

Modular Synthetic Platform for Interior-Functionalized Dendritic Macromolecules Enabled by the Palladium/Norbornene Catalysis

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ABSTRACT: Synthesis of interior-functionalized dendritic macromolecules is generally tedious and labor-intensive, which has been a key factor hampering their practical applications. Here, we have revisited this long-standing challenge and devised a modular and convergent platform to synthesize multifunctional dendrons with all-carbon backbones up to four generations via an *in situ* functionalization strategy. Enabled by the palladium/norbornene cooperative catalysis, different functional groups can be introduced to each generation of dendrons during the dendron growth, making it convenient for systematic comparison of their properties. The utility of this versatile platform is further showcased in the internal-functionalization-dependent properties of dendrons as organogels and aggregation-induced emission materials.

Materials with a demanding synthetic process are often avoided for practicality reasons, despite exhibiting promising properties. In general, it is until the synthetic burden is alleviated by a more efficient and user-friendly method that the value of these materials can be better recognized. One such example is multifunctionalized dendronized macromolecules (e.g., dendrimers, dendronized polymers).¹ Building on the unique properties of the bulky monodisperse dendronized three-dimensional architecture, the addition of multiple functional groups (FGs) to each layer can synergistically influence their solubility,^{2a,b} viscosity,^{2c} chain conformation,^{2d} core–shell compartmentation,^{2e} and other properties.² Thus, they offer an excellent platform for enabling high-end applications in drug delivery, sensing, and nanotechnology.³ Unfortunately, this promise is hampered by lengthy synthetic routes to access these materials and inefficiency of introducing FGs.^{1,2}

While it is straightforward to introduce FGs to the core of dendrimers or the periphery of dendrons,⁴ incorporating different FGs into interior layers (i.e., generations) of dendrons, which can maximize versatility offered by the layered architecture, has been challenging. To date, two strategies are known for internal functionalization of dendrons. The first one, namely, the prefunctionalization strategy, employs tetrafunctionalized monomers prepared in advance (Figure 1A).^{4a,5} The accessibility of such highly functionalized branched monomers could be a concern. In addition, the functionalization reaction needs to be chemically orthogonal to the dendron growth reaction, which is another strict requirement.^{4a} The alternative postfunctionalization strategy, FGs are coupled at dendrons' reactive sites after the macromolecule synthesis, was less time-consuming, yet unlikely suitable for generation-specific modification, and prone to defects (Figure 1B).^{4a,6} Hence, a more straightforward paradigm, in which the internal FGs are modularly installed onto a simple difunctionalized monomer during the dendron growth (Figure 1C), would serve as an almost ideal

