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High-Temperature Polymer Components Reimagined: Scalable Syntheses and *de novo* Routes to Structurally Versatile Precursors

Abstract

Developing efficient and scalable synthetic protocols for key polymer precursors is crucial to advancing high-performance materials designed to withstand severe thermal environments. In this article, we report on the development of solid, high-yield methods for preparing structurally diverse building blocks, including *s*-triazine derivatives, phenyl-borosilane alkynyl oligomers, phthalonitrile-based monomers, and novel diamine curing agents on multi-gram to multi-hundred-gram scales. These carefully optimized procedures use readily available starting materials, mild conditions, and well-known synthetic transformations, thus addressing the longstanding challenges associated with their practical upscaling. The resulting library of monomers and oligomers offers a broad range of reactive functional groups (e.g., nitriles, alkynes, borosilane motifs), enabling future combinatorial-like strategies for the formation of advanced co-polymers with enhanced thermal stability, mechanical strength, and tunable properties suitable for high-temperature applications.

Keywords: heat-resistant polymers; monomers; oligomers; curing agents; triazine; phthalonitrile; borosilane; diamine; synthesis

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Переосмислення компонентів високотемпературних полімерів: масштабований синтез і *de novo* шляхи до структурно різноманітних прекурсорів

Анотація

Розробка ефективних і масштабованих синтетичних протоколів для одержання ключових прекурсорів полімерних продуктів має вирішальне значення для подальшого вдосконалення цих матеріалів, зокрема розроблених з метою витримувати суворі термічні умови. У цій статті ми повідомляємо про розробку надійних, високопродуктивних методів синтезу структурно різноманітних білдинг-блоків, включно з похідними *s*-триазину, фенілборосилан-алкініловими олігомерами, мономерами на основі фталонітрилу та новими діаміновими затверджувачами в масштабах від кількох грам до кількох сотень грам. Ретельно оптимізовані процедури використовують легкодоступні вихідні матеріали, м'які умови проведення взаємодій та добре відомі синтетичні перетворення, таким чином вирішуючи проблеми, пов'язані з їх практичним масштабуванням. Отримана бібліотека мономерів і олігомерів пропонує широкий спектр реакційно-здатних функціональних груп (наприклад, нітрилів, алкінів, боросиланових фрагментів), що дозволяє в майбутньому

за допомогою комбінаторних стратегій створювати передові кополімери з підвищеною термічною стабільністю, механічною міцністю та регульованими властивостями.

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■ Introduction

The drive to develop heat-resistant polymers has been a major focus in material science due to the ever-increasing demands of industries like aerospace, electronics, and chemical processing that require materials capable of operating at high temperatures without degrading [1]. The inherent thermal stability of these materials is attributed to their molecular architecture, which often incorporates rigid aromatic backbones and robust heterocyclic structures specifically engineered to withstand high-temperature environments.

Among the various classes of heat-resistant polymers, several stand out and exhibit remarkable properties thanks to their unique chemical structures and bonding characteristics. Aromatic polyimides, as well as phthalonitriles, are highly valued for their mechanical robustness and thermal endurance [2–4] (**Figure 1**). These polymers are often synthesized using a two-step polymerization process that ensures high molecular weight and structural integrity [4, 5]. Similarly, polybenzoxazoles, polybenzimidazoles, and triazines-based polymers provide exceptional heat resistance and have been extensively studied for their application in harsher environments [3, 6]. The integration of elements like boron, silicon, and phosphorus has also been shown to significantly enhance thermal and oxidative stability, as explored in hybrid systems [3, 7, 8].
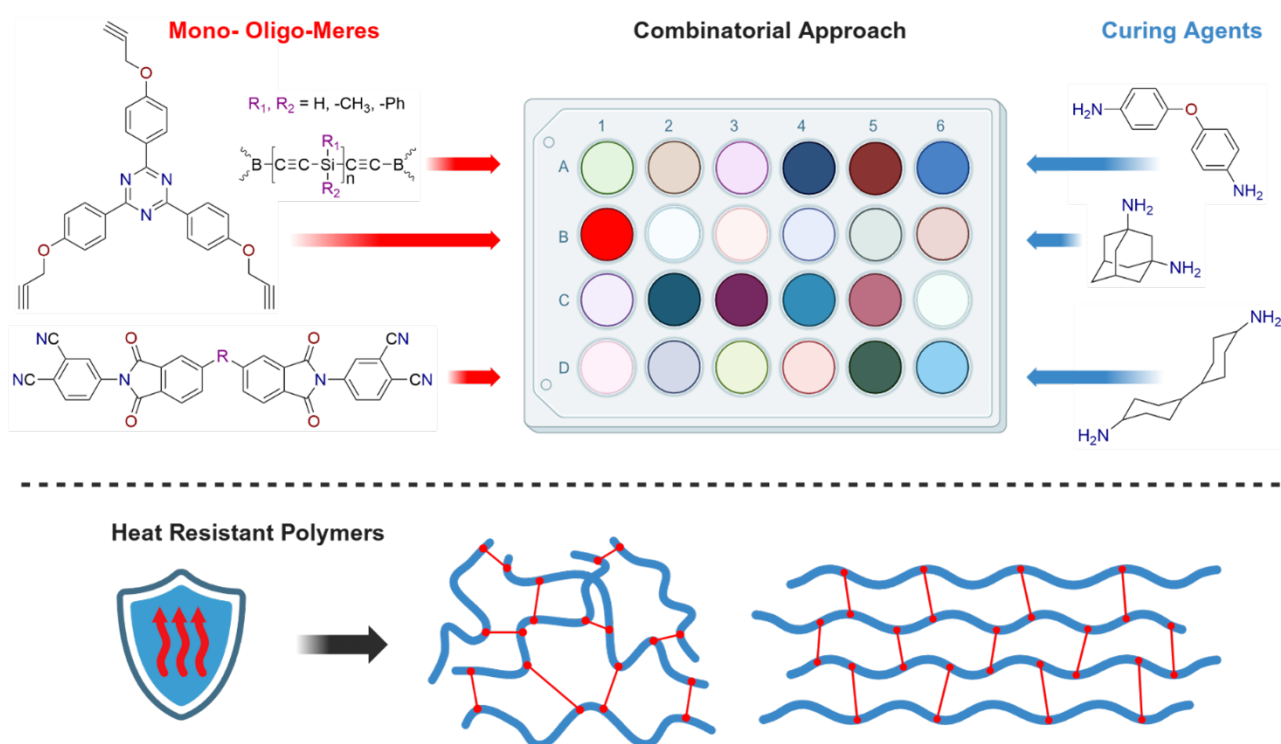

