, 300 MHz) of the protected macrocycle.



Figure S6. ¹³C-NMR (CDCl₃, 100 MHz) of the protected macrocycle.

1.4 Deprotection to afford the *bis*-urea macrocycle:



Scheme S5. Deprotection to afford the target *bis*-urea macrocycle.



Figure S7. ¹H-NMR (DMSO-d₆, 400 MHz) of the *bis*-urea macrocycle.



Figure S8. ¹³C-NMR (DMSO-d₆, 100 MHz) of the *bis*-urea macrocycle.

2. Self-assembly of the *bis*-urea macrocycle to afford host 1.

Self-assembly was carried out using following methods:

Method 1

The macrocycle (50 mg) was placed in a small scintillation vial and heated in \sim 10 mL DMSO to obtain a clear pale yellow solution. The small vial was placed inside a larger vial containing MeOH and sealed. Needle shaped pale yellow crystals were obtained after a week.

Method 2

The macrocycle (10 mg) was placed in a small scintillation vial and heated in ~ 2 mL DMSO to obtain a clear pale yellow solution. The small vial was placed inside a larger vial containing H₂O and sealed. Needle shaped pale yellow crystals were obtained after a few days.

Method 3

A small scintillation vial was charged with macrocycle (10 mg) and \sim 1 mL DMSO. The vial was placed in temperature controlled crystallization bath at 90 °C for 20 min to obtain a clear pale yellow color solution. Sample was slowly cooled (1 °C/h) to rt over few days to yield needle shaped pale yellow crystals.

Crystals obtained from all three methods were subjected to XRD analysis and yielded the same assembled structure with disordered solvent molecules. All studies were carried out using crystals obtained from method 1.

3. Additional single crystal X-ray diffraction information for 1 and 3.

3.1 Single crystal X-ray diffraction details for 1.

X-ray intensity data from a pale yellow needle crystal were collected at 100(2) K using a Bruker SMART APEX diffractometer (Mo Ka radiation, 1 = 0.71073 Å).² The crystals diffracted weakly because of size, needle morphology and disorder. No diffraction was observed above a 2 θ value of ca. 45°, and the data were truncated at that value. The raw area detector data frames were reduced using the SAINT+ program.² Final unit cell parameters were determined by least-squares refinement of 2962 reflections from the data set. The structure was solved by direct methods with SHELXS.³ Subsequent difference Fourier calculations and full-matrix least-squares refinement

against F2 were performed with SHELXL-2013/42³ using OLEX2.⁴ Corrections to the structure factors for the contribution of disordered species were performed with the Squeeze program in PLATON.^{5,6}

The compound crystallizes in the orthorhombic space group Pbcn as determined uniquely by the pattern of systematic absences in the intensity data. The asymmetric unit consists of half of one molecule, which is located on a crystallographic two-fold axis of rotation, and a tubular volume of disordered solvent species running along the crystallographic b axis. No reasonable disorder model could be achieved for the disordered guests after many trials. Their contribution to the scattering factors was accounted for with the Squeeze program.^{5,6} The solvent-accessible volume of the unit cell was calculated to be 1341.4 Å³ (28.6% of the total unit cell volume), corresponding to 342 electrons per unit cell. The reported F.W, dcalc and F(000) reflect only the known unit cell contents. Non-hydrogen atoms were refined with anisotropic displacement parameters. Hydrogen atoms bonded to carbon were placed in geometrically idealized positions and included as riding atoms. The two unique urea hydrogen atoms were located in difference maps and refined isotropically with their N-H distances restrained to be similar (SHELX SADI). The largest residual electron density peak in the final difference map is 0.20 e-/Å³, located 1.1 Å from C21.



Figure S9. 1D channels extended along the crystallographic *b* axis.

