**Porphyridin-Based Conjugated Microporous Polymer Tubes: Template-Free Synthesis and A Photocatalyst for Visible-Light-Driven Thiocyanation of Anilines**

Pengfei Zhang, Yucheng Yin, Zhengxin Wang, Chunyang Yu, Yizhou Zhu, Deyue Yan, Weimin Liu, and Yiyong Mai*

**ABSTRACT:** Conjugated microporous polymers (CMPs) represent an important type of functional materials. In this area, morphological engineering has remained a major challenge. Here, we report the synthesis of porphyrin-based CMP tubes (CMP-1) through a template-free protocol. A mechanism study reveals that the CMP tubes are formed by the scrolling and closing of ribbon-like structures. The tubes possess a high specific surface area of 495 m²/g, along with improved optical properties including broadened absorption in the visible-light region, longer triplet-state lifetime, and more stable photocurrent, compared to those of the irregular solid CMP counterpart. When serving as a metal-free photocatalyst for an undocumented visible-light-driven thiocyanation of anilines, CMP-1 exhibits excellent photocatalytic performance, with single chemoselectivity and high yields for the conversion of 25 types of anilines at ambient conditions. This study fills in the gap of the tubular morphological engineering of CMPs and broadens the scope of their potential applications.

**INTRODUCTION**

As a new class of emerging functional materials, conjugated microporous polymers (CMPs) have been synthesized by a number of coupling reactions including Sonogashira—Hagihara, Suzuki—Miyaura, Yamamoto, Heck, etc. In sharp contrast to porous nonconjugated materials and conventional nonporous conjugated polymers, CMPs generally combine extended π-conjugation with a microporous skeleton. Due to the advantages of high flexibility in molecular design of conjugated skeletons, high specific surface area, robustness, and thermal stability, CMPs have shown considerable potential in a wide range of applications, such as gas adsorption and separation, sensing, energy storage, and catalysis.

The functional performance of CMPs is dependent not only on their intrinsic compositions and porosity but also on their morphologies. So far, most of CMPs have been obtained in the form of irregular granules; well-defined structures such as spheres, cylinders, and tubes have been much less documented. However, studies on the morphological engineering of CMPs have shown that morphology can be a key factor determining their physicochemical properties and ultimate functions due to the morphologically governed diffusion pathways of guest molecules in the porous networks. Among the reported morphologies, CMPs with hollow structures such as hollow spheres can show improved performance in their applications including sensing of explosives, organic catalysis, and photocatalysis, compared to that of irregular or solid structures. The better performance of the hollow-structured photocatalysts generally
benefits from their advantages including improved light scattering and harvesting, reduced charge transfer distance, and abundant surface reactive sites. Nevertheless, the synthesis of most CMPs with hollow structures mainly relies on template methods, which suffers from the requirement of additional steps to remove the templates and the potential negative impact of the residual template on the physiochemical properties of the final product. Template-free synthesis of CMPs with well-defined hollow structures remains rarely reported.

Porphyrazines and their derivatives are unique chromophores with interesting photophysical properties such as strong visible-light absorption and tunable optical band gaps, which allow their potential applications in photocatalysis. Some irregular solid CMPs containing porphyrin units have been found to show visible-light-driven photocatalytic activity in water splitting, oxygen reduction reaction, and a number of important organic reactions such as Knoevenagel condensation. In contrast, porphyrin-based CMPs with hollow structures, to our knowledge, have not been explored for photocatalytic applications as yet. Even more, the synthesis of porphyrin-based CMP tubes has remained a vacancy. This inspires great interest to synthesize porphyrin-based CMP tubes and study their physicochemical properties and potential photocatalytic applications.