Figure 1. The visualization of the concept of the combinatorial chemistry-fashioned approach to the design of new heat-resistant materials

A particularly promising avenue is the development of composite polymers where combining different types of monomers and oligomers can lead to enhanced material properties. The compatibility of functional groups across these diverse classes allows for cross-linking and synergistic effects that optimize performance [9, 10]. This compatibility opens up opportunities for innovative composite designs that leverage the strengths of various polymer classes as seen in recent studies on silicon and boron-containing hybrids and *s*-triazine reinforced networks [7, 11] (**Figure 1**).

An effective strategy to further enhance the properties of these polymers may involve the use of polyamine curing agents of varying chemical nature, including aromatic, aliphatic, and saturated cage-like structures (**Figure 1**). These curing agents can react with functional groups present in the monomers and oligomers, such as nitriles and alkynes, facilitating cross-linking and the network formation [12, 13]. By selecting polyamines with different structural characteristics, it is possible to tailor the flexibility, cross-link density, and thermal properties of the resulting polymers. For example, aromatic polyamines can contribute to increased rigidity and thermal stability, while aliphatic and cage-like polyamines may improve toughness and impact resistance [14]. The incorporation of these diverse curing agents expands the potential of developing advanced materials with customized performance profiles suitable for demanding applications.

However, the synthesis of these monomers and oligomers, as well as amine curing agents, must be both efficient and scalable. Despite the availability of several synthetic pathways, few are optimized for large-scale production, which is crucial for practical applications. The challenge lies in developing protocols that maintain the integrity of the production sequence and use readily available and safe reagents in mild conditions, allowing for scale-up. It is critical to address this gap to transition these materials from the lab to industry, as highlighted in work on phthalonitriles, borosilane oligomers, and triazine-based precursors [4, 7, 11].

To address the need for scalable synthetic methods, our research focuses on developing robust, high-yield protocols for compounds, such as phthalonitriles, triazine-based monomers, aromatic borosilane oligomers, and a number of diamine curing agents [15]. These compounds are designed to participate readily in cross-polymerization reactions, leveraging their compatible functional groups to form complex, high-performance materials [10]. In the further stages of our research, through a parallel combinatorial-inspired series of polymerizations, we aim to assess the impact of each component on the final polymer characteristics (**Figure 1**). This systematic approach not only facilitates the identification of optimal polymer formulations, but also paves the way for novel applications in high-temperature environments.

Our effort to establish scalable synthetic protocols is motivated by the promising potential of these materials in various technological fields. By examining the interaction and effects of different polymer components, we seek to develop a comprehensive framework for producing advanced heat-resistant polymers that meet the stringent demands of modern industry.

