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Dendritic Ionic Liquids Based on Imidazolium-Modified Poly(aryl ether) Dendrimers

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Abstract: A series of dendritic ionic liquids (DILs) based on imidazolium-modified poly(aryl ether) dendrimers IL-Br-G*n* ($n=0$–3) were synthesized by a modified convergent approach and "click" chemistry. The resulting DILs exhibited high thermal resistance with decomposition temperatures up to 270 °C and low glass transition temperatures in the range of approximately −5–0 °C. All IL-Br-G*n* were found to be miscible with water at any ratio and could encapsulate hydrophobic molecules. The reversible phase transfer of the DILs between the aqueous and organic phases was accomplished by simple anion exchange between the hydrophilic Br^- anion and the hydrophobic bis(trifluoromethylsulfonyl)amide anion (NTf_2^-). IL-Br-G*n* could be used as transporters to shuttle hydrophobic molecules between the organic and aqueous phases efficiently. The present work provides a new kind of transporting materials with potential applications in substance separation, drug delivery, and biomolecule transport.

Keywords: dendrimers · ion exchange · ionic liquids · phase transfer · transporters

Introduction

Dendrimers are regularly and hierarchically branched macromolecules with excellent monodispersity, globular shape, interior pockets, and numbers of surface functionality.[1] The specific properties of dendrimers endow them with great potential in miscellaneous applications such as catalysis, supramolecular chemistry, and drug delivery.[2] Furthermore, the stepwise synthesis of dendrimers allows for a large degree of control over the molecular architecture. Desired functional groups can be accurately located at the core, focal point, periphery, or even at each branching point of the dendritic structure.[3]

Ionic liquids (ILs) nowadays have attracted rapidly increasing interest as a result of their unique properties, which include negligible vapor pressure, low flammability, ionic conductivity, low toxicity, and a wide electrochemical window, in addition to their potential for facile construction of highly multifunctional systems. Poly(ionic liquid)s (PILs), that is, polymerized ionic liquids, combining the properties of ionic liquids and the superior processability afforded by the polymer nature,[4] have been widely used in the fields of catalysis,[5] synthesis,[6] gas adsorption and separation,[7] electrochemistry,[8] and thermoresponsive materials.[9] Replacing polymers with special macromolecules such as hyperbranched polymers or dendrimers in PILs affords hyperbranched or dendritic ionic liquids (BILs or DILs). Various applications of BILs or DILs can be envisioned, such as sorbents, liquid separation media, catalyst scaffolds, dispersing agents, and transporters for shuttling functional materials. Recently, Ludwigs and co-workers reported a series of ionically functionalized branched polythiophenes with carboxylic acid or methylimidazolium end groups. The conjugated BILs exhibit characteristics of both conjugated polymers and polyelectrolytes, which implies potential applications in dye-sensitized solar cells and electrochemical devices.[10] Mülhaupt and co-workers developed new families of BILs with onion-like topology, containing a core of hyperbranched poly(1,3-diether), a polar inner imidazolium cation shell, and an nonpolar outer *n*-alkyl shell. BILs are very effective phase-transfer systems, and they enable extraction of water-soluble dyes and nanomaterials from an aqueous phase.[11] Up to now, only a few examples have dealt with DILs.[12] Our research group has developed carboxylate- and tetraethylene glycol terminated poly(aryl ether) dendrimers that can act as microreactors to control pathways of photochemical reactions.[13] In continuation of this research, we anticipate that the construction of imidazolium-terminated poly(aryl ether) dendrimers may provide macromolecules

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with the merits of both dendrimers and ILs, which will reinforce applications of dendritic ionic liquids in materials chemistry.

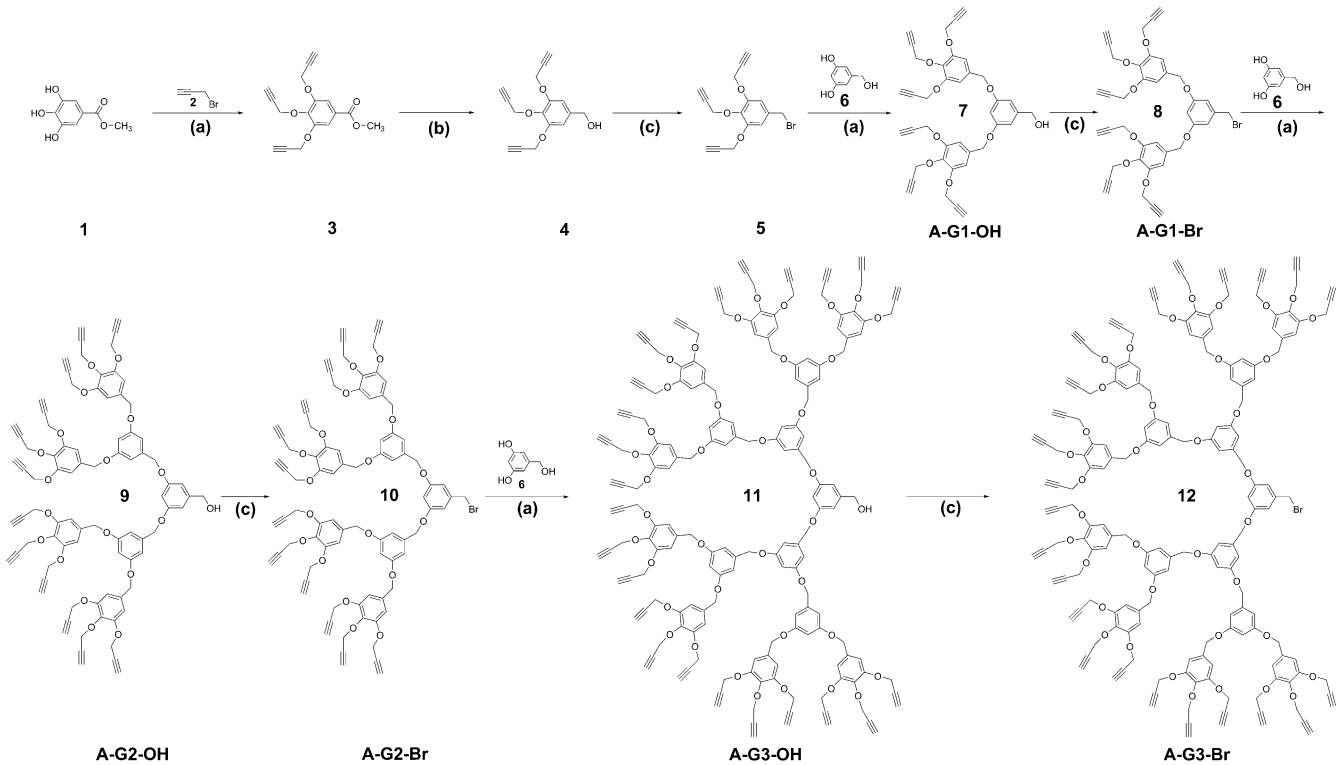
Herein, we attempt to take advantage of the dendritic architecture with numerous peripheral groups that could densely incorporate ionic liquid moieties to obtain DILs. Numerous ionic groups at the periphery will greatly affect the physical properties of the dendrimers, which should result in lower glass transition temperatures (T_g), reversible phase-transfer properties, and efficient transporting capabilities for hydrophobic molecules.