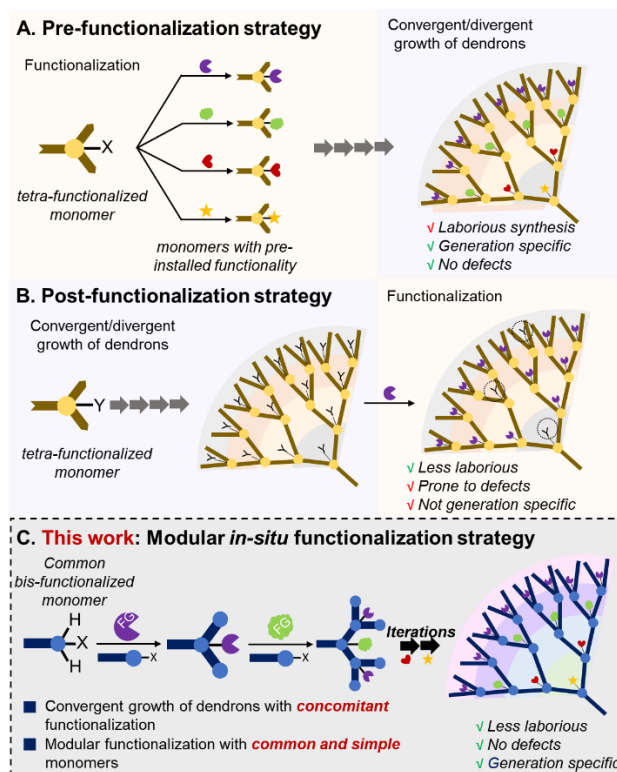


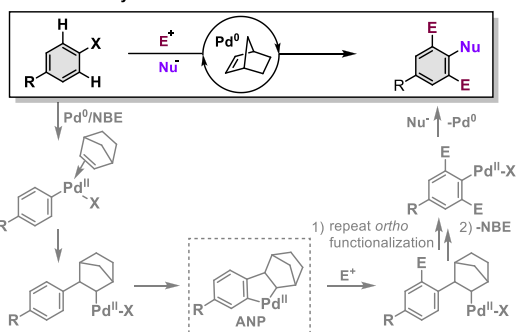
Figure 1. Synthetic strategies for the interior-layer functionalization of dendrons.

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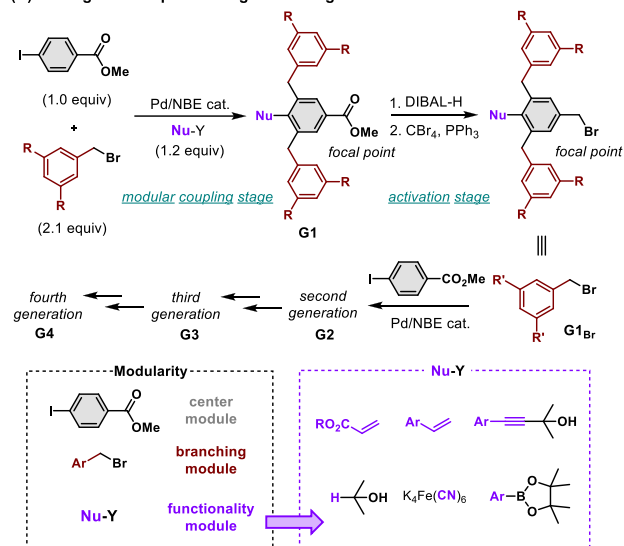


Scheme 1. Pd/NBE-Catalyzed Generation Growth of Interior-Functionalized Dendrons

(A) The Pd/NBE catalysis



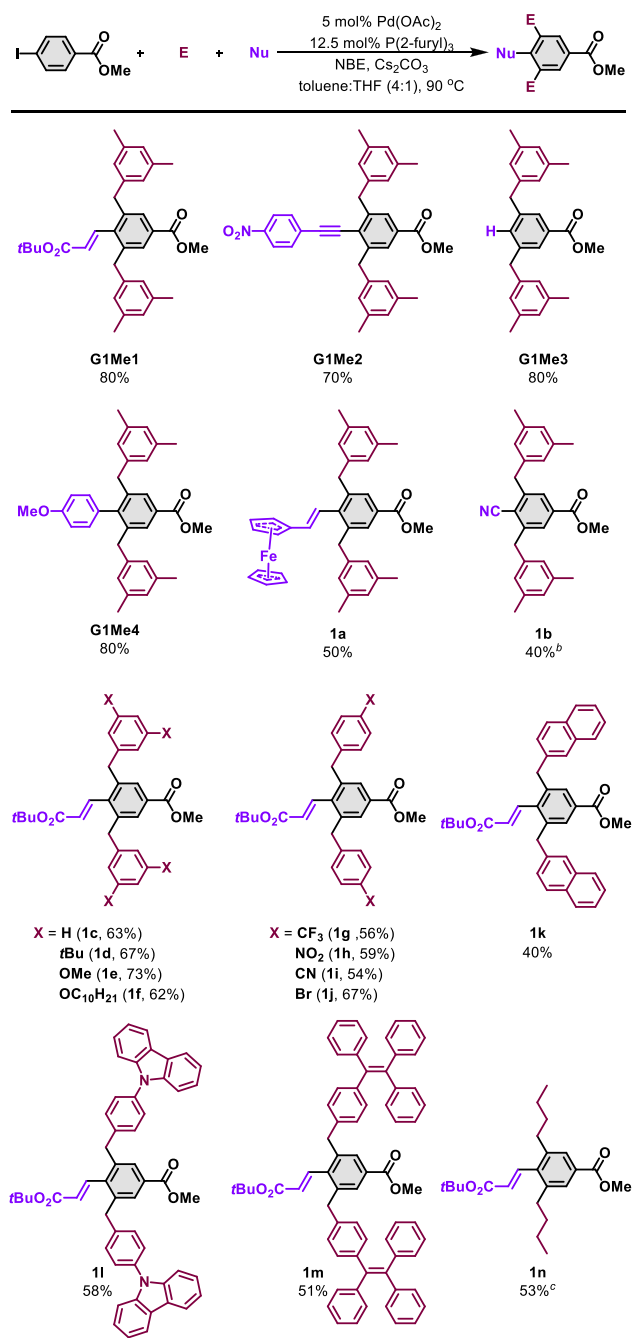
(B) Strategic development for generation growth of dendrons