■ Results and discussion

Monomers based on polynitriles, triazines with terminal alkynes, and borosilane alkynyl hybrid oligomers individually yield polymers renowned for their exceptional thermal and mechanical properties [4, 7, 11]. Each class contains functional groups that are chemically compatible for copolymerization, such as nitrile groups, terminal alkynes, and boron-silicon moieties. Grounding on the previous studies, we assume that when these monomers (oligomers) are combined in composite materials, the synergistic interactions among their functional groups can lead to enhanced properties, surpassing those of polymers derived from the individual components.

As the first step, we focused on the synthesis and study of the scale-up opportunities for *s*-triazines, particularly 2,4,6-*tris*(4-(prop-2-yn-1-yloxy)phenyl)-1,3,5-triazine (**3, Scheme 1**, *A*) proven high properties when used as the main component for polymerization [11] and borosilane alkynyl hybrid oligomers, which also exhibited excellent thermo-resistant performance [7]. For this purpose, we used reaction conditions similar to those described in the literature [11, 16], suggesting a two-step preparation using readily available components like 4-hydroxybenzonitrile (**1**) for the acid-catalyzed cyclization to 2,4,6-*tris*(4-(prop-2-yn-1-yloxy)phenyl)-1,3,5-triazine (**2**) at first, and then propargyl bromide for alkylating its phenol groups (**Scheme 1, A**). By optimizing reaction conditions, we were able to scale the preparation of triazine **3** to approximately 200 g per operation. Based on the scope of the
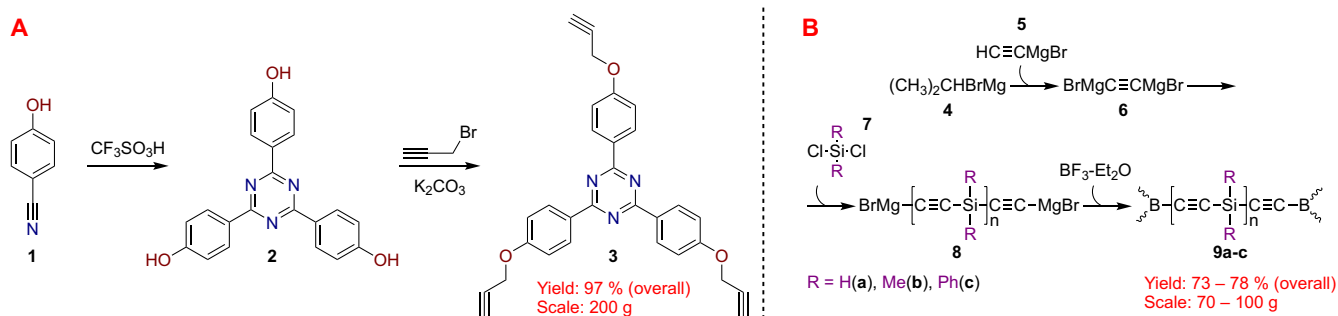
Scheme 1. The preparation of 2,4,6-*tris*(4-(prop-2-yn-1-yloxy)phenyl)-1,3,5-triazine (*A*, compound **3**) and phenyl-borosilane alkynyl hybrid oligomers (*B*, compounds **9a–c**)

borosilane alkynyl hybrid oligomers reported in the literature [7], we opted to prepare all three variants using different dichlorosilanes: dichloromethylsilane, dimethyldichlorosilane, and diphenyldichlorosilane. This approach was chosen to evaluate how various substituents influence the compatibility and, ultimately, the properties of the resulting polymers. The target oligomers (**9a**, **9b**, **9c**, **Scheme 1**, *B*) were synthesized *via* the Grignard reaction on a multigram scale, achieving high yields. To begin, a commercially available isopropylmagnesium bromide (1 equiv. of 3 M solution in 2-methyltetrahydrofuran (Me-THF), compound **4**, **Scheme 1**, *B*) was added to 1 equiv. of 3 M ethynylmagnesium bromide (**5, Scheme 1**, *B*) in the same solvent, and the mixture was refluxed for 2 h, forming a white precipitate of organic magnesium reagents. Utilizing commercial reagents significantly streamlined the process from a technological standpoint, and using Me-THF as a solvent enabled higher reaction temperatures, shorter reaction times, and improved yields while avoiding solvent decomposition products at every stage. To access three borosilane alkynyl hybrid oligomers (**9a–c, Scheme 1**, *B*), dichlorosilane, dimethyldichlorosilane, or diphenyldichlorosilane (0.45 equiv) in Me-THF were added dropwise over 30 min to the reaction mixture, which was then refluxed for additional 3 h.

Subsequently, boron trifluoride etherate (0.3 equiv.) was introduced, and the reaction proceeded for 5 more h at room temperature. Quenching with aqueous hydrochloric acid, extracting with ethyl acetate, washing to neutrality, drying over sodium sulfate, and concentrating gave the corresponding yellowish viscous oligomers. Under these conditions, yields ranged from 73% to 78% for three oligomers (**9a–c, Scheme 1**, *B*) on up to 100 g per the operation scale (**Scheme 1**, *B*).