Results and Discussion

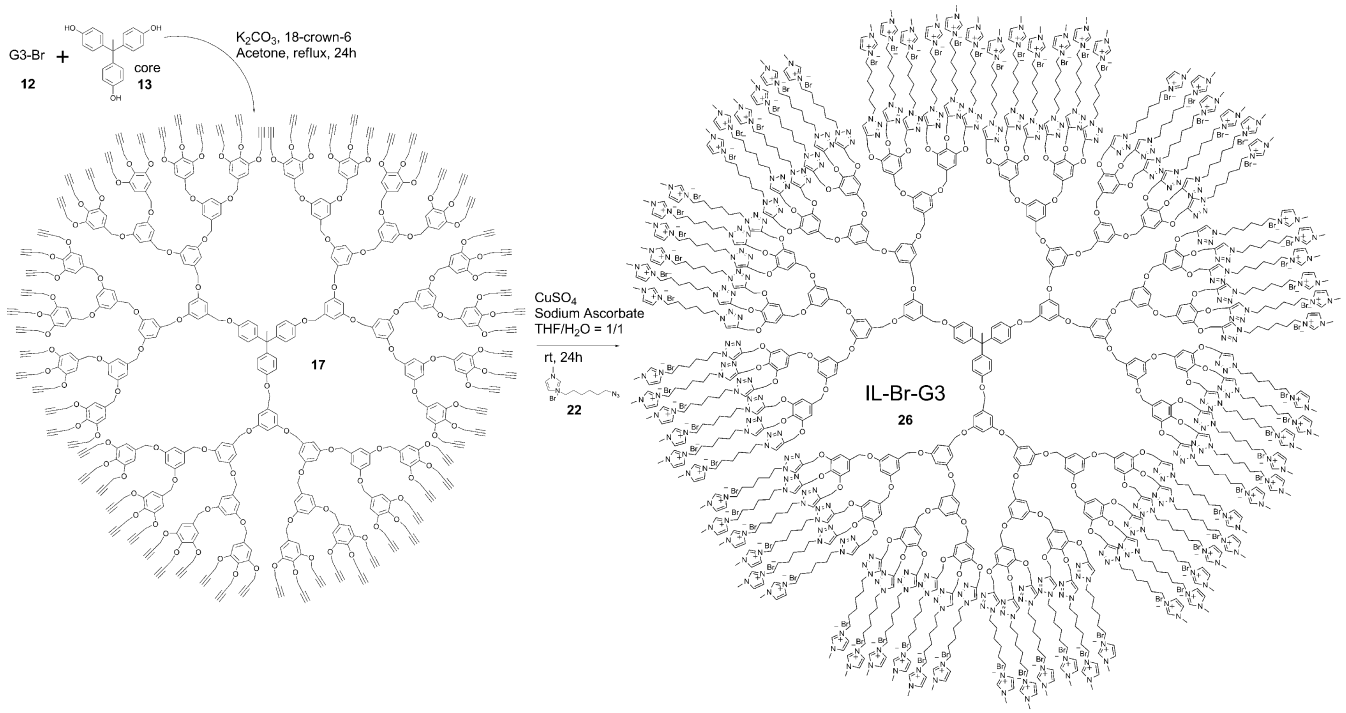
The design of DILs is based on the following ideas: One, the hydrophobic poly(aryl ether) dendritic backbone is adopted owing to its controllable synthetic method[3] and capability of encapsulating hydrophobic molecules;[1a,2a,13] two, alkynyl end groups are engineered to preinstall in the periphery of the precursor ready for the following "click" reaction; three, the efficient "click" reaction between azides and terminal alkynes is selected to attach the imidazolium groups to the periphery of the dendrimers completely.

The alkynyl-terminated poly(aryl ether) dendrons (A-G*n*-Br, $n=1$–3) were synthesized by the adapted convergent synthetic methodology[14] shown in Scheme 1. The reaction of methyl gallate (**1**) with propargyl bromide (**2**) was performed in the presence of potassium carbonate and 18-crown-6 in dry acetone, which gave desired compound **3** in 81% yield. Reduction of **3** with $LiAlH_4$, which was followed by bromination with PPh_3/CBr_4 afforded A-G0-Br (**5**) in 97% yield. Reaction of **5** with 3,5-dihydroxybenzyl alcohol (**6**) gave the first-generation dendritic alcohol A-G1-OH (**7**) in 91% yield after purification by column chromatography. By repeating bromination and reaction with **6**, first- to third-generation dendrons **8**, **10**, and **12** were prepared with 6, 12, and 24 alkynyl groups at their periphery, respectively. Details of the synthesis and characterization of the compounds are described in the Experimental Section. All of the compounds were characterized by ^1H NMR spectroscopy and mass spectrometry (MALDI-TOF or ESI).

The obtained dendrons were attached to a polyfunctional 1,1,1-tris(4′-hydroxyphenyl)ethane (**13**) core to build acetylene-terminated tris(phenolic)-cored dendrimers ([A-G*n*]$_3$-C) by using the same chemistry in constructing the dendrons, and the synthesis of the third generation is shown in Scheme 2. An acetone solution of dendron A-G3-Br (**12**, 3.2 equiv.) was heated at reflux with core molecule **13** (1.0 equiv.) in the presence of potassium carbonate and 18-crown-6. The desired acetylene-terminated tris(phenolic)-cored dendrimer [A-G3]$_3$-C (**17**) was obtained in 57% yield after simple purification by column chromatography. A similar reaction was performed to produce [A-G*n*]$_3$-C ($n=0$–2) by using the corresponding generation of dendrons with yields of 84, 80, and 77% for generations 0, 1, and 2, respec-



Scheme 1. Synthesis of alkynyl-terminated poly(aryl ether) dendrons. Reagents and conditions: a) acetone, K_2CO_3, 18-crown-6, reflux, 24 h; b) THF, $LiAlH_4$, RT, 3 h; c) THF, CBr_4, PPh_3, RT, 10 min.