Here, we demonstrate a template-free synthesis of porphyrin-based CMP tubes (denoted as CMP-1) via the Sonogashira reaction of 1,3,5-tris[4’-(ethynyl)phenyl]benzene and brominated porphyrin tethered with straight alkyl chains (Scheme 1). Meanwhile, irregular solid CMP granules (CMP-2) were also synthesized as a control sample by introducing phenyl rings with steric hindrance at the edges of the porphyrin building blocks. The CMP-1 tubes have an average diameter of 1.5 ± 0.6 μm and lengths at a micrometer scale. Their specific surface area reaches 495 m²/g, higher than that of the irregular CMP-2 (380 m²/g). Remarkably, CMP-1 exhibited apparent absorption in the visible-light region with two strong bands centered at 405 and 440 nm, along with a long triplet-state lifetime of 710 ns. Taking advantage of these optical properties, we employed the tubular CMP-1 as a metal-free catalyst for an unexplored photocatalytic thiocyanation of anilines. In the catalytic system, visible light was used as the driving force and O₂/air was employed as the oxidant. Strikingly, the utilization of only 15 wt % CMP-1 resulted in high yields (>80% mostly) for 25 types of anilines at room temperature within a 4 h reaction period. This photocatalytic reaction also showed single chemoselectivity, in which all of the products were C-4 thiocyanated anilines. The performance is much better than that of the irregular CMP-2, reflecting the advantage of the tubular structure in the photocatalytic reaction. In addition,
CMP-1 can be recycled at least 5 times with 92% amount left, indicating good recyclability of the catalyst. Our mechanism studies through control experiments and density functional theory (DFT) calculations unveiled the dual roles of CMP-1 in the photoredox catalysis process: one is to initiate the radical cations of anilines and the other is to form the •SCN free radicals; these two intermediates jointly completed the reaction.

■ RESULTS AND DISCUSSION

Synthesis and Characterizations of the Porphyrin-Based CMPs. The synthetic routes toward CMP-1 and CMP-2 are shown in Scheme 1 (experimental details and characterizations are given in the Supporting Information, Figures S1–S16). Alkyl porphyrins 3 (including 3-1 and 3-2) were synthesized by a condensation reaction of dipyrromethane 1 and different aldehydes 2. After the bromination of 3, the resultant compounds 4 (including 4-1 and 4-2), namely, the porphyrin building block, were subjected to Sonogashira coupling with arylacetylene 5 following a stoichiometric ratio of 3:2 in a mixture of tetrahydrofuran and triethylamine (3:2, v/v), yielding CMP-1 and CMP-2 depending on the substituting group (R) on the porphyrin building block.

Solid-state 13C nuclear magnetic resonance (NMR) and Fourier transform infrared (FTIR) spectroscopies demonstrate the successful coupling of 4 and 5 in the resulting CMPs (Figure 1 for CMP-1, Figures S14–S16 for CMP-2). In the solid-state 13C NMR spectrum of CMP-1 (Figure 1a), the peaks of both the aromatic carbon (120–150 ppm) and alkyl carbon (10–40 ppm) appear and there is no obvious change in the chemical shifts compared to that of the corresponding precursors. Moreover, the broad peak of the internal alkyne (70–75 ppm) in the CMP-1, which is the reaction site for the formation of CMPs, shows a significant change compared to that of the precursor 5 (two peaks at 78 and 82 ppm). This is a solid proof of the cross-linking of 4 and 5. FTIR spectra confirm the coupling of 4 and 5 (Figure 1b), in which the peak of the internal alkyne (2200 cm⁻¹) in CMP-1 exhibits a significant change compared to that of precursor 5 (2120 cm⁻¹). Moreover, inductively coupled plasma mass spectrometry (ICP MS) analysis proves the negligible amounts of the metal residues in the CMP samples. For CMP-1, the residual contents of Cu and Pd are 0.08 and 0.09%, while those of Cu and Pd in CMP-2 are 0.13 and 0.14%, respectively.

The morphology and inner porosity of the CMPs were investigated by optical microscopy (OM), scanning electron microscopy (SEM), transmission electron microscopy (TEM), and Brunauer–Emmett–Teller (BET) analysis. OM observation reveals a one-dimensional (1D) fiber-like structure of CMP-1, with an average length of 274 ± 260 μm and a mean width of 1.8 ± 0.8 μm (Figure 2a). SEM images show a cylindrical structure with a smooth surface for CMP-1; the
cylinders have an average diameter of 1.5 ± 0.6 μm (Figure 2b,c). Furthermore, TEM images reveal a hollow tubular structure for CMP-1 (Figure 2d,e), in which the average diameter of the hollow cavities is 400 ± 200 nm and the mean wall thickness is 550 ± 200 nm. Interestingly, for most of the tubes, both of the ends are closed, which has been very rarely found in tube formation. In addition, micrometer-scale CMP tubes have also been rarely documented thus far. In sharp contrast, CMP-2 shows an irregular agglomerate morphology, as observed by SEM (Figure 2f), owing to the different substituents on the porphyrin ring.