Polymers derived from tetranitriles, especially phthalonitriles, are renowned for their exceptional thermal stability and mechanical strength, making them highly valuable in advanced material applications. These superior properties arise from the extensive cross-linking facilitated by the multiple cyano-groups, which undergo cyclotrimerization to form stable triazine and phthalocyanine structures within the polymer matrix. Although the literature often treats phthalonitriles **11** and **17** (**Scheme 2**) as readily accessible [4], no single source actually describes their synthesis, even on the laboratory scale. To fill this gap, we started from inexpensive phthalimide (**12**) and converted it into the dicyanamine intermediate (**15**) in three straightforward steps. Using (**15**) and commercially available dianhydrides (**10** and **16**, **Scheme 2**) in refluxing DMF, we obtained target phthalonitriles **11** and **17** in
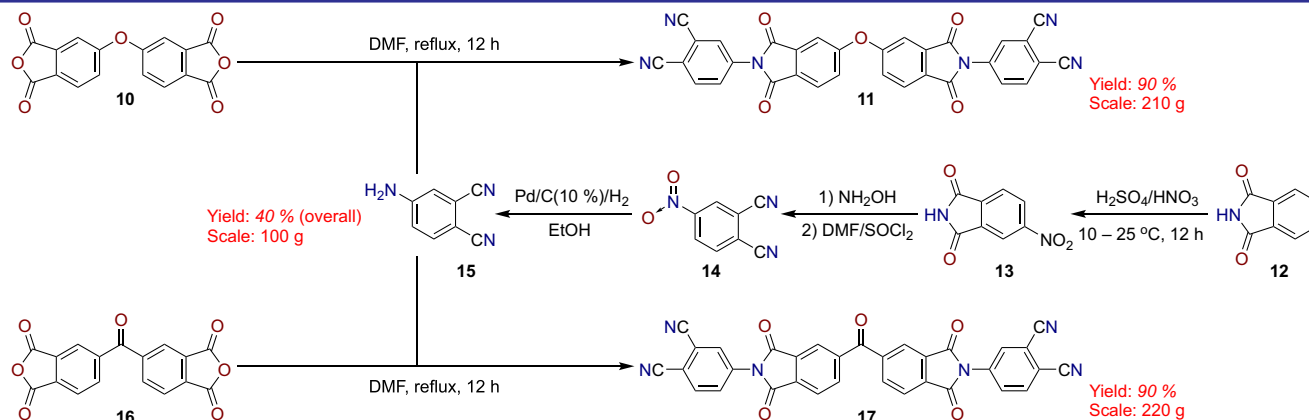
Scheme 2. The preparation of 4,4′-(oxybis(phthalimide))diphthalonitrile (**11**) and 4,4′-(carbonylbis(phthalimide))diphthalonitrile (**17**)
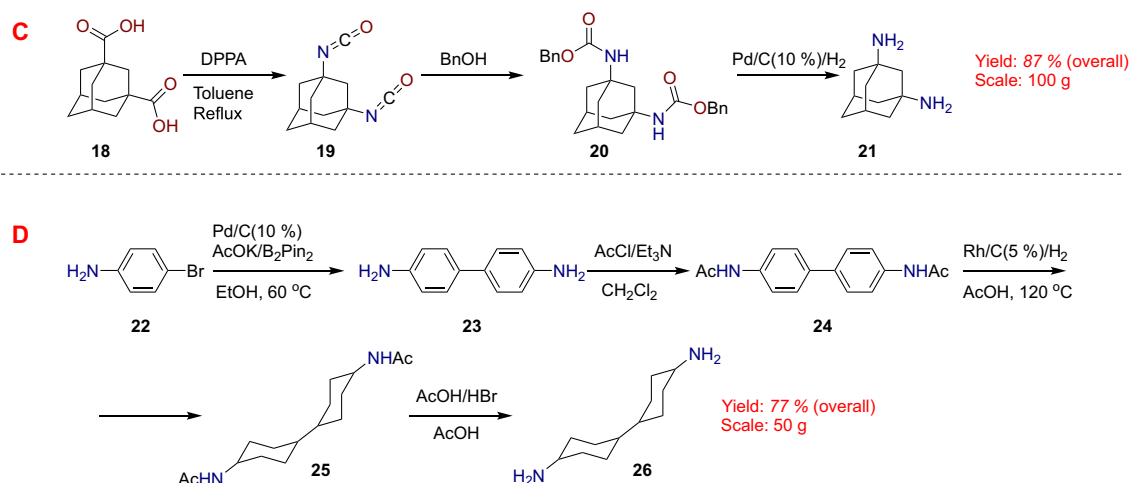
Scheme 3. The preparation of diamine-based curing agents: 1,3-diaminoadamantane (**21**) and 1,1'-bi(cyclohexane)]-4,4'-diamine (**26**)

the yield of about 90% each on over 200 g scale. This reliable, high-yield route not only provides these key phthalonitriles on a large scale, but also opens new opportunities for the subsequent (co-)polymerization studies and material development.