Scheme 2. Synthetic route to dendrimer **17** and IL-terminated tris(phenolic)-cored dendrimer IL-Br-G3 (**26**) with 72 imidazolium end groups.

tively. The copper(I)-catalyzed Huisgen 1,3-dipolar cycloaddition between azides and terminal alkynes is one of the most used "click" reactions, and it has many advantages such as high selectivity, functional group tolerance, mild reaction conditions, and quantitative yield.[15] Astruc's group functionalized the periphery of dendrimers by using the "click" reaction.[16] In the present case, the azide-substituted molecule $[N\text{-}C\text{-}Min]^+Br^-$ (**22**, Min = 1-methylimidazolium) was used as a coupling molecule to "click" with the acetylene-terminated tris(phenolic)-cored dendrimers to prepare imidazolium-terminated ones. The synthetic route for the synthesis of the third-generation DIL, IL-Br-G3 (**26**), is shown in Scheme 2 as a representative example. Click reaction of **17** with **22** afforded desired dendritic ionic liquid **26** in 68% yield. The ^{1}H NMR spectrum of **26** exhibits clearly the structure with two singlets at $\delta = 8.71$ and 7.38 ppm for the imidazolium protons. Compared with the ^{1}H NMR spectrum of **17**, the disappearance of the acetylene protons at $\delta = 2.46$ ppm further confirms the occurrence of the "click" reaction and the formation of the ionic-liquid-terminated structure. With a similar procedure, the lower generation DILs of IL-Br-Gn (n = 0–2; **23**, **24**, **25**) were prepared and characterized by ^{1}H NMR spectroscopy. We failed to obtain the molecular ion peak of IL-Br-G3 by MS, because of the limitation of the equipment for high molecular weights (calcd for $C_{1271}H_{1728}Br_{72}N_{360}$: 29588.2 $[M]^+$). IL-Br-G0 (**23**), IL-Br-G1 (**24**), and IL-Br-G2 (**25**) show ion peaks with multicharges at $m/z = 2928.6$ (calcd for $C_{158}H_{208}N_{45}O_{12}$: 2927.7 $[M-9Br^--8H^+]^+$), 5924.8 (calcd for $C_{317}H_{415}N_{90}O_{27}$: 5914.4 $[M-18Br^--17H^+]^+$), and 792.6 (calcd for $C_{635}H_{864}Br_{19}N_{180}O_{57}$: 789.6 $[M-17Br^-]^{17+}$) in the mass spectra.

The thermal properties of all the dendritic ionic liquids (IL-Br-Gn, n = 0–3) were measured by thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC) as shown in Figure 1. IL-Br-Gn (n = 0–3) exhibit excellent thermal resistance with decomposition temperatures (T_d) up to 270 °C and major weight changes at 270–360 °C (70–75%), which approximate to the weight percentage of saturated hydrocarbons formed by the elements in the molecules. Therefore, we speculate that the major weight loss corresponds to the decomposition of the molecules with residue of carbon. Similar thermal stability observed for different generations of IL-Br-Gn (n = 0–3) indicates little effect of the number of imidazolium groups on the thermal stability of the dendritic ionic liquids. A small weight loss below 100 °C can be ascribed to the trace amount of water within IL-Br-Gn (n = 0–3), and the water contents were estimated to be 1.1, 1.6, 1.9, and 2.0 wt% for generations 0, 1, 2, and 3, respectively. DSC analysis demonstrates that all four generations of IL-Br-Gn show similar glass transition temperatures in the range of approximately −5–0 °C. Evidently, peripheral functionalization with imidazolium groups decreases the value of T_g greatly in comparison with the corresponding acetylene-terminated dendrimers.[17] Generally, it is accepted that the absence of polar groups or ion pairs will minimize intermolecular interactions, which will thus lower T_g. In our DILs, the flexible poly(aryl ether) dendritic backbone tends to form a globular shape because of electrostatic repulsion of the peripheral imidazolium cation groups, which shields

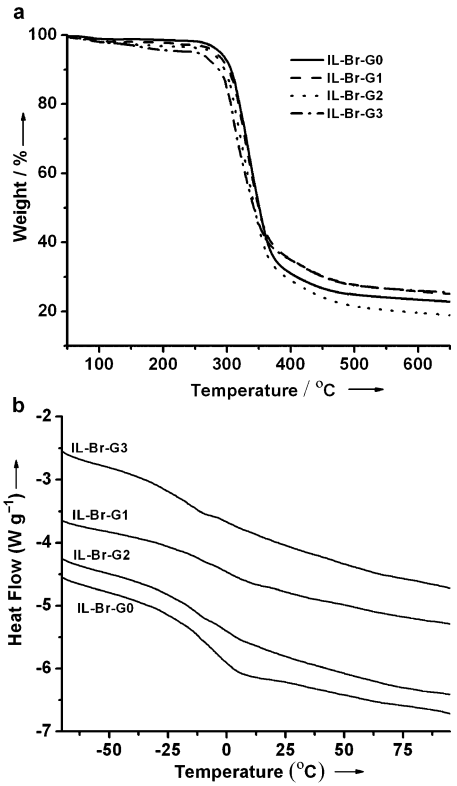
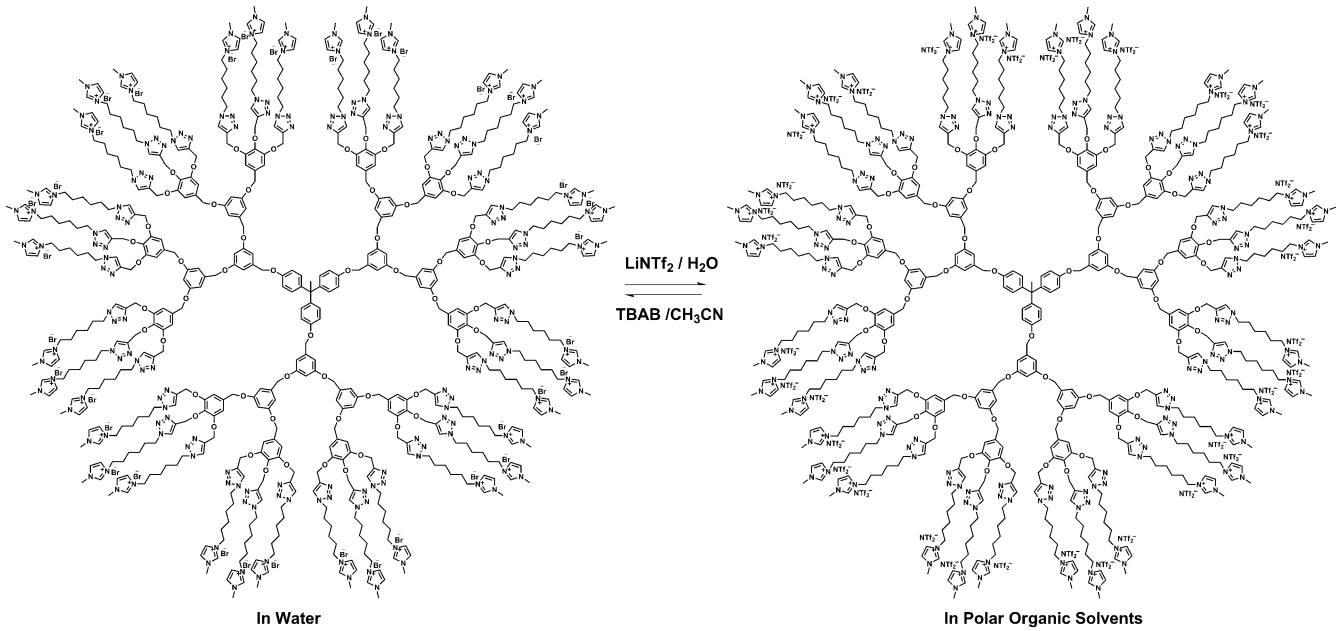


