

Inclusion Polymerization of Pyrrole and Ethylenedioxythiophene in Assembled Triphenylamine *Bis*-Urea Macrocycles

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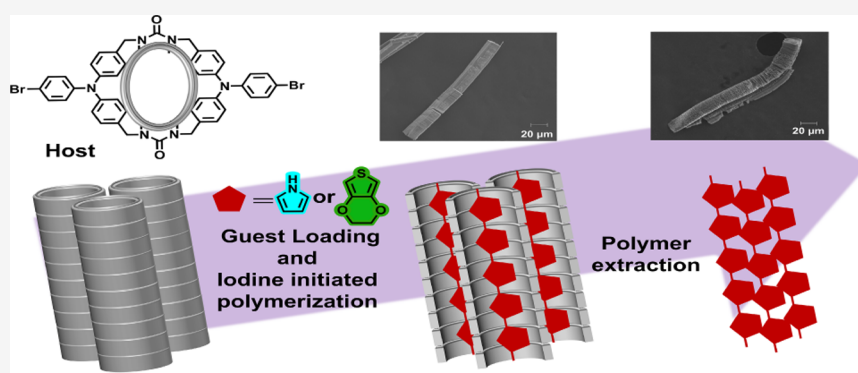
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ABSTRACT: Herein, two different monomers, pyrrole (Py) and ethylenedioxythiophene (EDOT), are loaded into a self-assembled *bis*-urea host **1** and oxidatively polymerized within its nanochannels, dramatically changing the properties of the crystalline complexes. Molecular dynamics (MD) simulation of both monomers within the channel demonstrates that they diffuse through the confinement upon applying thermal energy, which may facilitate the polymerization reaction. The structures of these host–guest complexes are characterized before and after polymerization using solid-state and photophysical measurements. The host maintains its columnar morphology during polymerization at 90 °C using iodine as an oxidizing agent. Intriguingly, upon dissolution of the host and recovery by filtration, the polymers exhibit memory of their nanoreactor environment, displaying unusual order by scanning electron microscopy, powder X-ray diffraction, and small- and wide-angle X-ray analysis. Solid-state ^{13}C cross-polarized magic angle spinning NMR suggests that polypyrrole (PPy) exhibits primarily α,α' linkages with some contributions from the quinoid form. Similarly, poly(ethylenedioxythiophene) (PEDOT) also exhibits formation of primarily α,α' linkages with minor quinoid contributions. Both the **1**•PPy and **1**•PEDOT crystals show a 10^3 -fold increase in conductivity to $\sim 10^{-6}$ S/cm versus host **1** crystals, which are nonconductive $\sim 10^{-9}$ S/cm. Overall, supramolecular polymerization strategies have the potential to readily modulate the properties of nanostructured materials.

INTRODUCTION

Polymerization of monomers confined within nanometer spaces <100 nm can influence the properties of the resulting polymers, altering their molecular weights, dispersity, glass-transition temperatures, and even generating stereoregular polymers.^{1,2} Nanoconfinement can be achieved through the incorporation of monomers into crystalline materials, including clathrates,³ porous silicates,⁴ porous coordination polymers,⁵ and metal–organic frameworks^{6,7} as well as in glasses,⁸ ultrathin films,⁹ porous anodized aluminum oxides (AAOs),¹⁰ and micelles.¹ Herein, we report the uptake of pyrrole (Py) and ethylenedioxythiophene (EDOT) monomers into extended cylindrical nanochannels of assembled triphenylamine *bis*-urea macrocycles, host **1** ($4.3 \text{ \AA} \times 6.5 \text{ \AA} \times \sim 250 \text{ \mu m}$), which is shown schematically in Figure 1. The

subsequent oxidative polymerization is then performed to generate polypyrrole (PPy) and poly(ethylenedioxythiophene) (PEDOT). The iodine-initiated polymerization mechanism is supported by energy-dispersive spectroscopy (EDS) measurements of **1**•PPy and **1**•PEDOT complexes. The host–polymer inclusion complexes and extracted polymers are then characterized and compared.

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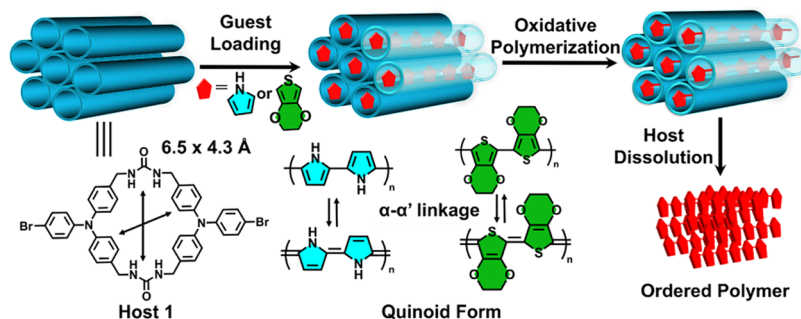


Figure 1. Schematic of loading of Py and EDOT inside the $\sim 6.5 \times 4.3$ Å pores of assembled triphenylamine *bis*-urea macrocycle host **1**. Subsequently, **1**·Py and **1**·EDOT crystalline complexes are subject to oxidative polymerization conditions forming polymers, which are extracted by the dissolution of the host. The polymers exhibit primarily α - α' linkage as well as their quinoid forms.

One-dimensional conducting polymers are of interest for sensing, as supercapacitors,¹¹ and in photothermal therapy.¹² PPy is a simple and well-studied example, which undergoes polymerization through radical cationic intermediates.¹³ The rapid rate of the reaction affords primarily α - α' connections as well as other C–C couplings, which lead to crosslinking that can modulate the conductivity of the resulting polymer.^{14,15} The polymerization of pyrrole has been studied in numerous confined spaces including in zeolites,¹⁶ AAOs,¹⁷ MOFs,^{18,19} and in coordination nanochannels.²⁰ Similarly, PEDOT has been synthesized in the pores of porous coordination polymers,^{21,22} nanochannels,^{23,24} SURMOFs,²⁵ and on nanoporous layer glass²⁶ to increase the conductivity of these materials.