3.2 Single crystal X-ray diffraction details for **3**.

X-ray intensity data from a pale yellow pale crystal were measured at 150(2) K on a Bruker SMART APEX diffractometer (Mo K α radiation, $\lambda = 0.71073$ Å).⁷ Raw area detector data frame integration was performed with SAINT+.⁷ Final unit cell parameters were determined by least-squares refinement of 3774 reflections from the data set. Direct methods structure solution, difference Fourier calculations and full-matrix least-squares refinement against F² were performed with SHELXTL.⁸

The compound crystallizes in the space group $P2_1/m$ as determined by the pattern of systematic absences in the intensity data and by achieving a reasonable solution and refinement of the structure. The asymmetric unit consists of half of one C₆₀H₅₆N₈O₂ molecule located on a crystallographic mirror plane, and half of one methylene chloride molecule also located on a mirror plane. The *tert*-butyl group C31-C34 is disordered across the mirror plane. The displacement ellipsoids of tert-butyl group C3-C5 also indicate slight disorder but this could not be modeled successfully. The methylene chloride molecule is disordered over multiple positions across the mirror plane. To account for this electron density, a disorder model involving one carbon atom position and five chlorine atom positions was refined. Occupancies for the carbon atom C1S and for Cl1 were fixed at 0.5. Occupancies for the remaining four chlorine sites were fixed manually such that they summed to 0.5 and gave reasonable displacement parameters. The reported methylene chloride hydrogen atom positions correspond to the major disorder fraction of this group, and some short C-Cl distances reflect the limitations of the disorder model. All non-hydrogen atoms were refined with anisotropic displacement parameters except for Cl3, Cl4 and Cl5 (isotropic). Hydrogen atoms were placed in geometrically idealized positions and included as riding atoms. The high R-factors are because of the *t*-butyl and solvent disorder in the crystal.



Figure S10. X-ray crystal structure of urea protected 1. (solvent CH_2Cl_2 omitted for clarity) (a) Top view of the macrocycle (b) View through the crystallographic *b* axis.

4. Hirshfeld surface analysis of 1 and comparison with 2.

Molecular Hirshfeld surface for **1** and **2** were constructed using Crystal Explorer 3.0.⁹ The Crystallographic Information File (.cif) of host **1** was imported into Crystal Explorer and a high resolution Hirshfeld surface was mapped with the function d_{norm} . Two dimensional (2D) fingerprints maps were obtained by calculating the distances from the Hirshfeld surface to the nearest nucleus inside the surface (d_i) to the outside surface (d_e) to analyze the molecular interactions around the nearest neighbor molecules. In 2D maps, green regions shows closer contacts and longer contacts indicated in blue color. The Hirshfeld surfaces of **1** and **2** were generated over a d_{norm} range -0.5 to 1.5. All surfaces constructed using d_{norn} function were illustrated as transparent hollow maps in order to clearly visualize the pyridine-phenylethynylene macrocycle inside the surface. The red spots on the surfaces represent the distances shorter than sum of vdW radii and blue regions correspond to the distances longer than sum of vdW radii.



Figure S11. Hirshfeld surface analysis of the macrocycle **1**. a) Bifurcated H bonding between macrocycles. b) CH-π interactions between neighboring macrocycle. c) Offset π- stacking interactions between neighboring macrocycle. d) Two dimensional map resolved into O...H/H...O contacts. e) Two dimensional map resolved to show C...H/H...C contacts. f) Two dimensional map highlighting the C...C contacts.



Figure S12. Hirshfeld surface analysis of the macrocycle **2**. a) Bifurcated H bonding between macrocycles. b) CH-π interactions between neighboring macrocycle. c) Offset π- stacking interactions between macrocycles. d) Two dimensional map resolved into O...H/H...O contacts. e) Two dimensional map resolved to show C...H/H...C contacts. f) Two dimensional map highlighting the C...C contacts.

5. TGA analysis of host 1.

TGA analysis of host 1 was carried out using two methods:

Method 1:

Freshly crystalized host 1 (~ 15 mg) was heated at 2 $^{\circ}$ C/min from rt to 120 $^{\circ}$ C under He atmosphere and kept isothermally for 2 h.

Method 2:

Freshly crystalized host 1 (~ 15 mg) was heated at 2 $^{\circ}$ C/min from rt to 170 $^{\circ}$ C under He atmosphere and kept isothermally for 1 h.