Figure 1. a) TGA and b) DSC curves of the dendritic ionic liquids. Heating rate: 10 °C min^{-1}, under a nitrogen atmosphere.

the coulombic interactions among the dendritic molecules and, consequently, decreases T_g. Additionally, the alkyl linkage between the dendritic backbone and the imidazolium groups may facilitate the motion of the dendritic building blocks at relatively lower temperatures.

The solubility of imidazolium-containing materials can be easily modulated by exchanging the corresponding counterions.[18] The introduction of imidazolium cations to the periphery of the dendritic structures should also result in phase-transferable DILs. The phase-transfer process of DILs was achieved through sequential anion exchanges (generation two as a representative example is shown in Scheme 3). Two molar equivalents of lithium bis(trifluoromethylsulfonyl)amide ($LiNTf_2$) based on the terminal groups of DIL was dissolved in water (≈ 50 mg mL^{-1}), and the solution was added to an aqueous solution of IL-Br-G2 dropwise. A white precipitate formed immediately owing to substitution of the hydrophilic anion (Br^-) by the hydrophobic anion (NTf_2^-) within the DIL. The resulting hydrophobic IL-NTf_2-G2 was isolated and readily redissolved in polar aprotic solvents such as acetonitrile (MeCN), dimethylformamide (DMF), tetrahydrofuran (THF), and *N*-methylpyrrolidone (NMP). Furthermore, IL-NTf_2-G2 dissolved in organic solvents was transferred to the aqueous phase in a similar way by the addition of appropriate salts containing hydrophilic anions such as tetrabutylammonium bromide (TBAB). Thereby, reversible phase transfer of second-generation DILs between the aqueous and organic phases was accomplished by simple anion-exchange treatments. The same reversible phase-transfer phenomenon was observed for other generations of DILs.

The reversible phase transfer of DILs caused by anion exchange was further confirmed by validation of the structures of the hydrophobic IL-NTf_2-G*n* ($n = 0$–3). IL-NTf_2-G*n* ($n =$ 0–3) were full characterized by NMR and IR spectroscopy and MALDI-TOF or ESI mass spectrometry (Supporting Information). The ^{1}H NMR, ^{13}C NMR, and ESI mass spectra of IL-NTf_2-G2 in CD_3CN are shown in Figure 2 as an example to illustrate the anion exchange of the DILs. The



Scheme 3. Phase-transfer process for a second generation DIL between the aqueous and organic phases by anion exchange.

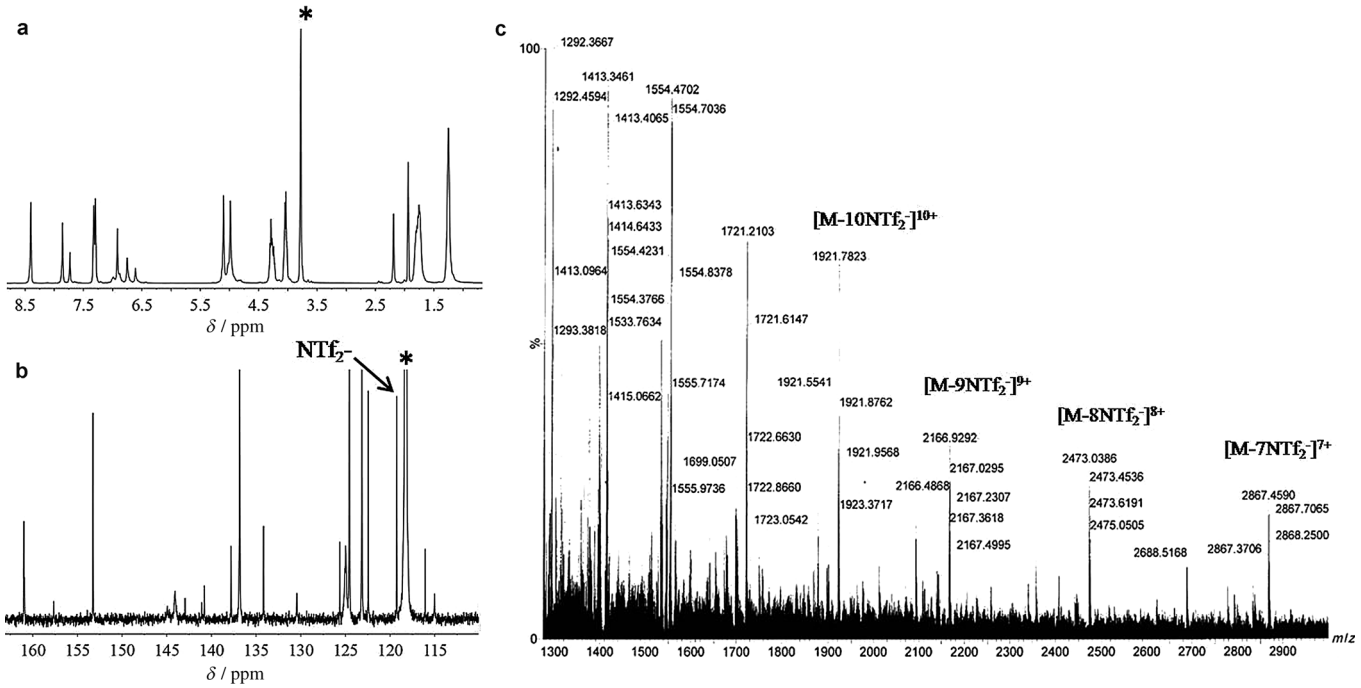


Figure 2. NMR and mass spectra of IL-NTf_2-G2. a) ^{1}H NMR and b) ^{13}C NMR spectra in CD_3CN; c) ESI-TOF mass spectrum.