One strategy to control the morphology of the growing polymer is inclusion polymerization. First demonstrated by Clasen, nanoconfinement-guided polymerization of dimethylbutadiene was achieved in thiourea clathrates.²⁷ Radiation-initiated polymerization of diene-type monomers such as 1,3-butadiene, vinyl chloride, cyclohexadiene encapsulated in urea,²⁸ and thiourea²⁸ clathrates have since been reported. The Shimizu group employs ureas and two C-shaped spacers to construct *bis*-urea macrocycles.²⁹ The rigid macrocycles assemble efficiently into columnar structures facilitated by urea hydrogen bonding and can encapsulate guests within their crystalline structures, much like clathrates. For example, triphenylamine *bis*-urea macrocyclic **1** assembles at room temperature from DMSO (2.5 mg/mL) upon vapor diffusion of dimethoxyethane (DME).³⁰ The **1**·DME crystals are activated by heating under vacuum to remove the DME from the nanochannels and the host is ready to absorb a new guest by vapor treatment or by soaking.³¹ ¹²⁹Xe NMR and ¹²⁹X pulsed field gradient NMR experiments established the restricted diffusion of Xe in the channels.³⁰ Previously, electron acceptors including benzothiadiazole and benzoquinones have been loaded into these robust triphenylamine assemblies to study the reversible host-to-guest electron transfer.³² Herein, we probe the uptake and dynamics of Py and EDOT within narrow linear channels of **1**, which are <1 nm in diameter. The structures of host **1**·Py and host **1**·EDOT are analyzed, and the oxidative polymerization of these monomers within the host crystals are examined. Finally, we examine the effect of confinement on the structure of the resulting oligomers/polymers.

RESULTS AND DISCUSSION

Freshly prepared crystals of **1**·DME were heated at 90 °C under vacuum to afford activated host **1**. The colorless needle-like crystals of **1**·DME, activated host **1**, and all subsequent host–guest complexes are isostructural, crystallizing in the monoclinic space group $P2_1/c$. Figure 2A displays the

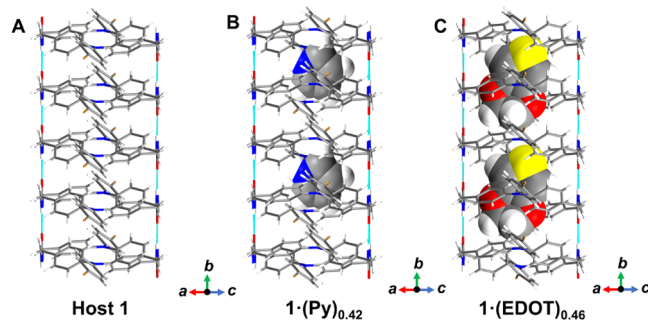


Figure 2. Crystal structures of (A) activated host **1**,³⁰ (B) **1**·(Py)_{0.42}, and (C) **1**·(EDOT)_{0.45}.

columnar structure of **1**, which is organized through urea hydrogen bonds ($d(\text{N}(\text{H})\cdots\text{O}) = 2.845(2)$ and $2.915(2)$ Å). The columns run parallel to the crystallographic *b* axis and adopt a pseudohexagonal rod-packing arrangement (see Figure S14). Next, host **1** (5–10 mg) was exposed to guest vapor by heating the guests to their sublimation temperature (40 °C for Py and 90 °C for EDOT) under vacuum for ~ 24 h.^{25,33} The resulting host–guest complexes remained colorless, and their structures were evaluated by single-crystal X-ray diffraction (SC-XRD).

After absorption of pyrrole, the structure remains similarly organized with urea hydrogen-bonding distances of $d(\text{N}(\text{H})\cdots\text{O}) = 2.848(3)$ and $2.929(3)$ Å. Figure 2B shows the Py arrangement inside the columns. The guest is disordered over multiple crystallographic sites with a refined occupancy of 0.42 Py per host molecule. The bulk crystals were lightly ground and examined by PXRD. Figure S34 compares the experimentally observed PXRD pattern with the pattern simulated from the structure using Mercury.³⁴ The two patterns are nearly identical, suggesting that the bulk powder is single phase. In host **1**·EDOT, the EDOT guest is also disordered inside the hydrogen-bonded columns ($d(\text{N}(\text{H})\cdots\text{O}) = 2.857(3)$ and $2.942(3)$ Å) with a host–guest ratio of 1:0.46 as refined from the SC-XRD data. Again, a comparison of the bulk and simulated PXRD patterns suggests a single-phase bulk powder sample (Figure S33).