Amine curing agents are effectively utilized in the copolymerization of polynitriles with terminal alkynes to form highly cross-linked polymer networks with enhanced thermal and mechanical properties [17]. The amine groups react with nitrile functionalities through nucleophilic addition, forming amidine linkages, and they facilitate cyclization reactions that incorporate heterocyclic structures, such as triazine rings, into the polymer backbone [12]. Additionally, amines can interact with terminal alkynes via the hydroamination or addition reactions, further increasing the cross-link density [17]. This synergistic approach not only accelerates the polymerization process, but also allows for tailoring material properties, making it valuable for advanced applications in high-performance composites and adhesives. In this part of our study, we focused on saturated diamines, considering that aromatic counterparts like 4,4'-oxydianiline [4] were readily available from commercial sources. Two complementary synthetic routes (**Scheme 3,** *C* and *D*) were developed to access structurally diverse amine curing agents on a multi-gram scale, giving adamantane-based diamine (**21**) and diamine (**26**) featuring a flexible bis-cyclohexane backbone. In route **C** (upper pathway, **Scheme 3**), 1,3-adamantanedicarboxylic acid (**18**) was converted into a diisocyanate intermediate (**19**) *via* the reaction with diphenyl phosphoryl azide (DPPA) in refluxing toluene. The treatment of **19** with benzyl alcohol (BnOH) gave a Cbz-protected derivative (**20**), and the subsequent Pd/C-catalyzed

hydrogenation allowed to completely remove the protecting group, yielding diamine **21** [15] in an excellent overall yield of 87% at a 100 g scale. In route **D** (lower pathway, **Scheme 3**), at the first step, a Suzuki coupling between 4-bromoaniline (**22**) and 4-aminophenylboronic acid pinacol ester (generated *in situ* from **22** and *bis*(pinacolato)diboron) yielded *bis*-aniline **23** (**Scheme 3**). A direct Rh-(or Pd-)-catalyzed hydrogenation of diamine **23** did not allow to completely reduce the substrate and led to the inseparable mixtures of the products. To address this issue, we first prepared the corresponding diacetyl amide (**24**). After optimizing the catalytic conditions, the Rh(5% on Carbon)-catalyzed hydrogenation was applied to fully saturate the aromatic rings, giving diacetamido-*bis*-cyclohexane (**25**) with a quantitative yield. After evaluating various hydrolysis conditions for **25**, including both acidic and basic protocols, we found that the HBr-mediated hydrolysis in acetic acid provided the best outcome. Under these optimized conditions, diamine **26** (**Scheme 3, B**) could be obtained in the 77% overall yield over five steps on a 50 g scale. It is worth noting that [1,1'-bi(cyclohexane)]-4,4'-diamine (**26, Scheme 3**) was synthesized for the first time using a *de novo* developed protocol. Together, routes **C** and **D** demonstrated robust, scalable methods for accessing diamines with distinct structural features.

■ Conclusions

This study has substantially advanced the methods available for producing critical building blocks of high-temperature polymers. We have shown that by fine-tuning synthetic conditions, employing cost-effective and readily available raw materials, and integrating mild reaction conditions,

it is possible to achieve reliable multi-gram to multi-hundred-gram scale preparations of structurally diverse intermediates, ranging from s-triazine derivatives and phthalonitriles to borosilane oligomers and novel diamine curing agents. Unlike many reports that focus solely on polymerization outcomes, our work has focused on developing reproducible procedures and adapting them to industrially significant quantities. This has allowed us to demonstrate that even complex components can be obtained in high yields, high purity, and at scales that transcend typical bench-level experiments.

Such an expanded synthetic toolkit promises a significant impact on the rational design of future advanced materials. Although we did not perform polymerizations here, the compounds prepared open the door to tailor-made architectures with specifically tuned properties. The presence of multiple reactive functionalities, including nitriles, alkynes, boron-silicon motifs, and amine groups, encourages a combinatorial-like approach to explore various cross-linked networks. This combinatorial exploration may help researchers systematically correlate structural modifications with the thermal, mechanical, and oxidative characteristics of the resulting polymers. Over time, this knowledge is expected to guide the development of new classes of polymers optimized for extreme operational conditions.

Ultimately, our work provides a practical foundation for bridging the gap between conceptual molecular designs and real-world material applications. The scalable production of key polymer precursors will be instrumental in ensuring a steady pipeline of innovative components, paving the way for next-generation materials with enhanced longevity, durability, and reliability in demanding high-temperature settings.