Nitrogen adsorption−desorption analyses showed type IV isotherms with typical microporous character for both resulting CMPs.\textsuperscript{45,46} The tubular CMP-1 possesses a higher specific surface area (495 m\textsuperscript{2}/g) compared to that (380 m\textsuperscript{2}/g) of the irregular CMP-2 (Figure 2g). This is attributed to the presence of hollow cavities in the CMP-1 tubes.\textsuperscript{31} In addition, pore-size distribution curves, calculated by the DFT method, indicate that CMP-1 has pore diameters in the range of 1.0−3.0 nm, with an average value of 1.9 nm (Figure 2h). CMP-2 shows a similar pore-size distribution with a mean diameter of 1.8 nm. Thermal gravimetric analysis (TGA) revealed that CMP-1 is thermally stable up to 300 °C (Figure 2i). Powder X-ray diffraction (XRD) studies revealed an amorphous characteristic for both CMP-1 and CMP-2 (Figure S17).

To understand the formation process of the CMP tubes, we tracked the morphology of the intermediates formed during the synthesis of CMP-1 at increasing reaction time. The SEM image of the intermediate after the Sonogashira coupling of 4-1 and 5 for 5−20 min showed a two-dimensional (2D) ribbon-like structure with a slight bending along the radial direction (Figure 3a). With an increase in the reaction time to around 30 min, the scrolling of the ribbons to tubes almost completed, with thin apertures on the surfaces (Figure 3b). Over 60 min, intact tubes formed eventually (Figure 3c).

This tube formation process is exceptional. As the molecular packing mode in the amorphous microporous polymer is unable to know, we speculate that the formation of the initial
2D structure is probably induced by the presence of small angles of rotation between the arylacetylene and porphyrin building units as well as the interactions between the alkyl chains. Over time, possibly entropy drives the ribbons to scroll, as previously known for the formation of supramolecular tubes or microporous polymers. Afterward, the continuous cross-linking of the monomers at the ends and the two edges of the scrolled ribbons leads to the formation of the closed tubes. For CMP-2, the steric hindrance of the side phenyl rings with the porphyrin units possibly induces a significant twist, thus leading to limited π-conjugation and consequently the formation of the irregular aggregates.

### Photophysical Properties of the Porphyrin-Based CMPs.**

UV-vis spectra show that both CMPs in tetrahydrofuran (THF) exhibit intense absorptions at 440 nm in addition to the peak at 405 nm, which can be assigned to the Soret bands of the porphyrin rings (Figure 4a). This red-shifted peak of Soret band results from the J-aggregation of the porphyrin units, which broadens the absorption of the CMPs in the visible-light region. Moreover, the Q-bands of CMP-1 in the range of 500–800 nm appear stronger than those of CMP-2; this can be due to the more extended π-conjugation of the porphyrin blocks in the ordered 1D tubular structure. In the irregular CMP-2, the steric hindrance of the side phenyl rings probably limits the π-conjugation of the porphyrin units.

Fluorescence emission spectra of both CMP-1 and CMP-2 in THF exhibit two peaks in the wavelength window of 625–750 nm, the positions are basically identical to those in the spectrum of the porphyrin monomer (compound 4-1, Figure S18). However, the fluorescence intensity of CMP-2 is nearly 3 times higher than that of CMP-1 under similar conditions. The obvious fluorescence attenuation of CMP-1 suggests its more efficient charge separation compared to both CMP-2 and the porphyrin monomer due to the more ordered structure of the CMP-1 tube. Further, we studied the triplet-state lifetime of the two CMPs by transient absorption spectroscopy (Figures 4c and S19). As shown in Figure 4c, CMP-1 exhibits apparently a longer triplet-state lifetime (710 ns) than that (350 ns) of CMP-2. This difference can be attributed to the fact that the more disordered aggregation of the porphyrin units in the irregular CMP-2 can easily quench the triplet excited state. The long lifetime of the triplet excited state can be more favorable for the porphyrin units in CMP-1 to produce the active oxygen species (ROS) by electron or energy transfer. Photocurrent curves reveal that the photocurrent intensity of CMP-1 is higher and more stable than that of CMP-2 (Figure 4d), suggesting a stronger capability of the CMP-1 tubes for generating and separating photogenerated electrons, which favors the transport of the photoexcited electrons from the CMPs to the guest molecules.