approach to prepare interior-functionalized dendritic macromolecules. Herein, we describe the first and preliminary development of a modular *in situ* functionalization strategy for convergent synthesis of dendritic macromolecules containing generation-specific FGs and all-carbon backbones.

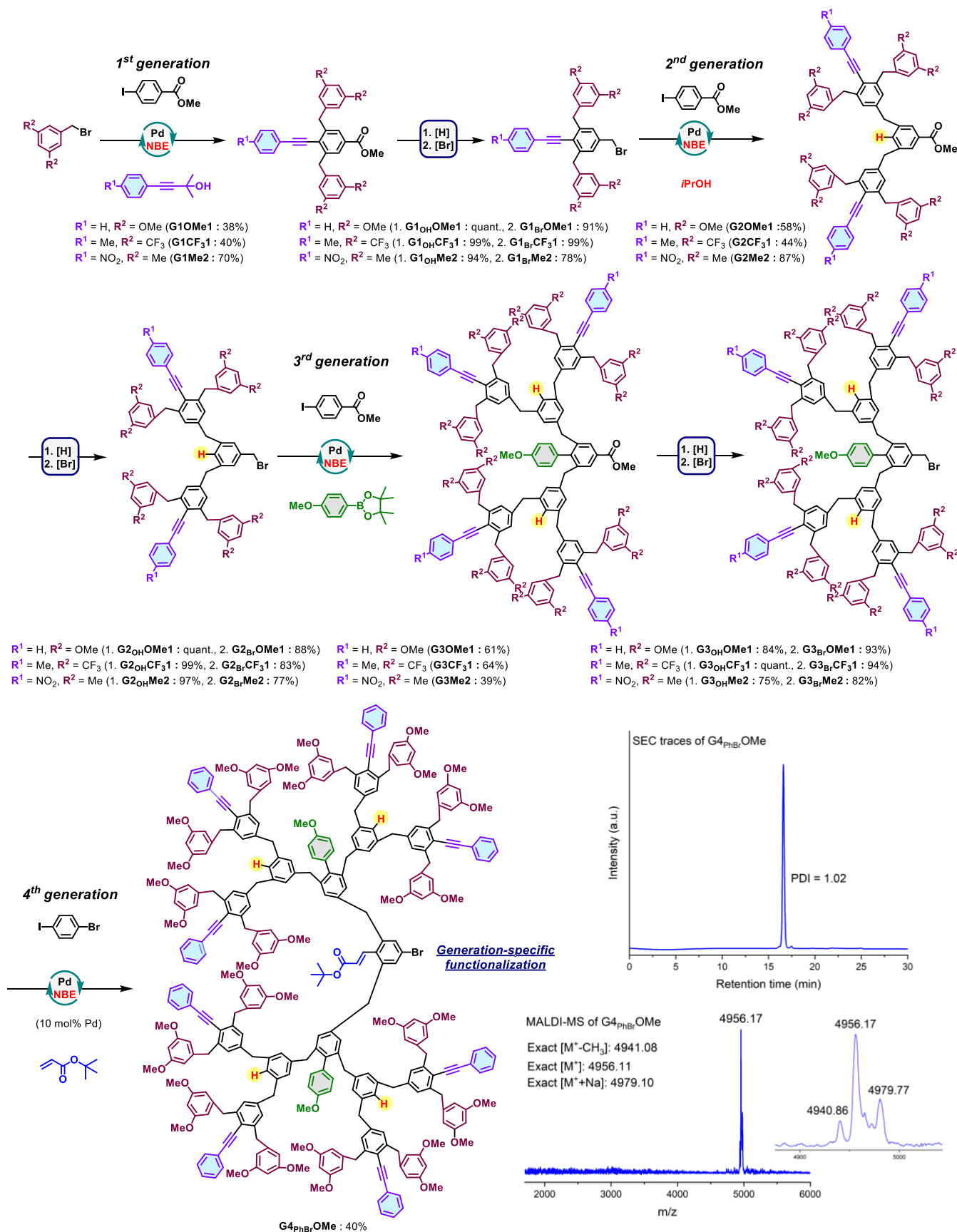
Palladium/norbornene (Pd/NBE)-catalyzed functionalization of *para*-substituted aryl halides provides a unique and efficient method to install three adjacent FGs to the aromatic core (Scheme 1A).⁷ Through an aryl-norbornenyl palladacycle (ANP) intermediate, various electrophiles and various nucleophiles (including alkenes) can be coupled at the *ortho* and *ipso* positions, respectively.⁸ The branching selective coupling mode renders the Pd/NBE catalysis well suited for the development of modular *in situ* functionalization synthesis of interior-functionalized dendritic macromolecules.