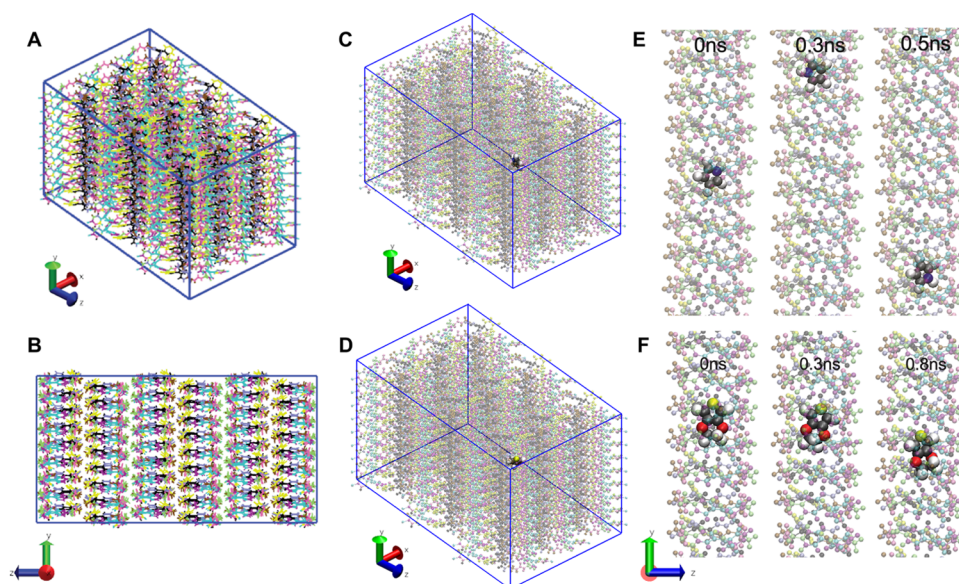


Figure 3. Molecular dynamics simulation of Py and EDOT inside the cavity of host **1**. (A, B) MD simulation of the activated host **1**, (C, D) simulation of Py and EDOT guests in the host cavity, and (E, F) diffusion of Py and EDOT inside the cavity of host **1** in different time scales (0–1 ns). Periodic boundary conditions were used in all simulations.

The polymerization of Py and EDOT in the crystals of host **1** starts with the motion of individual pyrrole and EDOT monomers through the channel. Therefore, atomistic simulations were performed to study the mobility of pyrrole and EDOT in confinement. The samples in the simulations were built with the aid of LigParGen web server.³⁵ The interactions in the host–guest systems were modeled using the classical OPLS All-Atom force field,³⁶ and the simulations were performed using the simulation package LAMMPS (see the SI for further details).³⁷ Host **1** was simulated in a box containing 162 macrocyclic molecules corresponding to 18 channels along the *b*-axis direction with nine layers of macrocycle stacks in each channel. (Figure 3A,B). The simulation was carried out at constant temperature and constant volume using the Nosé–Hoover thermostat (NVT) with a characteristic time of 50 fs. In the temperature range $T = 27$ – 90 °C, host **1** has small vibrational motions, but its center of mass does not move, which suggests that the host is stable enough to keep intact its columnar structure, consistent with the experimental observations of single-crystal-to-single-crystal guest exchange.^{25,33}

Next, the host–guest system was built by inserting a Py or EDOT molecule into the host **1** domain. The initial position of the monomer was sandwiched by two hosts that faced each other. To remove the distortion and overlap of atoms induced by the insertion, energy minimization was performed. The subsequent simulation of a monomer in the crystal was performed at constant temperature (T) and constant volume using the NVT with a characteristic time of 50 fs. The simulation of the host–guest complexes demonstrates that both Py and EDOT monomers move along the channel formed by the macrocycles rather than in the space between two layers of the macrocycles in the crystal, as shown in Figure 3C–F. For the temperature range $T = 300$ – 363 K, where the crystalline structure remains stable in the simulations, the mobility of the guests increases with increasing T for both Py and EDOT, as the larger thermal energy at higher T facilitates the overcoming of the energy barrier for diffusion. Py shows no

mobility at $T = 40$ °C, but at $T = 60$ °C, pyrrole diffuses freely through the channel. However, at the same T , the mobility of EDOT through the channel is lower than that of Py, as EDOT is larger in size and experiences more hindrance. Thus, a higher energy barrier is expected for diffusion of EDOT within the channel. This was observed in our simulations. At $T = 90$ °C, EDOT exhibits some mobility through the confined channels. However, $T \sim 160$ °C is needed for EDOT to freely diffuse through the channels. The mobility of both monomers through the confinement suggests that both are amenable to polymerization inside the channel upon application of thermal energy and suitable polymerization methods.

Oxidative polymerization of Py within the loaded crystals **1**•(Py)_{0.42} and EDOT in the **1**•(EDOT)_{0.45} was carried out using iodine as auxiliary oxidizing agent. Preliminary exposure of crystal samples of **1**•(Py)_{0.42} and **1**•(EDOT)_{0.45} complexes (~ 5 mg each) to I_2 vapor at room temperature turned the crystals brown. The crystals were dissolved in DMSO- d_6 and evaluated by 1H NMR. For **1**•EDOT, only resonances corresponding to the host and unreacted EDOT were observed in the 2:1 ratio (Figure S5). In the case of **1**•Py, a tiny amount of insoluble black precipitate was observed, which was separated by filtration. However, 1H NMR of the dissolved sample was consistent with host and pyrrole in an $\sim 2:1$ ratio, indicating a very low level of reaction (Figure S6).

MD simulations suggested that elevated temperatures were required for guest mobility. Therefore, the host–guest complexes were subjected to oxidative polymerization at 90 °C for 24 h. This resulted in a dramatic color change in both **1**•Py and **1**•EDOT crystals from colorless to black (Figure S11), a primary indication of the formation of the π -conjugated polymers. Unfortunately, the crystals no longer diffracted by SC-XRD. However, diffuse reflectance spectra showed an emergent broad band beyond 600 nm for both the complexes upon polymerization, which is typical for these conducting polymers, PPy and PEDOT (Figures S23 and S24). The structures of these complexes before and after polymerization were compared using scanning electron microscopy (SEM),