Figure S13. Thermogravimetric analysis of host 1. (a) Using method 1. (b) Using method 2.

All studies were carried out using host material obtained from method 1.

6. Isoprene loading studies, photo irradiation and product isolation.

Isoprene monomer was purified using an alumina plug prior to loading studies. Monomer loading experiments were performed under high vacuum using a loading apparatus (Figure S9).



Figure S14. Loading of isoprene, photo irradiation and product isolation. a) Loading apparatus used in the study. b) Photoreaction and isolation of *trans*-1,4-polyisoprene.

Host 1 (20 mg) was place in a 10 mL flask and evacuated under high vacuum for 3 h. Isoprene 5 mL was placed in the second flask and degassed using at least 4 freeze pump thaw cycles. Isoprene absorbed from its vapor phase under reduce pressure at room temperature for 24 h, conditions which likely lead to an equilibrium for diffusion. Next, the isoprene treated host 1 (host 1•isoprene) was frozen and vacuum sealed. The sealed vial was transferred into Rayonet reactor for UV irradiation. Sample was irradiated at 350 nm for 24 h at room temperature. The product was extracted with CHCl₃ using an ultra sound sonicator for 30 min. The suspension of the host and product was filtered and host 1 recovered. The filtrate was concentrated *in vacuo*, and polyisoprene was precipitated by adding ice-cold methanol drop wise.

7. UV-vis spectral study.

UV–Vis diffuse reflectance spectroscopy data of host **1** and host **1**.isoprene were collected on a PerkinElmer Lambda 35 UV–Vis scanning spectrophotometer equipped with an integrating sphere over the range of 200–900 nm at room temperature. Although the absorption band of the isoprene treated sample is broadened, the two spectra have a very similar shape with λ_{max} at 354 nm (host 1) and 350 nm (host 1.isoprene).



Figure S15. Solid state UV-visible spectra of host 1 (black) and host 1 isoprene (red).

8. Characterization of the photoproduct.



Figure S16. ¹H-NMR (CDCl₃, 400 MHz) of *trans*-1, 4-polyisoprene.



Figure S17. ¹³C-NMR (CDCl₃, 125 MHz) of *trans*-1,4-polyisoprene.



Figure S18. GPC trace of *trans*-1,4-polyisoprene. (Eluent: THF, calibrated to polystyrene standards)

¹H-NMR: (300 MHz, CD₃Cl δ): olefinic H atoms for 1,4-motif: 5.11 (s, *br*, 1H); aliphatic H atoms for 1,4-motif: 2.06 (m, 2H), 1.97 (m, 2H), 1.68 (s, 3H), 1.60 (s, 3H); ¹³C-NMR: (125 MHz, CD₃Cl δ): olefinic H atoms for 1,4-motif: 134.96, 124.26, 39.77, 26.75, 16.04; SEC chromatography (eluent: THF, Polystyrene standards): *Mn* = 4400 g/mol, *D* = 1.39. Selectivity¹⁰ *trans*-1,4 = 96.7%, *cis*-1,4 = 3.3%.

9. Bulk anionic polymerization of isoprene

Anionic polymerization technique is widely used to polymerize isoprene. The results are summarized in the table S1.

Table S1. Microstructure composition of polyisoprene produced by anionic polymerization with two different initiators in cyclohexane at 30 °C gives low selectivity.¹¹

Initiator	Selectivity (%)			
	cis-1,4	trans-1,4	3,4	1,2
Butyllithium	80	15	5	-
Sodium	29	29	42	-

10. Characterization of isoprene in host 1



Figure S19. ¹H-NMR (DMSO-d₆, 300 MHz) of dissolved crystals of host **1**•isoprene. A host guest ratio of 1:1 was found by averaging the host **1** peaks vs. isoprene.



Figure S20. Thermogravimetric analysis of isoprene in host **1**. Freshly loaded host **1** (\sim 5 mg) kept isothermally for 15 min, heated at 4 °C/min from rt to 180 °C, and kept isothermally for 5 min all under He (g). A host guest ratio of 1:0.7 was found in this trial with an average of 1:0.9 of two trials.

11. References

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