■ Experimental section

The general information and materials

The solvents were purified according to the standard procedures. All starting materials were obtained from Enamine Ltd. Melting points were measured on an automated melting point system. ^{1}H, ^{11}B, ^{13}C, and NMR spectra were recorded on a Bruker Avance 500 spectrometer (at 500 MHz for ^{1}H, 160 MHz for ^{11}B and 126 MHz for ^{13}C) and Varian Unity Plus 400 spectrometers (at 400 MHz for ^{1}H, 128 MHz for ^{11}B and 101 MHz for ^{13}C). Tetramethylsilane (^{1}H, ^{11}B, ^{13}C) was used as a standard. HPLC analyses were done on Agilent 1200. Mass spectra were recorded on an Agilent 1100 LCMSD SL instrument (chemical ionization (APCI)). Column chromatography was performed with silica gel (200–300 mesh).

Experimental protocols
4,4',4''-(1,3,5-Triazine-2,4,6-triyl)triphenol (2)

In a dry flask, 200 g (1.68 mol) of *p*-cyanophenol (**1**) was dissolved in a minimal portion of dry chloroform, and 300 mL (2-fold molar excess) of trifluoromethanesulfonic acid was added slowly at stirring as one portion. During the first two hours of stirring at room temperature, a brown precipitate of target 4,4',4''-(1,3,5-Triazine-2,4,6-triyl)triphenol (**2**) was formed. The precipitate was collected and washed with several portions of cold water, upon which it turned pale yellow. Additional washes with hot chloroform were performed to stripe off the residual starting material, then product **2** was collected and dried on air. The yield of purified triazine (**2**) was 195 g (98%).

2,4,6-Tris(4-(prop-2-yn-1-yloxy)phenyl)-1,3,5-triazine (3)

Triazine **2** (150 g, 0.42 mol) was partially dissolved in 1500 mL of anhydrous acetonitrile (acetone may be used as an alternative solvent). Potassium carbonate (176 g, 3.1-fold excess) was then slowly added to the reaction mixture in one portion while stirring. The resulting mixture was brought to a gentle reflux, and an excess of propargyl bromide (156 g, 100 mL, 3.1 mol) was introduced as a slow stream *via* a dropping funnel. The heating at 80 °C continued for 24 h. After the completion, the mixture was poured into water, and the precipitated solid product was collected by filtration. The crude product **3** was thoroughly washed with several portions of cold water, followed by several portions of cold hexane. The final yield of triazine **3** was 198 g (99%).

Borosilane alkynyl hybrid oligomer (9b)

Under an argon atmosphere, 0.5 M solution of acetylene magnesium bromide **5** in Me-THF (700 mL, 0.45 mol) was placed in a dry flask. 2 M solution of isopropylmagnesium bromide **4** in Me-THF (245 mL, 0.5 mol) was then added dropwise, monitoring the course of the reaction by gas evolution (propane release). Once the gas evolution ceased, a white precipitate (**6**) formed, indicating the reaction had reached its completion. Next, dichlorodimethylsilane (**7**) (53.2 g, 0.21 mol) was added dropwise. As the addition proceeded, the white precipitate partially dissolved, and the mixture became nearly clear.

The reaction was stirred at room temperature for 5 h. Afterward, boron trifluoride etherate (20.3 g, 0.14 mol) was introduced gradually, and the mixture was stirred for an additional 15 h. Upon the completion, the reaction was quenched by cautiously adding dilute hydrochloric acid under continuous stirring. The resulting mixture was transferred to a separation funnel and extracted with ethyl acetate. The combined organic phase was washed with water until a neutral state, dried over sodium sulfate, and concentrated under reduced pressure to give a thick brown liquid. To remove impurities, the product was reprecipitated from ethyl acetate into hexane. After the evaporation of the solvents, the borosilane oligomer (**9b**) was obtained as a brown oil, which crystallized upon standing. The yield of oligomer (**9b**) was 80 g (75%).

Borosilane alkynyl hybrid oligomer (9a) was prepared according to the protocol used for the preparation of **9b**, its yield was 68 g (73%).

Borosilane alkynyl hybrid oligomer (9c) was prepared according to the protocol used for the preparation of **9b**, its yield was 97 g (78%).

4-Nitrophthalimide (13)

Phthalimide (**12**) (240 g, 1.63 mol) was added into the mixed acid, which was prepared from the fuming nitric acid (65%, 300 g) and the concentrated sulfuric acid (98%, 1500 g) at 10 °C. The reaction mixture was then allowed to warm slowly to 25 °C. After 12 h, the reaction product was precipitated by pouring into ice, filtered and washed with water until it was free of acid, and purified by crystallization from ethanol. The yield was 294 g (94%).