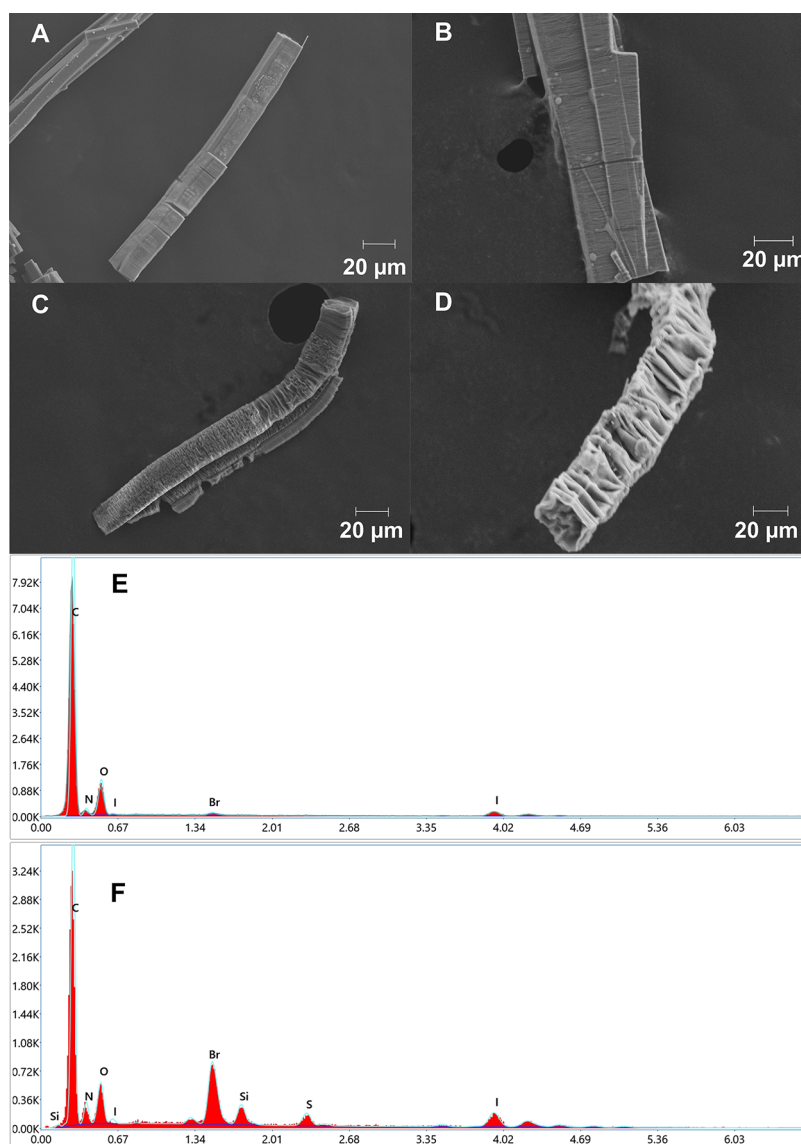


Figure 4. SEM images of (A) 1•PPy, (B) 1•PEDOT, (C) extracted PPy, and (D) extracted PEDOT. (E) EDS spectrum of the 1•PPy and (F) EDS spectrum of 1•PEDOT.

energy-dispersive X-ray spectroscopy (EDS), ^{13}C cross-polarized magic angle spinning (CP-MAS) NMR, powder X-ray diffraction (PXRD), and wide- and small-angle X-ray scattering (WAXS and SAXS).

SEM measurements of 1•PPy and 1•PEDOT indicated that the needle-like morphology of the crystals is retained during polymerization (Figure 4A,B). However, the crystals show fractures across the needle axis (the crystallographic [010] direction); see Figures 4A,B, S10, and S38. These fractures are likely the reason why the crystals were no longer suitable for SC-XRD. Elemental mapping *via* energy-dispersive X-ray spectroscopy (EDS) of the 1•PPy and 1•PEDOT displayed iodine at ~ 0.67 , 3.937 keV (Figure 4E,F), consistent with an iodine-initiated polymerization. Previous reports on the computational studies on the mechanisms of pyrrole polymerization suggest that weak bases are needed to deprotonate at the α position.¹⁵ It is certainly possible that iodide ion may be serving this role in addition to I_2 serving as the oxidant. Further analysis of the EDS spectra of both the polymer complexes

revealed the presence of expected elements, for example, sulfur in PEDOT and the Br of host.

The crystals 1•PPy and 1•PEDOT were dissolved separately in $\text{DMSO}-d_6$ (2.5 mg/mL). In both cases, a black precipitate remained, which was recovered by filtration. The ^1H NMR spectra of both filtrates were consistent with the presence of the recovered host 1, suggesting the host is stable to the polymerization reaction. Resonances for the Py or EDOT guests were notably absent (Figures S7 and S8), indicating no monomer remained.

SEM analysis of the recovered black solids tentatively identified as PPy (Figure 4C) and PEDOT (Figure 4D) showed fibers with similar dimensions as the crystalline complexes. However, compared to the rigid nature of the host–polymer complexes (Figure 4A,B), both the extracted polymers exhibit soft structure with some surface roughness (Figures 4C,D, S39, and S40). For PPy, polymer fibers are closely packed, while PEDOT shows porous networks on its surface (Figure S38). In comparison, bulk PPy and PEDOT are typically amorphous and granular in nature.³⁸ The size and