^{1}H NMR spectrum gave more specific information than that of IL-Br-G2 in D_2O; it exhibits clearly the structure with a singlet at $\delta = 8.40$ ppm and a doublet at $\delta = 7.32$ ppm for the imidazolium protons (Figure 2a). Compared with the ^{13}C NMR spectrum of IL-Br-G2, a singlet at $\delta = 119.3$ ppm can be clearly observed in the spectrum of IL-NTf_2-G2 (Figure 2b), which is assigned to the carbon atom of NTf_2^- according to the literature.[19] Multicharged ion peaks of IL-NTf_2-G2 are observed at $m/z = 2867.5$, 2473.0, 2166.9, and 1921.8 for $[M-7NTf_2^-]^{7+}$, $[M-8NTf_2^-]^{8+}$, $[M-9NTf_2^-]^{9+}$, and $[M-10NTf_2^-]^{10+}$, respectively, in its ESI-TOF mass spectrum (Figure 2c). Similar to IL-Br-G3, the molecular ion peak of IL-NTf_2-G3 was not observed in its MALDI-TOF or ESI-TOF mass spectrum as a result of equipment limitations for high molecular weights. All the characterizations unambiguously confirm the formation of IL-NTf_2-Gn ($n = 0$–3); this indicates that anion exchange is the cause of the reversible phase transfer of DILs. Notably, the values of T_g for IL-NTf_2-Gn are almost the same as those of IL-Br-Gn, and thus, the anions have little effect on the thermal properties of the DILs (Figure S39, Supporting Information).

Transporters of small organic molecules play a crucial role in biological processes, drug delivery, and catalysis. Meijer's early work indicated that dendrimers could be used as a box to encapsulate and release different dyes stepwise.[20] The novel DILs, IL-Br-Gn ($n = 0$–3), which contain an inner hydrophobic poly(aryl ether) branch unit and a hydrophilic outer imidazolium shell, may have the capability to serve as effective transporters of small organic molecules. Prior to detecting the capability of DILs as transporters, understanding the encapsulation ability of DILs is essential. Nile Red was chosen as a probe to detect the interior of IL-Br-Gn ($n = 0$–3). The UV/Vis absorption spectra of Nile Red in water and aqueous solutions of IL-Br-Gn were measured (Figure S40). The solubility of Nile Red is very low in water and is evidently enhanced in the presence of IL-Br-Gn ($n =$ 0–3). According to the absorption data, the solubility of Nile Red is approximately 1.7, 17, 23, and 73 times higher for generations 0, 1, 2, and 3 DILs, respectively. The average numbers of Nile Red molecules encapsulated within each IL-Br-Gn molecule were estimated to be 0.03, 0.3, 0.4, and 1.4 for generations 0, 1, 2, and 3, respectively; this is consistent with other water-soluble poly(aryl ether) dendrimers.[13a,21] These results indicate that IL-Br-Gn are capable of encapsulating hydrophobic molecules, and the encapsulation ability increases with the generation. There is a steep increase in the encapsulation ability of the third-generation DIL relative to that of the second-generation DIL. Therefore, we infer that IL-Br-G3 has better transporting ability.

The ability of IL-Br-G3 to serve as a transporter was further estimated by using Nile Red as a model of hydrophobic substance. A IL-Br-G3/water mixture (33 wt%) was used as the phase-transfer agent for Nile Red because of the high viscosity of IL-Br-G3 at room temperature. The process for transporting Nile Red from the hexane organic phase into the aqueous phase is shown in Figure 3. A n-hexane solution of Nile Red was added to the IL-Br-G3/water mixture as a top, yellow organic phase (Figure 3a). After shaking, the upper organic layer was almost colorless (Figure 3b); this indicated that Nile Red was transferred completely from the n-hexane phase to the aqueous phase (IL-Br-G3/water mixture) immediately. Back transportation of Nile Red from the aqueous phase to another organic phase was performed

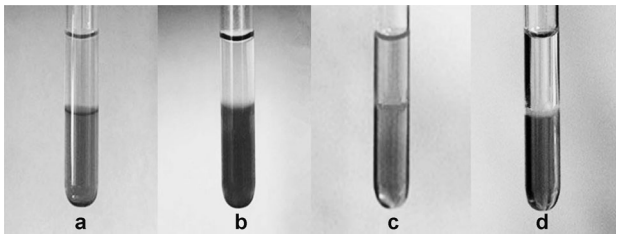


Figure 3. Photograph of transporting Nile Red between different phases: a) before shaking (the upper layer: Nile Red/hexane solution, bottom layer: DILs/H_2O mixture); b) after shaking; c) back transport to EtOAc (the upper layer: Nile Red/EtOAc solution, bottom layer: DILs/H_2O mixture); d) the second time for back transport with EtOAc. The concentrations of Nile Red and IL-Br-G3 were 1.0×10^{-4} M and 33 wt%, respectively.

by adding ethyl acetate (same volume of *n*-hexane) to the IL-Br-G3/water mixture encapsulating Nile Red. Nile Red was completely back transferred to the ethyl acetate organic phase after shaking (Figure 3c), which was validated by the almost colorless organic layer of the second back-transporting experiment (Figure 3d). The phase transfer of Nile Red from the organic phase to the aqueous phase and then to another organic phase in the presence of IL-Br-G3 indicates that IL-Br-G3 is an effective phase transporter (color photograph shown in Figure S41). More importantly, the IL-Br-G3 phase-transporting agent exhibits excellent cyclability and can be reused without any loss after the back-transporting experiment. Notably, the brown-orange color of IL-Br-G3 itself is caused by oxidation and decomposition of the N-heterocycles during heating or long-term storage,[5e] although its ^{1}H NMR spectrum exhibits no change.

Conclusions

In summary, we accomplished the synthesis of a series of dendritic ionic liquids (DILs) based on imidazolium-modified poly(aryl ether) dendrimers by a modified convergent approach and "click" chemistry. The ionic end groups attached to the periphery of the dendritic structures had a major impact on the physical properties of the DILs, and high thermal resistance and low glass transition temperatures were obtained. The DILs were miscible with water at any ratio, and the reversible phase transfer of the DILs between the aqueous and organic phases was achieved by simple anion exchange between the hydrophilic anion (Br^-) and the hydrophobic anion (NTf_2^-). The DILs showed the ability to serve as transporters to transfer hydrophobic substances efficiently between the organic and aqueous phases, and they could be reused without any loss; this is in accordance with the concept of "green chemistry". This work provides a new kind of transporting materials with potential applications in substance separation, drug delivery, and biomolecule transport.