4-Nitrophthalonitrile (14)

Step 1. 4-Nitrophthalimide (**13**, 220 g, 1.14 mol) was suspended in 2 L of ethanol in a 5 L round-bottom flask equipped with a mechanical stirrer and a reflux condenser. A 25% aqueous hydroxylamine solution containing 3.42 mol NH_2OH (3.0 equiv. relative to 4-nitrophthalimide **13**) was added dropwise with vigorous stirring. The mixture was heated to 75–80 °C under reflux for 5 h, ensuring the complete conversion as monitored by HPLC. After cooling to room temperature, the mixture was further chilled in an ice bath to facilitate precipitation. The resulting solid was collected by the vacuum filtration, washed thoroughly with cold ethanol followed by cold water, and then dried under reduced pressure to give 4-nitrophthalamide 14 with the yield of 90% (200 g). The product was taken to the next step without the additional purification.

Step 2. Thionyl chloride (3.81 mol, 453 g, 278 mL) was added slowly to *N,N*-dimethylformamide (667 mL) at a temperature below 5 °C under the argon atmosphere. After the addition was complete, 4-nitrophthalamide from the previous step (200 g) was introduced slowly in one portion, and the mixture was stirred for 18 h at room temperature. The reaction mixture was then poured into ice-cold water, causing the product to precipitate. The solid was collected by filtration, washed thoroughly with cold water, and dried under reduced pressure to give the desired product in the yield of 89% (178 g).

4-Aminophthalonitrile (15)

4-Nitrophthalonitrile **14** (125 g, 0.72 mol) and Pd/C (10% on carbon, 18 g) were suspended in 5 L of 95% ethanol in a hydrogenation vessel. Hydrogen gas was passed through the vigorously stirred suspension for 3 h at ambient temperature and pressure. After the completion, the catalyst was removed by filtration through celite, and the solvent was evaporated under reduced pressure to yield 4-aminophthalonitrile as an off-white solid (97 g, 97% yield).

4,4'-(Oxybis(1,3-dioxoisoindoline-5,2-diyl))diphthalonitrile (11)

In a 5 L round-bottom flask, *bis*-anhydride **10** (124 g, 0.70 mol) was combined with 4 L of glacial acetic acid and heated to reflux at 120 °C while stirring. Dinitrile **15** (94.7 g, 0.65 mol) was then added, and the reaction was maintained by stirring under reflux for an additional 12 h. Initially, the solution was clear and yellow, and as the reaction proceeded, a white precipitate of imide **11** formed. After the completion of the reaction (monitored by HPLC), the mixture was cooled to room temperature, and the solid was collected by filtration. The precipitate was thoroughly washed with water to remove residual acetic acid, then with ethyl acetate and finally with hexane. Drying the white solid under reduced pressure gave 210 g of imide **11** (95% yield).

4,4'-(Carbonylbis(1,3-dioxoisoindoline-5,2-diyl))diphthalonitrile (17)

In a 5 L round-bottom flask, compound **16** (132 g, 0.75 mol) was combined with 4.5 L of glacial acetic acid and heated to 120 °C under reflux while stirring. Dinitrile **15** (80 g, 0.54 mol) was then introduced, and the reaction mixture was stirred under reflux for an additional 12 h. Initially, the solution was clear and yellow; as the reaction progressed, imide **17** precipitated from the mixture. After the completion, the reaction was cooled to room temperature, and the

solid was collected by filtration. The precipitate was thoroughly washed with water to remove residual acetic acid, then with ethyl acetate, and finally with hexane. Drying the white solid under reduced pressure gave 220 g of imide **17** (95% yield).

Dibenzyl-(adamantane-1,3-diyl)dicarbamate (20)

In a 2 L round-bottom flask, 1,3-adamantanedicarboxylic acid (**18**) (50.5 g, 0.23 mol) was dissolved in 900 mL of toluene and heated to 80 °C under reflux. Triethylamine (70 mL, 50 g, 0.49 mol) was added, followed by the careful dropwise addition of diphenyl phosphorazidate (DPPA; 97 mL, 110 g, 0.35 mol). The reaction mixture was maintained at 80 °C for 1 h until the gas evolution ceased. The solution of benzyl alcohol (60 mL, 61 g, 0.56 mol) in triethylamine (70 mL, 50 g, 0.49 mol) was then introduced, and the mixture was kept at 80–85 °C for 48 h. After cooling to room temperature, the mixture was poured into cold water, the layers were separated and the aqueous layer was additionally extracted twice with ethyl acetate, and the combined organic layers were dried and concentrated under reduced pressure. The recrystallization of the residue from ethanol gave 96 g (99% yield) of carbamate **20**.