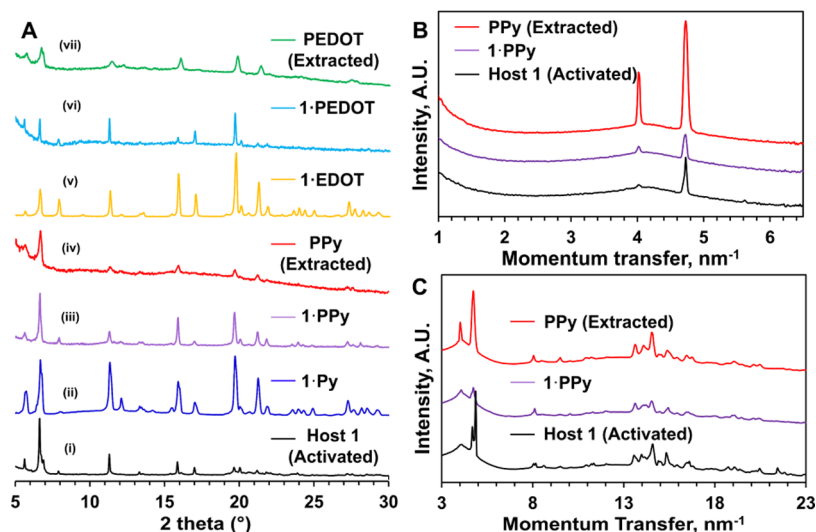


Figure 5. Comparison of host **1** and host–guest complexes by PXRD and SAXS. (A) PXRD patterns of (i) host **1**, (ii) **1**·Py, (iii) **1**·PPy, (iv) extracted PPy, (v) **1**·EDOT, (vi) **1**·PEDOT, and (vii) extracted PEDOT. (B) SAXS data for host **1**, **1**·PPy and extracted PPy. (C) WAXS data for host **1**, **1**·PPy, and extracted PPy.

morphology of the extracted polymers suggest some memory of their nanoencapsulation is retained. The EDS analysis of both the polymers revealed the presence of expected elements, for example, sulfur at 2.307 keV in PEDOT. A residual peak of Br (*L* α) at 1.480 keV indicates that a small quantity of the host or its degradation products is still present in the extracted polymers (Figures S45 and S46).

Therefore, a second recovery procedure was carried out. Fresh samples of **1**·PPy and **1**·PEDOT (~ 5 mg/10 mL DMSO) were first heated up to 90°C and sonicated for 2 h at room temperature, and the black precipitates were recovered by filtration. Again, the ¹H NMR spectra of the filtrates were consistent with the recovered host. SEM images of the recovered PPy show that similar PPy structures were obtained from the two recovery procedures (Figure S41). In comparison, the second method for PEDOT recovery affords polymer columns with some spaced networks, which may be due to the loss of host **1** or due to swelling of the polymers in solvent (Figure S42).³⁹ These open networks of polymer chains may allow easy introduction of dopants, which are of interest for future studies. EDS of both the extracted polymers shows the presence of all of the expected elements. However, the presence of Br at 1.480 keV suggests that a small amount of host likely remains in the extracted polymers. (Figures S47 and S48)

Next, PXRD analysis was performed for the host–guest complexes before and after oxidative treatment and compared with the host and extracted polymer. Figure 5 (pattern i) compares the bulk activated host **1** powder pattern with *d*-space values of 15.71, 13.29, 7.82, 5.58, 5.19, 4.51, and 4.42 Å with the host **1**·Py complex (Figure 5, pattern ii). Only slight shifts are observed to lower *d*-space values of 15.32, 13.21, 7.80, 5.55, 4.48, and 4.17 Å. This guest is relatively small (6.8 Å $\times$ 6.6 Å) compared with the elliptical pores (4.3 Å $\times$ 6.5 Å) that connect to form unidirectional channels in host **1**. Interestingly, these low-angle peaks remain very similar after oxidative treatment (Figure 5, pattern iii, *d*-spacing = 15.59, 13.25, 7.79, 5.56, 4.51, and 4.18 Å), indicating the crystal structure was maintained during the polymerization process. Once again, the PXRD of the extracted PPy (Figure 5, pattern

iv) also showed similar *d*-spacing values (15.59, 13.25, 7.79, 5.55, 4.49, 4.17 Å) but with lower intensity and broadened peak profiles. These peaks are consistent with the PPy guest maintaining the same rod-packing arrangements of columns as the host. In comparison, loading of the larger monomer EDOT (8.3 Å $\times$ 5.9 Å) affords a **1**·EDOT sample (Figure 5A, pattern v), the PXRD of which exhibits a new peak at *d*-spacing = 11.18 Å corresponding to the presence of the guest as well as similar small shifting ($\sim 0.7\%$) of the other key peaks in the *d*-spacing range (15.59, 13.21, 11.18, 7.79, 5.57, 5.19, 4.49, and 4.15 Å). Upon polymerization, the **1**·PEDOT complex shows higher *d*-spacings (15.71, 13.29, 11.20, 7.84, 5.58, 5.22, 4.51, and 4.42 Å, Figure 5, pattern vi) suggesting retention of some host–guest complex crystal structure. Surprisingly, the extracted polymer also exhibits a similar PXRD pattern albeit with lower intensity and broader peak profiles with *d*-spacing values = 15.27, 13.10, 11.21, 7.71, 5.51, 5.21, 4.47, and 4.15 Å (Figure 5, pattern vii), again indicating the structural memory preservation of the host by the polymer.

To gain more insight into potential templating effects, both SAXS and WAXS analyses were performed on host **1**, host–polymer complexes, and extracted polymers (Figures S35 and S36). The SAXS pattern for empty host **1** exhibited two sharp diffraction peaks located at $q = 4.0$ and 4.7 nm⁻¹, corresponding to the 100 and 002 reflections from the parallelogram arrangement of columns. These in-plane dimensions correspond to column-to-column spacings of 1.5 and 2.6 nm in the 100 and 001 directions, respectively. Similarly, by SAXS, **1**·PPy complex exhibited identical peak positions as the empty host for the 100 and 002 scattering peaks as well as many of the other in-plane *h*0*l* (Figure 5B,C). Indeed, it is curious that the removal of host **1** is not accompanied by a crystallographic rearrangement of columns. This symmetry preservation suggests that either a trace amount of the host remains or the resulting polymer columns have periodic interconnections in between template molecules.