At this initial stage of exploration, the Pd/NBE-catalyzed double *ortho*-C–H alkylation using benzyl bromides was employed as the dendron growth reaction to access branching networks (Scheme 1B). 4-Iodobenzoate serves as an excellent center module because it can be easily converted to a benzyl bromide moiety after a sequence of reduction and bromination in high efficiency, which can participate in the Pd/NBE reaction again as the branching module for the growth of the next-generation dendron. In each dendron generation synthesis, different FGs can be introduced to the *ipso* position using different nucleophiles. This approach should provide dendrons with all-carbon backbones, which, to the best of our

Table 1. Reaction Scope of Various Electrophiles and Nucleophiles^a

knowledge, have not been accessed previously with the traditional dendron synthesis methods. The benzyl-linked framework is also structurally complementary and chemically adaptable to the benzyl ether-based dendrons pioneered by Hawker and Fréchet, which also utilizes benzyl-type electrophiles.⁹ Additionally, the robust all-carbon dendritic scaffold offers the

Scheme 2. Synthetic Pathways to Access Three Prototypes of Multifunctional Dendrons



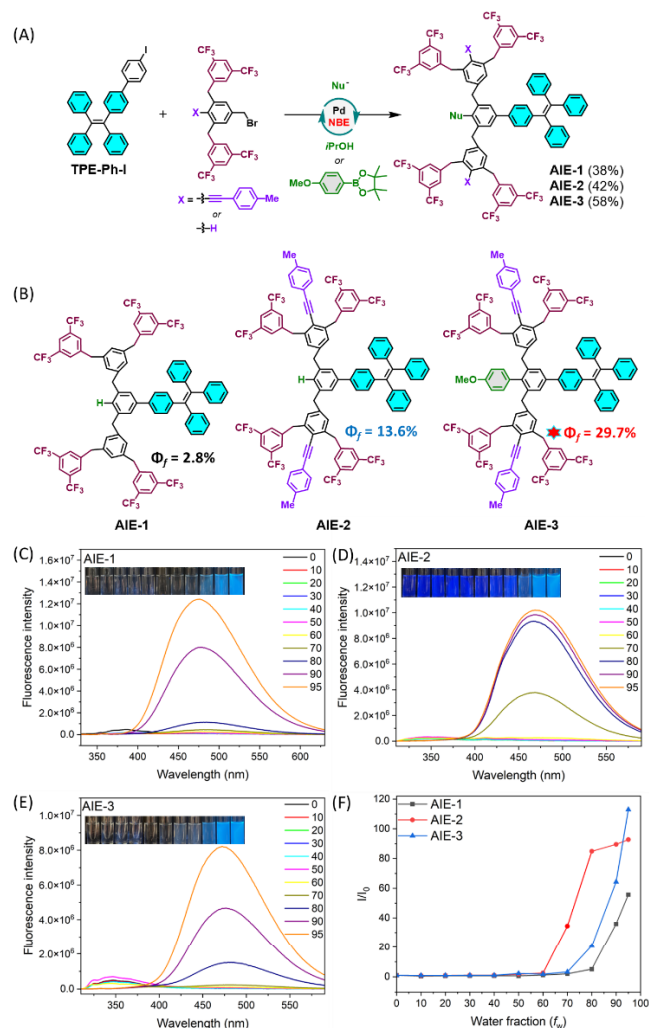


Figure 2. Structure–property relationship study of the AIE effect of second-generation dendrons: (A) Rapid synthesis of the dendritic AIE compounds. (B) The chemical structures of three dendrons along with their respective fluorescence quantum yields. Fluorescence intensity of (C) AIE-1 (excitation: 327 nm, emission = 475 nm), (D) AIE-2 (excitation: 300 nm, emission = 470 nm), and (E) AIE-3 (excitation: 300 nm, emission = 473 nm) with varying f_w . Inset: fluorescence images of THF-H₂O mixtures (from left to right, f_w = 0 to 95 vol %) taken under 365 nm UV illumination. (F) Relative increase in fluorescence intensity compared to that of the material in pure THF solution (I_0).

opportunity for postmodifications under harsher conditions that benzyl ethers may not survive (see Figure S2).¹⁰

To make the Pd/NBE catalysis more suitable for dendron synthesis, our initial effort was to optimize the *ortho*-C–H benzylolation of 4-iodobenzoate with 3,5-dimethylbenzyl bromide as the electrophile to achieve higher efficiency (see the Supporting Information). Palladium acetate and tri(2-furyl)-phosphine were found to be a better combination of catalyst and ligand. Only 2.1 equiv of the benzyl bromide electrophile were needed. A survey of the solvent effect revealed that 20% THF in toluene was optimal. To understand the scope of FGs that can be introduced to the peripheral and interior positions, different nucleophiles and alkyl electrophiles as functionality and branching modules, respectively, were explored (Table 1). First, alkenyl (G1Me1 and 1a), alkynyl (G1Me2), hydrogen (G1Me3), aryl (G1Me4), and cyano (1b) groups can all be