Adamantane-1,3-diamine dihydrochloride (21)

In a 2 L round-bottom flask, carbamate **20** (98 g, 0.32 mol) was dissolved in methanol (1.5 L). Palladium on carbon (Pd/C, 10%, 9.8 g) was added, and the flask was purged with hydrogen. The hydrogen atmosphere (1 atm) was maintained above the solution, ensuring a hydrogen supply of 110 mL per gram of substrate **20**. The mixture was stirred at room temperature for 18 h. After the completion, the catalyst was removed by filtration through celite, and the solvent was evaporated under reduced pressure, yielding a white powdery diamine **21**. Diethyl ether (500 mL) was added, followed by dioxane/HCl until the mixture became acidic. The resulting suspension was stirred, and the precipitated diamine **21** as a dihydrochloride salt was collected by filtration, washed, and dried under reduced pressure to give 96 g (98% yield) of the desired product.

1,1'-Biphenyl-4,4'-diamine (benzidine, 23)

4-Bromoaniline (107 g, 0.62 mol) was combined with *bis*(pinacolato)diboron (249 g, 0.94 mol) and potassium acetate (183.6 g, 1.87 mol) in anhydrous ethanol (1 L) within an argon-flushed, three-necked, 2 L round-bottom flask. To this mixture, 10% Pd/C catalyst (6.6 g) was added,

and the reaction mixture was stirred and heated to 60 °C. The mixture was maintained at this temperature with continuous stirring for the duration necessary to achieve the complete consumption of the starting materials, as confirmed by HPLC. After the reaction was complete, the reactor was cooled to room temperature, and the reaction mixture was filtered through celite to remove the catalyst. The filtrate was concentrated under reduced pressure, and the residue was taken up in dichloromethane (3 × 0.5 L). The combined organic layers were then washed twice with water (2 × 0.5 L) and once with brine (0.25 L). The organic phase was dried over anhydrous magnesium sulfate and concentrated under reduced pressure to yield a thick brown residue. This crude product was purified by flash chromatography on silica gel using petroleum ether as an eluent. The purified *bis*-aniline **23** was obtained as a white solid in the amount of 54 g, corresponding to the yield of 94%.

N,N'-([1,1'-biphenyl]-4,4'-diyl)diacetamide (24)

In a 2 L round-bottom flask, compound **23** (66 g, 0.36 mol) was dissolved in 600 mL of dichloromethane at room temperature. Triethylamine (99 mL, 72 g, 0.71 mol) was added, followed by the dropwise addition of acetyl chloride (50 mL, 55.7 g, 0.71 mol) under ice-cooling. The mixture was stirred for 5 h, then the solvent was removed under reduced pressure. The resulting residue was washed thoroughly with water multiple times. After drying, diacetamide **24** was obtained in a quantitative yield (100%) as 96 g of the solid.

N,N'-([1,1'-bi(cyclohexane)]-4,4'-diyl)diacetamide (25)

N,N'-([1,1'-biphenyl]-4,4'-diyl)diacetamide **24** (100 g, 0.37 mol) was dissolved in glacial acetic acid (1 L) and transferred into an autoclave equipped with mechanical stirring. Rhodium on carbon (Rh/C) catalyst (5 g of 5% Rh/C) was added, and the vessel was sealed under hydrogen at 120 °C. The mixture was stirred under these conditions for 7 days, and the reaction progress was monitored by ^{1}H NMR until aromatic signals completely disappeared, indicating the full hydrogenation to *N,N'*-([1,1'-bi(cyclohexane)]-4,4'-diyl)diacetamide (**25**). After cooling to room temperature, the mixture was filtered to remove the catalyst, and the solvent was evaporated under reduced pressure to give the product as an oil. The yield was 99%, providing 103 g of fully saturated acetamide **25**.

[1,1'-Bi(cyclohexane)]-4,4'-diamine (26)

N,N'-([1,1'-bi(cyclohexane)]-4,4'-diyl)diacetamide (**25**) (59.8 g, 0.21 mol) was dissolved in a mixture (1:1, *v/v*) of glacial acetic acid (1 L) and hydrobromic acid (1 L) and heated at 115 °C for 5 days. During the hydrolysis, water (100 mL) and additional HBr (50 mL) were added as needed. After the complete hydrolysis was confirmed by the mass spectrometric analysis, the mixture was concentrated under reduced pressure. The residue was neutralized with an aqueous base and extracted three times with MTBE (3 × 500 mL). The combined organic extracts were dried and evaporated to yield an oily residue, which was dissolved in anhydrous MTBE (200 mL). The dioxane/HCl solution was added until an acidic state, causing the precipitation of diamine **26** as dihydrochloride (white solid). After the filtration and drying, 55 g of the product was obtained, corresponding to a yield of 92%.

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