Experimental Section

General methods

All reagents were obtained from Acros, TCI, or Beijing Chemicals and were used without further purification unless otherwise noted. Tetrahydrofuran (THF) and acetone were dried with sodium and anhydrous potassium carbonate (K_2CO_3), respectively, and were distilled under a N_2 atmosphere. ^{1}H NMR (400 MHz) and ^{13}C NMR (100 MHz) spectra were obtained by using a Bruker Avance Π-400 spectrometer with tetramethylsilane as the internal standard. MS spectra were measured by using a Bruker BIFLEX III spectrometer (MALDI-TOF) or a Waters LCT Premier XE spectrometer (ESI-TOF). Absorption spectra were run with a Shimadzu UV-1601PC spectrometer. Chromatographic purifications were performed by column chromatography on silica gel (200–300 mesh). IR spectra were measured as KBr pellets by using a Varian Excalibur 3100 spectrometer. The glass transition temperature (T_g) was measured with a TA Instruments Q2000 modulated differential scanning calorimeter (DSC) at a heat/cool rate of 10 °C min^{-1} under a N_2 atmosphere for heat/cool/heat cycles. TGA was performed on a TA Instruments Q600 at a heating rate of 10 °C min^{-1} under a N_2 atmosphere.

Syntheses

3: Potassium carbonate (37.5 g, 271.5 mmol) and 18-crown-6 (0.05 g, 0.2 mmol) were added to a solution of methyl gallate (**1**; 10 g, 54.3 mmol) and propargyl bromide (**2**; 28.4 g, 238.9 mmol) in acetone (60 mL). The mixture was heated at reflux under an atmosphere of nitrogen for 24 h. The mixture was allowed to cool and was then evaporated to dryness under reduced pressure. The residue was partitioned between H_2O and CH_2Cl_2, and the aqueous layer was extracted with CH_2Cl_2 (3×50 mL). The combined organic layer was then dried and evaporated to dryness. The crude product was purified by recrystallization (methanol) to give **3** as a white solid (13.1 g, 81%). M.p. 84–85 °C; ^{1}H NMR (400 MHz, $CDCl_3$): $\delta=7.47$ (s, 2H, Ar), 4.82 (d, $J=2.4$ Hz, 2H, *p*-CH_2), 4.80 (d, $J=2.4$ Hz, 4H, *m*-CH_2), 3.91 (s, 3H, CH_3), 2.53 (t, $J=2.4$ Hz, 2H, *m*-C≡CH), 2.45 ppm (t, $J=2.4$ Hz, 1H, *p*-C≡CH).

4: Lithium aluminum hydride (4.1 g, 107.3 mmol) was added to anhydrous THF (250 mL) in small portions, and a solution of **3** (12.8 g, 42.9 mmol) in anhydrous THF (50 mL) was added dropwise at 0 °C. The mixture was then stirred at ambient temperature for 3 h. Subsequently, the reaction was quenched with an excess amount of H_2O (200 mL) and was extracted with CH_2Cl_2 (3×100 mL). The combined organic layer was dried with anhydrous $MgSO_4$. After removal of the solvent under reduced pressure, the residue was purified by recrystallization (methanol) to produce a white solid (10.9 g, 94.0%). M.p. 95–97 °C; ^{1}H NMR (400 MHz, $CDCl_3$): $\delta=6.79$ (s, 2H, Ar), 4.77 (d, $J=2.4$ Hz, 4H, *m*-CH_2), 4.73 (d, $J=2.4$ Hz, 2H, *p*-CH_2), 4.66 (s, 2H, $ArCH_2O$), 2.51 (t, $J=2.4$ Hz, 2H, *m*-C≡CH), 2.45 ppm (t, $J=2.4$ Hz, 1H, *p*-C≡CH).

General procedure for the bromination

Triphenylphosphine (1.5 equiv.) was added to a mixture of dendritic benzyl alcohol (1.00 equiv.) and carbon tetrabromide (1.5 equiv.) in a minimum amount of dry THF required to dissolve the above reagents. The mixture was stirred under an atmosphere of nitrogen for 15 min. For the second and third generations, larger excess amounts of CBr and PPh_3 were required to force the reaction to completion. The reaction was quenched with H_2O, and the mixture was extracted with CH_2Cl_2 ($3\times$); the combined extract was dried and evaporated to dryness. The residue was purified by column chromatography on silica gel to afford the desired product.

General procedure for the synthesis of dendritic benzyl alcohols

A mixture of the appropriate dendritic benzyl bromide (2.1 equiv.), 3,5-dihydroxybenzyl alcohol (**6**, 1.0 equiv.), dry potassium carbonate (2.50 equiv.), and 18-crown-6 (0.2 equiv.) in dry acetone was heated at reflux and was stirred under an atmosphere of nitrogen for 24 h. The mixture was allowed to cool and was evaporated to dryness under reduced pressure. The residue was partitioned between H_2O and CH_2Cl_2. The combined organic layer was then dried and evaporated to dryness.

The residue was purified by column chromatography on silica gel to afford the desired product.

A-G0-Br (**5**): Prepared by the reaction of alcohol **4** (2.4 g, 8.9 mmol), carbon tetrabromide (4.4 g, 13.3 mmol), and triphenylphosphine (3.5 g, 13.3 mmol) upon stirring at ambient temperature for 10 min according to the general procedure. Purification by column chromatography on silica gel (CH_2Cl_2/petroleum ether = 1:1) afforded **5** as a white solid (2.9 g, 97%). M.p. 64–65 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 6.80 (s, 2H, *o*-Ar), 4.77 (d, J = 2.4 Hz, 4H, *m*-CH_2), 4.73 (d, J = 2.4 Hz, 2H, *p*-CH_2), 4.45 (s, 2H, CH_2Br), 2.53 (t, J = 2.4 Hz, 2H, *m*-C≡CH), 2.46 ppm (t, J = 2.4 Hz, 1H, *p*-C≡CH).

A-G1-OH (**7**): Prepared from 3,5-dihydroxybenzyl alcohol (**6**) and bromide **5** according to the general procedure. Purification by column chromatography on silica gel (CH_2Cl_2/EtOAc = 20:1) afforded **7** as a white solid (91%). M.p. 104–106 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 6.83 (s, 4H, *o*-Ar), 6.62 (s, 2H, *o*-Ar), 6.53 (s, 1H, Ar), 4.98 (s, 4H, $ArCH_2O$), 4.76 (d, J = 2.1 Hz, 8H, *m*-CH_2C≡C), 4.73 (d, J = 2.3 Hz, 4H, *p*-CH_2C≡C), 4.63 (s, 2H, CH_2OH), 2.49 (s, 4H, *m*-C≡CH), 2.46 ppm (s, 2H, *p*-C≡CH).