smoothly installed at the *ipso* position. Next, a range of benzyl bromides with various substituents at the *meta* positions such as hydrogen (1c), methyl (G1Me1), *tert*-butyl (1d), methoxy (1e), and long alkoxy chain (1f), proved to be feasible coupling partners. In addition, electron-withdrawing groups at the *para* position, including trifluoromethyl (1g), nitro (1h), cyano (1i), and bromide (1j), can be tolerated. Gratifyingly, extended π systems such as naphthalene (1k), phenyl carbazole (1l), and tetraphenyl ethylene (1m) were also compatible to the Pd/NBE catalysis. Besides benzylation, *ortho*-C–H alkylation with *n*-butyl iodide was successfully achieved (1n), using 1,4-dioxane as solvent.

To demonstrate the feasibility of this *in situ* functionalization platform for dendritic molecule synthesis, three prototypes of higher-generation multifunctional dendrons containing different FGs at the periphery/interior/core were prepared (Scheme 2). For the peripheral functionalization, we employed benzyl bromides bearing –OMe, –Me, or –CF₃ FGs as branching modules, and three different masked alkynes as functionality modules. To our delight, the first-generation synthesis proceeded smoothly to afford G1OMe1, G1CF₃1, and G1Me2 on a multigram scale, and all the products can be purified by recrystallization without chromatography.¹¹ The following ester reduction and Appel reactions afforded all three G1Br compounds in high yields (73 to 98% over two steps). Afterward, these G1Br compounds were subjected to the next generation synthesis of G2 dendrons, in which hydrogen is introduced to the *ipso* position using isopropanol as the hydride source. The same reduction and bromination sequence was applied to prepare G2Br compounds. Similarly, the third-generation dendrons (G3) were synthesized by the same iteration, except using the *ipso*-Suzuki quench in the Pd/NBE catalysis to introduce an aryl FG. Lastly, 1-bromo-4-iodobenzene was used as a center module to connect two G3 dendrons, generating the fourth-generation dendritic macromolecule (G4_{PhBr}OMe). Notably, the *ipso*-position was still functionalized even in this more sterically hindered environment after adjusting the cosolvent ratio (toluene:THF) from 1:4 to 4:1. The remaining aryl bromide moiety in G4_{PhBr}OMe can potentially be used for further functionalization. The structure of G4_{PhBr}OMe was characterized and supported by NMR spectroscopy, MALDI-MS, and size exclusion chromatography (SEC).