### Visible-Light-Driven Photocatalytic Thiocyanation of Anilines.**

Thiocyanated anilines have been widely used to synthesize various sulfur-containing compounds, which are indispensable intermediates in the synthesis of many vital natural products or pharmaceuticals with excellent HIV protease activity. However, to our knowledge, the photocatalytic thiocyanation of anilines has remained unexplored. Taking advantage of the photophysical properties of CMP-1, we utilize CMP-1 as a photocatalyst for the visible-light-driven catalytic thiocyanation of anilines. First, we selected the readily available N,N-dimethylaniline 6a and ammonium thiocyanate 7 as the model substrate and thiocyanating agent, respectively, to explore the optimal experimental conditions for the photocatalytic reaction. As shown in Table 1, after 12 h reaction in the presence of 5 wt % KSCN was used to replace NH4SCN. In dark. NR: no reaction. Entries 10–12 are control experiments.

<table>
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<tr>
<td>12</td>
<td>CMP-1</td>
<td>THF</td>
<td>O2</td>
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| CMP-1 under the irradiation with an 18 W white-light-emitting diode (LED) light in CH2Cl2, N,N-dimethyl-4-thiocyanatoaniline 8a was obtained in a yield of 53% under an air atmosphere (Table 1, entry 1). A reason for the moderate yield was that with a trace amount of water in the air, a demethylation byproduct (N-methyl-4-thiocyanatoaniline, 25% yield) was formed by the hydrolysis of an iminium ion of 8a (Figure S20), which was generated by photocatalytic one-electron oxidation. In contrast, under a pure O2 atmosphere, the yield of 8a increased to 72% without any demethylation byproduct (Table 1, entry 2). Therefore, pure oxygen was used to ensure an anhydrous atmosphere for achieving high chemoselectivity and yields for the conversion of anilines with methyl substituent(s) on a N atom such as 6a. However, we also found that the conversion of anilines without methyl substituent(s) on the N atom could be preceded with high chemoselectivity and yields of products under an air atmosphere (see Scheme 2). In comparison, when CMP-2 or the porphyrin precursor 4-1 was employed as the control photocatalyst (Table 1, entries 3 and 4), the selectivity and yields of the products were obviously lower than those obtained using CMP-1. For CMP-2, 45% product 8a and 45% reactant 6a were obtained after the reaction under a pure oxygen atmosphere for the same period. The lower conversion rate can be explained by the lower specific surface area of CMP-2 and a number of photophysical features unfavorable for the photocatalysis compared to CMP-1, as discussed in the previous section. Similar results were obtained when using the porphyrin precursor 4-1 as the catalyst (Table 1, entry 4), only 40% product 8a and 55% reactant 6a yielded, which can be explained by the less absorption of the precursor 4-1 in the visible-light region compared to CMP-1. Moreover, a series of experiments for selecting the optimal solvent (Table 1, entries 5–7) proved that THF is the best one for the reaction (87%, Table 1, entry 7) due to the excellent dispersibility of CMP-1 in THF. Further, an increase in the content of the photocatalyst...
to 15 wt %, accompanied with a reduction of the reaction time to 4 h, produced 8a with a much higher yield of 91% (Table 1, entry 8). This yield is comparable to those obtained by traditional thermal catalytic methods that need special SCN reagent-assisted multistep synthesis and equivalent oxidants, or uneconomical metal catalysts, or higher temperatures (>55 °C) (Table S1). We then used KSCN to replace NH4SCN as the sulfur source for the reaction (Table 1, entry 9). 

However, the yield reduced to 75%, which reflected that the presence of a proton in the sulfur source is beneficial to this reaction. Finally, several more control experiments including the lack of oxygen, photocatalyst, or light irradiation were also conducted (Table 1, entries 10–12); the results demonstrated the essential roles of these three key elements in the photocatalytic thiocyanation of anilines.