A-G1-Br (**8**): Prepared from benzyl alcohol **7** according to the general procedure for bromination. Purification by column chromatography (CH_2Cl_2) gave bromide **8** as a white solid (82%). M.p. 115–116 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 6.83 (s, 4H, *o*-Ar), 6.64 (d, J = 2.2 Hz, 2H, *o*-Ar), 6.52 (s, 1H, *p*-Ar), 4.98 (s, 4H, $ArCH_2O$), 4.75 (s, 8H, *m*-CH_2C≡C), 4.73 (s, 4H, *p*-CH_2C≡C), 4.41 (s, 2H, CH_2Br), 2.49 (s, 4H, *m*-C≡CH), 2.46 (s, 2H, *p*-C≡CH).

A-G2-OH (**9**): Prepared from 3,5-dihydroxybenzyl alcohol (**6**) and bromide **8** (2.1 equiv.) according to the general procedure for alkylation with potassium carbonate and 18-crown-6 in acetone. The crude product was purified by column chromatography (CH_2Cl_2/EtOAc = 20:1) to give alcohol **9** as a colorless glass (90%). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 6.82 (s, 8H, *o*-Ar), 6.65 (d, J = 2.0 Hz, 4H, *o*-Ar), 6.59–6.52 (m, 4H, *o*-Ar and *p*-Ar), 6.46 (s, 1H, *p*-Ar), 4.98 (m, 12H, $ArCH_2O$), 4.74 (m, 24H, CH_2C≡C), 4.62 (s, 2H, CH_2OH), 2.47 ppm (m, 12H, C≡CH); MS (MALDI-TOF): m/z: calcd for $C_{85}H_{68}O_{19}Na$: 1415.4 $[M+Na^+]^+$; found: 1415.5.

A-G2-Br (**10**): Prepared from alcohol **9** according to the general procedure with CBr_4 (2.0 equiv.) and PPh_3 in anhydrous THF. The crude product was purified by column chromatography (CH_2Cl_2/EtOAc = 100:0 to 20:1) to give bromide **10** as a white solid (78%). M.p. 93–95 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 6.84 (s, 8H, *o*-Ar), 6.68 (d, J = 1.5 Hz, 4H, *o*-Ar), 6.64 (d, J = 1.6 Hz, 2H, *p*-Ar), 6.57 (s, 2H, *o*-Ar), 6.52 (s, 1H, *p*-Ar), 4.99 (m, 12H, $ArCH_2O$), 4.76 (m, 24H, CH_2C≡C), 4.43 (s, 2H, CH_2Br), 2.49 ppm (m, 12H, C≡CH).

A-G3-OH (**11**): Prepared from 3,5-dihydroxybenzyl alcohol (**6**) and bromide **10** (2.1 equiv.) according to the general procedure for alkylation with potassium carbonate and 18-crown-6 in acetone. The crude product was purified by column chromatography (CH_2Cl_2/EtOAc = 20:1) to give alcohol **11** as a colorless glass (69%). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 6.81 (s, 16H, *o*-Ar), 6.76 (s, 1H, *p*-Ar), 6.64–6.66 (m, 12H, *o*-Ar), 6.58 (s, 2H, *o*-Ar), 6.52–6.53 (m, 6H, *p*-Ar), 4.96 (s, 28H, $ArCH_2O$), 4.73 (m, 48H, CH_2C≡C), 4.58 (s, 2H, CH_2OH), 2.46 ppm (m, 24H, C≡CH); MS (MALDI-TOF): m/z: calcd for $C_{177}H_{140}O_{39}Na$: 2911.9 $[M+Na^+]^+$; found: 2917.2.

A-G3-Br (**12**): Prepared from alcohol **11** according to the general procedure with CBr_4 (2.5 equiv.) and PPh_3 in anhydrous THF. The crude product was purified by column chromatography (CH_2Cl_2/EtOAc = 100:0 to 20:1) to give bromide **12** as a colorless glass (71%). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 6.81 (s, 16H, *o*-Ar), 6.76 (s, 1H, *p*-Ar), 6.64–6.66 (m, 12H, *o*-Ar), 6.62 (d, J = 2.0 Hz, 2H, *o*-Ar), 6.54 (s, 6H, *p*-Ar), 4.96 (s, 28H, $ArCH_2O$), 4.73 (m, 48H, CH_2C≡C), 4.38 (s, 2H, CH_2Br), 2.46 ppm (m, 24H, C≡CH).

General procedure for the synthesis of acetylene-terminated tris(phenolic)-cored dendrimers

A mixture of the appropriate dendritic benzyl bromide (3.3 equiv.), 1,1,1-tris(4-hydroxyphenyl)ethane (**13**, 1.0 equiv.), anhydrous potassium carbonate (5.0 equiv.), and 18-crown-6 (0.3 equiv.) in dry acetone was heated at reflux and stirred under an atmosphere of nitrogen for 48 h. The mixture was allowed to cool and was evaporated to dryness under reduced pressure. The residue was partitioned between H_2O and CH_2Cl_2. The combined organic layer was then dried and evaporated to dryness. The residue was purified by column chromatography on silica gel to afford the desired product.

[A-G0]$_3$-C (**14**): Prepared from 1,1,1-tris(4-hydroxyphenyl)ethane (**13**) and propargyl bromide **5** (3.3 equiv.) according to the general procedure for alkylation with potassium carbonate and 18-crown-6 in acetone. The crude product was purified by column chromatography (CH_2Cl_2/EtOAc = 100:0 to 20:1) to give **14** as a pale yellow glass (84%). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.01–6.99 (d, J = 8.8 Hz, 6H, *o*-Ph), 6.87–6.85 (d, J = 8.9 Hz, 6H, *m*-Ph), 6.83 (s, 6H, *o*-Ar), 4.98 (s, 6H, $ArCH_2O$), 4.76 (d, J = 2.4 Hz, 12H, *m*-CH_2C≡C), 4.73 (d, J = 2.4 Hz, 6H, *p*-CH_2C≡C), 2.47–2.46 (m, 9H, C≡CH), 2.11 ppm (s, 3H, CH_3C); MS (MALDI-TOF): m/z: calcd for $C_{68}H_{54}O_{12}Na$: 1085.4 $[M+Na^+]^+$; found: 1085.5.