Owing to the high versatility of the Pd/NBE catalysis, this *in situ* functionalization platform allows convenient exploration of structure–property relationships in some applications, which is difficult to achieve otherwise. For example, considering that benzyl ether-based dendrons are known to form organogels as light harvesting or stimuli-responsive materials,¹² seven different interior-functionalized second-generation dendritic “gelators” were prepared using this method (see the Supporting Information for details). The driving forces for gelation (π – π and C–H/ π interactions)¹³ were reported to be affected by structural variations, such as dendron generations, peripheral FGs, or substitution patterns,^{14,15} and yet the effect of interior-functionalization on gelation efficiency remains unexplored. Interestingly, the dendrons with *ipso*-functionalization at the first generation exhibited superior gelation ability compared to the corresponding nonfunctionalized one. In contrast, the *ipso*-functionalization at the second generation had a negative impact on gelation efficiency, and this negative impact was even higher when the *ipso*-position was functionalized with more electron-deficient groups (Table S2).

Figure 2 illustrates another example of using the interior functionalization to enhance the aggregation-induced-emission (AIE) effect by introducing more steric bulk around the rotatable benzyl or phenyl groups (Figure 2).¹⁶ The aryl iodide attached to a well-investigated AIE moiety (Figure 2A, TPE-Ph-I), tetraphenylethylene,¹⁷ successfully provided three dendron variants: a nonfunctionalized dendron (AIE-1), a dendron with *ipso*-functionalization at the first generation (AIE-2), and a dendron *ipso*-functionalized in both generations (AIE-3) (Figure 2B). The AIE behavior of each dendron was examined by measuring the fluorescence in THF/H₂O mixed solvents upon varying the volume fraction of water (f_w) (Figure 2C–F). The formation of aggregates upon increasing f_w was confirmed using UV–vis absorption spectroscopy (Figure S1). For AIE-1, upon increasing f_w to 95%, emission intensity was approximately 56-fold higher than that of the emission in pure THF. Gratifyingly, interior-functionalized dendrons AIE-2 and AIE-3 exhibited a greater enhancement in emission intensity at $f_w = 95\%$, approximately 93- and 113-fold, respectively. The absolute quantum yields (ϕ_f) exhibited a similar pattern, giving 2.8%, 13.6%, and 29.7% for AIE-1, AIE-2, and AIE-3, respectively. These two examples clearly showed that changes of the *ipso*-functionalization in such benzyl-type dendrons could make a significant difference in their properties. This highlights the importance of interior functionalization for dendritic material development, as well as the convenience of this new synthetic platform for studying structure–property relationship.

In summary, we have described the first use of the Pd/NBE catalysis for synthesis of dendritic macromolecules, enabling generation-specific multilayered interior functionalization in a streamlined and scalable manner. This unique platform simplifies the access to a series of dendrons with similar structures but having different internal and peripheral FGs precisely installed, showing potential to build dendron libraries for systematic structure–property relationship studies. It is our hope that, by mitigating the synthetic burdens, this convenient platform could catalyze a renaissance in the field of advanced multifunctional dendritic macromolecules.

■ ASSOCIATED CONTENT

SI Supporting Information

The Supporting Information is available free of charge at <https://pubs.acs.org/doi/10.1021/jacs.4c06090>.

Detailed experimental procedures, characterization data, gelation test of dendrons, UV–vis spectra, fluorescence spectra, stability test of dendrons, NMR spectra of compounds, MALDI-tof spectra of compounds (PDF)

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Author Contributions

S.C. and K.-Y.Y. contributed equally to this work.

Notes

The authors declare no competing financial interest.

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