The intensity of the transmission-corrected SAXS and WAXS data was used to validate the incorporation of the guest species in the columnar host arrangements. As the guest was incorporated, the overall scattering length density (SLD)

contrast ($\propto$ intensity) is expected to decrease as the host is filled with guest molecules. Indeed, this was observed as the intensity from the anticipated host 1 002 reflection at 4.7 nm^{-1} lowering from $\sim 0.35 \text{ au}$ for the empty host macrocycle to $\sim 0.20 \text{ au}$ for the 1•PPy complex. Thus, SAXS data were consistent with preservation of the columnar arrangements and host filling with guest molecules. The SAXS data for the extracted PPy exhibited two sharp peaks at 4.0 and 4.7 nm^{-1} , corresponding to the 100 and 002 reflections of the host structure factor, as well as a number of higher-order $h0l$ peaks. Again, note that the preservation of the rod-packing arrangement after removal of the host is consistent with either retention of some of the host molecules as spacers or additional deposition of PPy, either in between columns or at grain boundaries. For the case of additional deposition, the scattered intensity is expected to increase going from host–guest to guest alone. The transmission-corrected intensity for the 002 reflection increased from $\sim 0.2 \text{ au}$ for the 1•PPy host–guest to $\sim 0.34 \text{ au}$ for the resulting PPy, host removal. Thus, the SAXS and WAXS data were consistent with the removal of some of the template molecules.

FTIR spectra (Figures S17 and S18) were compared for host 1, 1•Py, 1•PPy, 1•EDOT, and 1•PEDOT. All samples exhibit the characteristic peaks for host 1, providing further evidence that the host is stable to oxidative polymerization. Furthermore, comparison of the FTIR spectra of the extracted PPy with the corresponding bulk PPy, prepared by oxidative polymerization in hexanes, exhibits peaks corresponding to C–H out of plane deformation at ~ 816 , $\sim 750 \text{ cm}^{-1}$, the C–N stretching of pyrrole ring at $\sim 1440 \text{ cm}^{-1}$, C–C stretching vibration of the pyrrole ring at $\sim 1502 \text{ cm}^{-1}$, C–H or N–H in-plane deformation modes at $\sim 1265 \text{ cm}^{-1}$, and the C–N and N–H in-plane deformation at ~ 1177 and $\sim 1042 \text{ cm}^{-1}$, respectively. For comparison, EDOT was oxidatively polymerized with iodine in toluene to give a bulk PEDOT sample. In the case of the extracted PEDOT, the spectra show typical bands for PEDOT. The bands observed are as follows: 1501 , 1428 , 1358 , 1176 , 1069 , 948 , and 818 cm^{-1} . The band at 1501 cm^{-1} can be corresponding to the asymmetric stretching of the C=C characteristic of the quinoid form of the PEDOT, while the band at $\sim 1428 \text{ cm}^{-1}$ can be corresponding to the symmetric stretching of the C=C of the thiophene ring.⁴⁰ Bands at ~ 1176 and $\sim 1069 \text{ cm}^{-1}$ correspond to the C–O–C stretching of ethylenedioxy group. In addition, C–C stretching at $\sim 1358 \text{ cm}^{-1}$ and the C–S bond of thiophene ring ~ 948 and $\sim 818 \text{ cm}^{-1}$ were observed. Raman spectra also support the polymer formation (Figures S19–S22). The extracted PPy and bulk PPy showed similar stretching at 1546 cm^{-1} corresponding to the π conjugated structure. In the case of the extracted PEDOT and bulk PEDOT, 1503 and 1428 cm^{-1} peaks were observed corresponding to C=C asymmetric and symmetric stretching.

Solid-state ^{13}C CP-MAS NMR of the host and host–guest complexes were recorded to compare these structures. In the host and its inclusion complexes, the CP-MAS NMR spectra are sharp and well resolved. The host resonances are nearly identical in all samples, again demonstrating the stability of the urea macrocycle. The 1•Py complex (Figure 6, ii) has the resonance for the pyrrole monomer at 119 ppm (α carbon) and 107.5 ppm (β carbon). Upon polymerization, 1•PPy (Figure 6, iii) shows a loss of the 107.5 ppm resonance and an obvious broadening in the carbon resonance from 120 to 135 ppm , which indicates the formation of PPy. The extracted PPy

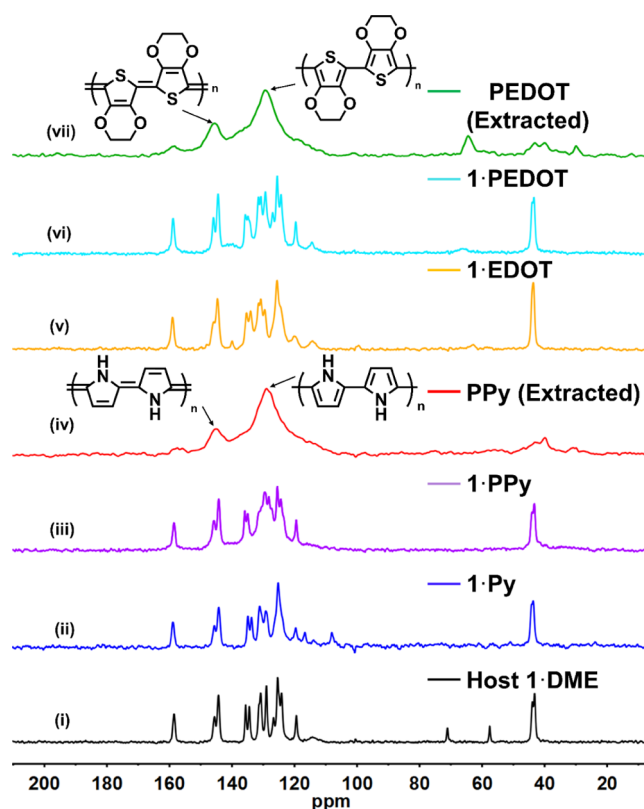


Figure 6. Comparison of ^{13}C CP-MAS NMR of the host–guest complexes. (i) Solid-state NMR of host 1•DME, (ii) Solid-state NMR of 1•Py, (iii) Solid-state NMR of 1•PPy, (iv) Solid-state NMR of extracted PPy, (v) Solid-state NMR of 1•EDOT, (vi) Solid-state NMR of 1•PEDOT, (vii) Solid-state NMR of extracted PEDOT.