*Reaction was performed under an air atmosphere. Reaction time was 24 h. Reaction conditions: Anilines (0.5 mmol), NH4SCN (1.0 mmol, 2 equiv), CMP-1 (15 wt %), THF (5 mL), oxygen atmosphere, and irradiation under an 18 W white LED at room temperature for 4 h.*
By employing the identified optimal reaction conditions (Table 1, entry 8), the applicable scope of this reaction was investigated. As shown in Scheme 2, this photocatalytic reaction is applicable for a wide range of substrates including tertiary, secondary, and primary anilines. For tertiary amines, regardless of the substituents on the benzene ring of N,N-dimethylaniline (6a–6e) or the substituents on the N atom (6f–6k), most of them could be converted to the corresponding 4-thiocyanated products with high chemoselectivity and yields (8a–8k, 74–92%), under an oxygen or air atmosphere. However, the compounds 8d (50%) and 8j (43%) have a lower yield due to the presence of steric hindrance substituents on the adjacent sites of the para position of an amine group or the existence of a hydroxyl group. The similar results were also obtained in the photocatalytic conversion of the secondary amines (8l–8u). In the selected substrates, anilines with electron-deficient groups (6l–6n) or electron-donating groups (6o–6p), at the ortho and meta positions on the benzene ring, could undergo efficient thiocyanation to give the products in high yields (63–82%). The results are similar for the substrates with different alkyl substituents on the N atom (8q–8u, 55–76%). It is noted that this conversion is also applicable for the substrates with vinyl and hydroxyl groups (products 8t and 8u). Regarding the primary aniline, 8w was formed in a relatively low yield (50%) with nearly 50% aniline left, even upon the visible-light irradiation for 24 h. Finally, when more reaction sites were introduced (e.g., 6w and 6x), it is interesting that only the products with a single SCN substituent were obtained (52% for 8w and 40% for 8x) after reaction for 24 h. Impressively, all of the products of the above-discussed reactions were para-thiocyanated compounds, which were confirmed by the 1H NMR analyses (part 6 in the Supporting Information). These results indicate an ultrahigh chemoselectivity of this photocatalytic thiocyanation of anilines.

To further verify the high chemoselectivity of the para-position substitution in the photocatalytic thiocyanation, we conducted several control experiments. First, when the C-4 position was occupied by −CH3 (6a-1) or the electron-donating group −N(CH3)2 (6a-2), no product was obtained under similar conditions (Scheme 3a), which was confirmed by 1H NMR analyses (Figure S21). Interestingly, when N,N-dimethylaniline (6a) was changed to phenetole (6y), both of which have similar electron density on the benzene ring, there were no products either (Scheme 3b and Figure S22). When the substrate 6z containing both −N(CH3)2 and −OC2H5 groups was employed as the reactant, a C-4 thiocyanated product (8z) was obtained (Scheme 3c and Figure S23). These results indicate that the N atom on the aromatic amine is essential with an orientation effect (para-position of the aromatic amine) on the photocatalytic thiocyanation.

**Reaction Mechanism.** To study the reaction mechanism, we chose 6i (with the highest yield to obtain 8i in Scheme 2) as the reactant (Scheme 4). When 3 equiv of 2,6,6-tetramethylpiperidyl-1-oxyl (TEMPO), a radical scavenger, was added to the photocatalytic thiocyanation reaction, the transformation was inhibited (Scheme 4a and Figure S24). This phenomenon suggests that the thiocyanation reaction proceeded via a radical pathway. When control experiments were performed in the absence of 6i (Scheme 4b), we noticed that TEMPO would disappear under UV-light (λ = 254 nm) irradiation for 12 h, suggesting that some radicals were trapped by TEMPO. Gas chromatography-mass spectrometry (GC-MS) analysis proved that the trapped radical was *SCN (Figures S25–S27). This is a line of evidence for the radical pathway of the photocatalytic thiocyanation. Furthermore, it was found that TEMPO could exist in the absence of either NH4SCN or CMP-1 (Scheme 4c,d and Figure S27), indicating that the excited state of CMP-1 could be one of the crucial elements to initiate the *SCN free radical.