(Figure 6, iv) displays much broader spectra, exhibiting a main peak at 128 ppm , which corresponds to α – α' linkage of pyrrole. There is also a high-frequency peak at 144 ppm which can be associated with the quinoid form of the polypyrrole. Notably, the peaks for α – β' or β – β' was absent in the NMR suggesting the polymerization proceeded through α – α' linkage.⁴¹ The ^{13}C CP-MAS NMR spectra of the 1•EDOT complex (Figure 6, v) display a characteristic resonance at 62 ppm for the ether carbon of the monomer. Upon polymerization (Figure 6, vi), this resonance shifts slightly to 66 ppm after oxidative polymerization. In addition, there is obvious broadening in the aromatic region from 120 to 140 ppm . Again, the resonances of host 1 remain sharp and are not altered by the reaction. The spectra of the extracted PEDOT (Figure 6, vii) show the main aromatic carbon resonance at 128 ppm with a higher-frequency peak at 145 ppm while the ether carbon peak arrives at 64 ppm .⁴² The broad higher-frequency peak can be assigned to the sp^2 carbons of the quinoid form of the conductive PEDOT.⁴³

Thermogravimetric analysis of the extracted polymers versus the bulk polymerized controls suggests that inclusion polymerization affords polymers with greater thermal stability. For example, extracted PPy shows a one-step 4% weight loss from 25 to $50 \text{ }^\circ\text{C}$, which is attributed to the loss of the solvent; however, the material is then quite stable up to $314 \text{ }^\circ\text{C}$. In comparison, the bulk polymerized PPy shows that a polymer exhibits a similar initial weight loss (4%) between 25 and $50 \text{ }^\circ\text{C}$, followed by a 25% weight loss between 70 and $300 \text{ }^\circ\text{C}$ (Figure S28). The higher stability of the extracted PPy may be

due to the enhanced π - π interaction between the quinoid form of the pyrrole ring.^{44,45} Similarly, the extracted PEDOT shows a 9% weight loss between 20 and 300 °C, whereas the bulk PEDOT has a one-step desorption between 25 and 280 °C with a 49% weight loss. Again, the higher stability may be due to π - π stacking interaction between the quinoid backbone of the PEDOT extracted polymers.

While the host itself should be nonconductive, formation of conductive polymers such as PPy and PEDOT within the nanochannels is expected to dramatically increase the electrical conductivity. A two-probe method was used to probe the conductivity of host **1** and its polymer inclusion complexes. Single crystals were deposited on a glass surface, and both ends of the crystals were coated with conducting Ag paste. Figure 7

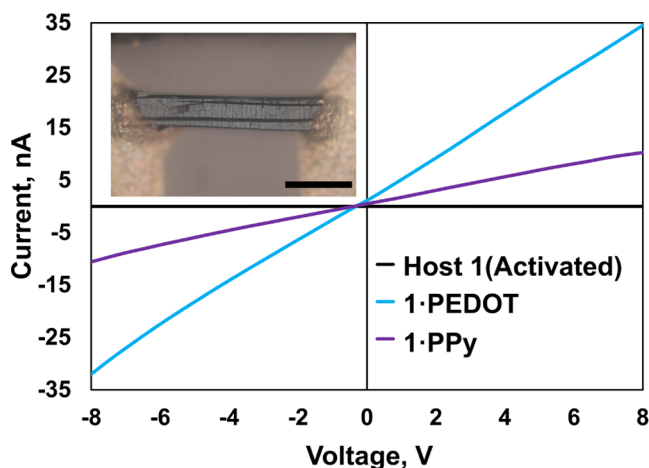


Figure 7. I - V curves measured for representative host and host-guest complex crystals (black) host **1**, (purple) **1**•PPy, (blue) **1**•PEDOT. (Inset) Picture of a representative single crystal mounted on a glass surface with silver paste on both ends. Scale bar-250 μm .

shows I - V curves measured from single crystals of host **1**, **1**•PPy, and **1**•PEDOT. The electrical conductivity of the samples was calculated from I - V curves and dimensions of the single crystals (see the SI for detailed calculations). From the conductivity measurements, host **1** shows very little to no conductivity upon three trials with a highest conductivity calculated as $6.72 \times 10^{-9} \text{ S cm}^{-1}$ with an average of $3.1 \times 10^{-9} \text{ S cm}^{-1}$. However, after polymerization of the pyrrole, single crystals of **1**•PPy shows an almost 10^3 -fold increase in conductivity. The highest conductivity of **1**•PPy crystals was calculated as $1.11 \times 10^{-5} \text{ S cm}^{-1}$ and an average of $4.7 \times 10^{-6} \text{ S cm}^{-1}$. Upon three trials, the single crystals of the **1**•PEDOT complex displayed a maximum conductivity value of $1.15 \times 10^{-5} \text{ S cm}^{-1}$ with an average of $8.2 \times 10^{-6} \text{ S cm}^{-1}$ (Figure S51 and Table S4). Previous works on the oxidative polymerization of pyrrole and EDOT reported that the conductivity of the host-polymer complexes ranges from 10^{-1} to $10^{-7} \text{ S cm}^{-1}$ depending on the morphology and properties of the host (MOFs, PCPs, etc.). The conductivity of the **1**•PPy and **1**•PEDOT complexes lies closer to the single crystals of the terpyrrole cationic polymers confined in the cyclodextrin MOFs.¹⁹ Considering that morphological defects (crack or bend) of the single crystals of **1**•PPy and **1**•PEDOT will tend to lower their conductance, the conductivity values observed here may represent a lower bound on what is achievable. We note that most of the reported conductivity values for host-

polymer complexes are measured using bulk crystals or thin films known to have closer polycrystalline packing.

Next, we probed the amount of iodine present in both the complexes immediately after polymerization. Fresh samples of **1**•Py ($\sim 3 \text{ mg}$) and **1**•EDOT ($\sim 1.5 \text{ mg}$) were oxidatively polymerized, then the samples were separately stirred in ethanol (10 mL) in the dark. The concentration of I_2 was monitored by recording the UV/vis spectra over time (Figure S54). After 3 days, the absorbance at $\lambda = 230 \text{ nm}$ reached a maximum. A calibration curve was used to estimate the amount of I_2 released (Figure S53). From the measurement, it was found that both the complexes are heavily doped with iodine after polymerization. These estimates suggest that the **1**•PPy sample contains $\sim 51 \text{ wt } \%$ I_2 . In comparison, the I_2 content is lower, $\sim 40 \text{ wt } \%$ in **1**•PEDOT. The high level of doping may also enhance the conductivity values of the crystals.

CONCLUSIONS

In summary, these studies show that TPA *bis*-urea macrocycle crystals are robust and can be used as a nanoreactor for the oxidative polymerization of Py and EDOT. Single-crystal X-ray diffraction studies confirm the incorporation of the monomers into the narrow channels of the host without disruption of the assembled framework. MD simulations suggest that the monomers diffuse linearly through single channels with elevated temperatures (40–90 °C). Therefore, the oxidative polymerizations were carried out at 90 °C with iodine and resulted in the crystals changing color and showing enhanced conductivity. SEM images of the crystals post polymerization show that they retain their general columnar morphology, although the crystals show fractures along the needle axis, likely due to applied thermal energy for polymerization reaction or introduction of strain in the polymer product. The extracted polymers exhibited fibers with similar dimensions as the crystalline complexes.

Solid-state ^{13}C cross-polarized magic angle spinning (CP-MAS) NMR of **1**•PPy and **1**•PEDOT complexes retain the resonances for the host while displaying new resonances corresponding to polymers. Solid-state ^{13}C CP-MAS NMR of both the extracted polymers showed characteristic peaks for their respective α - α' linked oligomers as well as new resonances for their quinoid forms. IR and Raman spectra of the extracted polymers versus bulk samples are also consistent with the formation of the polymers.

The polymers were easily recovered from the host and the DMSO-soluble macrocycles were recrystallized for reuse. Intriguingly, structural studies with three X-ray diffraction techniques (PXRD, SAXS, and WAXS) suggest that the extracted polymer retains some order indicative of their formation within the nanochannels of the host, while the bulk polymer materials are amorphous. For example, PXRD exhibits a similar peak position with similar d -spacing for the extracted polymers to the host molecules. Additionally, the SAXS data shows the retention of the host morphology in the polymers, consistent with the host acting as a template for the polymerization reaction.

Inclusion polymerization is a strategy to postmodify the porous host crystals, which are typically nonconductive. Such postmodification may be of interest for sensing and other applications. Indeed, measurements on single crystals of **1**•PPy and **1**•PEDOT showed a dramatic 10^3 -fold increase in conductivity versus host **1** crystals. Given recent optimized

synthesis of the host based on dynamic covalent methods based on work from Cheng's group,⁴⁶ we are now focused on scaling up the macrocycle synthesis. The availability of sizeable quantities of host **1** will allow us to explore the effects of confined polymerization on a wider range of monomers as well as provide more material for full characterization of polymer properties including glass-transition temperatures, stress-strain measurements, and introduction of dopants.

■ ASSOCIATED CONTENT

SI Supporting Information

The Supporting Information is available free of charge at <https://pubs.acs.org/doi/10.1021/acs.macromol.2c02042>.

Product characterization, X-ray data for **1**·Py and **1**·EDOT (CCDC no. 2206565-2206566), MD simulation details, SEM, EDS, and conductivity measurements (PDF)

MD simulation video 1 (MPG)

MD simulation video 2 (MPG)

MD simulation video3 (MPG)

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Author Contributions

L.S.S. initiated the study. E.A., A.B.G., M.F.I., P.K., P.J.P., M.S., E.R.W., and L.S.S. planned experiments, analyzed data, and contributed to the manuscript. E.A., M.F.I., P.J.P., M.D.S., A.W., E.R.W., S.Z., and T.G. performed experiments/contributed to the MD simulation. The manuscript was written through contributions of all authors. All authors have given approval to the final version of the manuscript.

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Notes

The authors declare no competing financial interest.

■ ABBREVIATIONS USED

EDOT, ethylenedioxythiophene; Py, pyrrole; PPy, polypyrrole; PEDOT, poly(ethylenedioxythiophene); TPA, triphenylamine; PXRD, powder X-ray diffraction; SEM, scanning electron microscopy; EDS, energy-dispersive spectroscopy; WAXS, wide-angle X-ray spectroscopy; NMR, nuclear magnetic resonance; MAS, magic angle spinning; MD, molecular dynamics; SAXS, small-angle X-ray scattering; TGA, thermogravimetric analysis; DMSO, dimethylsulfoxide; FTIR, Fourier transform infrared

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