Furthermore, density functional theory (DFT) calculations were conducted to further understand the reaction mechanism, and the results are shown in Table S2 and Figure S28. In the calculated energy diagram (Figure S28), the lowest unoccupied molecular orbitals (LUMO) of representative model compounds of CMP-1 are all lower than the highest occupied molecular orbital (HOMO) of *SCN, which allows the transfer of a single electron from *SCN to the exited CMP-1.
(denoted as CMP-1*), thus leading to the formation of a free radical intermediate *SCN. Moreover, the singly occupied molecular orbitals (SOMO) of the reduced model components CMP-1− were higher than the LUMO orbital of oxygen, which ensured a pathway for the reduced model components CMP-1− going back to the ground state CMP-1 and thus completing the photoredox cycle. In the experiment, a valence band (VB) and a conduction band (CB) of CMP-1 were obtained (Figure S29) by the electrochemical Mott–Schottky63 along with the optical band gap (1.5 eV) calculated from the absorption peak in the range of 710−800 nm (Figure 4a). The experimental result also supported that CMP-1 could complete the photoredox cycle. Finally, we conducted the kinetic experiments by choosing 6i as the typical example at two different initial concentrations to obtain the relationship between the product yield and reaction time (Figure S30). The results indicate first-order kinetics of the photocatalytic reactions.

Based on the above-discussed results and DFT calculations, a plausible reaction mechanism is illustrated in Scheme 5. Initially, CMP-1 was excited to CMP-1* by visible light. The CMP-1* would prompt two different single electron transfer (SET) processes: one would oxidize aromatic amine (6a) to a radical cation 3a including intermediate A and its resonance structure (B) and the other would convert the *SCN anion (7) to a *SCN free radical. Then, the excited CMP-1* was converted to the CMP-1** radical anion. The photoredox cycle was completed by the molecular oxygen oxidation of CMP-1** to the ground state of CMP-1. Meanwhile, the *SCN free radical bonded with the radical cation B, generating the cationic intermediate C. Finally, the rearomatization of the intermediate C by losing a proton produced the para-thiocyanated product 8a. The proton exchange process was completed by O2*, thus the sulfur source like NH4SCN that can generate protons is better than those that cannot produce protons such as KSCN. On the other hand, DFT calculations of the radical cation B reveal that the para position of aromatic amine has the lowest atom polar tensor-based (APT) charge and thus can preferentially bond with the *SCN free radical; meanwhile, the formed cation C has the lowest energy compared with other cationic intermediates D and E. These calculation results account for the single chemoselectivity of the products.

**Recyclability.** The thiocyanated products are soluble in most of the conventional solvents, while CMP-1 is not. This solubility difference provides a chance to recover the photocatalyst by simply filtering the reaction mixture in an appropriate solvent such as methanol. In this work, we chose 6i (with the highest yield to obtain 8i in Scheme 2) as the reactant and studied the recyclability of CMP-1. Remarkably, the yield of 8i remained over 90% in each cycle, and the amount of the recycled CMP-1 was more than 92 wt % after five catalytic cycles (Figure S31), suggesting the excellent recyclability of CMP-1. The solid-state 13C NMR spectrum revealed no obvious alteration in the characteristic peaks of CMP-1 (Figure S32), and both SEM and TEM images showed the retention of its tubular morphology (Figure S33). These results demonstrate the excellent chemical and structural stabilities of CMP-1 during the catalytic cycles.

**CONCLUSIONS**

In summary, this study demonstrated a template-free synthesis of porphyrin-based CMP tubes (CMP-1). The tubes had an average length of 274 ± 260 μm and a mean width of 1.5 ± 0.6...
μm, which were formed by the scrolling and closing of 2D ribbon-like structures. Compared to the irregular CMP counterpart, CMP-1 exhibited a higher specific surface area and advantageous photophysical properties, including broadened absorption in the visible-light region, longer triplet-state lifetime, and more stable photocurrent. When serving as a metal-free photocatalyst for a visible-light-induced catalytic thiocyanation of anilines, the addition of 15 wt % CMP-1 resulted in high chemoselectivity and yields (>80% mostly) for the conversion of 25 types of anilines at ambient conditions within 4 h reaction period. The excellent recyclability of this photocatalyst enabled its repeated utilization. The study of the reaction mechanism revealed dual roles of CMP-1 in the photocatalytic thiocyanation. The CMP tubes hold promise in serving as recyclable carriers of single-atom catalysts for a wide range of catalytic applications.

ASSOCIATED CONTENT

Supporting Information
The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acs.macromol.1c00190.

Materials and measurements; synthesis of CMPs; general procedure for thiocyanation of anilines; 1H NMR and 13C NMR spectra; and MALDI-TOF spectra (PDF)

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Notes
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