[A-G1]$_3$-C (**15**): Prepared from 1,1,1-tris(4-hydroxyphenyl)ethane (**13**) and bromide **8** (3.3 equiv.) according to the general procedure. The crude product was purified by column chromatography (CH_2Cl_2/EtOAc = 100:0 to 20:1) to give **15** as a colorless glass (80%). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.01–6.99 (d, J = 8.8 Hz, 6H, *o*-Ph), 6.86 (s, 6H, *m*-Ph), 6.83 (s, 12H, *o*-Ar), 6.68 (d, J = 1.9 Hz, 6H, *o*-Ar), 6.55 (s, 3H, *p*-Ar), 4.98 (s, 12H, $ArCH_2O$), 4.96 (s, 6H, $ArCH_2O$), 4.76–4.73 (m, 36H, CH_2C≡C), 2.48–2.45 (m, 18H, C≡CH), 2.11 ppm (s, 3H, CH_3C); MS (MALDI-TOF): m/z: calcd for $C_{137}H_{108}O_{27}Na$: 2207.7 $[M+Na^+]^+$; found: 2208.1.

[A-G2]$_3$-C (**16**): Prepared from 1,1,1-tris(4-hydroxyphenyl)ethane (**13**) and bromide **10** (3.3 equiv.) according to the general procedure for alkylation with potassium carbonate and 18-crown-6 in acetone. The crude product was purified by column chromatography (CH_2Cl_2/EtOAc = 20:1) to give **16** as a colorless glass (77%). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.00–6.98 (d, J = 8.0 Hz, 6H, *o*-Ph), 6.86 (d, J = 8.6 Hz, 6H, *m*-Ph), 6.84–6.81 (m, 24H, *o*-Ar), 6.66 (s, 18H, *o*-Ar and *p*-Ar), 6.54–6.52 (d, J = 6.0 Hz, 9H, *o*-Ar and *p*-Ar), 4.98–4.94 (m, 42H, $ArCH_2O$), 4.76–4.71 (m, 72H, CH_2C≡C), 2.46–2.44 (d, J = 8.2 Hz, 36H, C≡CH), 2.09 ppm (s, 3H, CH_3C); MS (MALDI-TOF): m/z: calcd for $C_{275}H_{216}O_{57}Na$: 4452.4 $[M+Na^+]^+$; found: 4448.0.

[A-G3]$_3$-C (**17**): Prepared from 1,1,1-tris(4-hydroxyphenyl)ethane (**13**) and bromide **12** (3.2 equiv.) according to the general procedure. The crude product was purified by column chromatography (CH_2Cl_2/EtOAc = 10:1) to give **17** as a colorless glass (57%). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 6.98–6.96 (d, J = 8.7 Hz, 6H, *o*-Ph), 6.83–6.73 (m, 54H, *m*-Ph and *o*-Ar), 6.66–6.58 (m, 42H, *o*-Ar), 6.53–6.51 (m, 21H, *p*-Ar), 4.96–4.92 (m, 90H, $ArCH_2O$), 4.73–4.70 (m, 144H, CH_2C≡C), 2.45–2.43 (m, 72H, C≡CH), 2.17 ppm (s, 3H, CH_3C); MS (MALDI-TOF): m/z: calcd for $C_{551}H_{432}O_{117}Na$: 8941.8 $[M+Na^+]^+$; found: 8940.1.

1-Azido-6-bromohexane (**20**): A solution of 1,6-dibromohexane (**18**; 18.8 g, 76.9 mmol) and sodium azide (**19**; 5 g, 76.9 mmol) in DMF (20 mL) with H_2O (5 mL) was stirred at 60 °C for 24 h. The aqueous phase was extracted with CH_2Cl_2 (3×50 mL), dried with $MgSO_4$, and evaporated to dryness to give **20** as a pale yellow oil (9.6 g, 61%). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 3.41 (t, J = 6.7 Hz, 2H, CH_2Br), 3.28 (t, J = 6.8 Hz, 2H, CH_2N_3), 1.84–1.91 (m, 2H, CH_2CBr), 1.48–1.58 (m, 2H, CH_2CN_3), 1.37–1.41 ppm [m, 4H $C(CH_2)_2C$].

[N-C-Min]$^+$Br$^-$ (**22**): A solution of 1-azido-6-bromohexane (**20**; 4.6 g, 22.3 mmol) and 1-methylimidazole (**21**; 2.2 g, 26.8 mmol) in toluene (10 mL) was stirred at 60 °C for 24 h. The mixture was partitioned between toluene and oil. The oil was extracted with EtOAc (5×5 mL) and evaporated to dryness to give **22** as a pale yellow viscous oil (6.0 g, 94%). ^{1}H NMR (400 MHz, D_2O): δ = 8.71 (s, 1H, NCHN in imidazole), 7.47 (s, 1H, imidazole), 7.43 (s, 1H, imidazole), 4.20 (t, J = 7.1 Hz, 2H, NCH_2), 3.89 (s, 3H, NCH_3), 3.31 (t, J = 6.8 Hz, 2H, N_3CH_2), 1.94–1.83 (m, 2H, CH_2 in hexyl), 1.64–1.54 (m, 2H, CH_2 in hexyl), 1.46–1.27 ppm (m, 4H, CH_2 in hexyl).

General procedure for the click reaction

A solution of sodium ascorbate (2.0 equiv.) and $CuSO_4$·H_2O (2.0 equiv.) in H_2O was added to a mixture of the appropriate acetylene-terminated tris(phenolic)-cored dendrimer (1.0 equiv.) and coupling molecule **22** (

≈18–144 equiv.) in H_2O/THF (*v/v* = 1:1). The mixture was stirred at ambient temperature for 48 h. After removal of the organic solvents, the crude product was further purified by repeated anion exchange to afford the desired product.

General procedure for the anion exchange

An aqueous solution of $LiNTf_2$ (2.0 equiv. to Br^-) was added dropwise to an aqueous solution of IL-Br-G*n* (1.0 equiv., crude product). The mixture was stirred vigorously at ambient temperature for 2 h, and a white precipitate formed immediately. After filtration, the residue was washed with H_2O (3×) to afford the corresponding IL-NTf_2-G*n*. The IL-NTf_2-G*n* was redissolved in MeCN and the anion was exchanged again with tetrabutylammonium bromide (TBAB) to afford pure IL-Br-G*n*.

IL-Br-G0 (**23**): Acetylene-terminated dendrimer **14** (0.5 g, 0.47 mmol) and $[N{-}C{-}Min]^+Br^-$ (**22**; 2.4 g, 8.47 mmol) were added a H_2O/THF mixture (1:1 *v/v*, 10 mL). Then, a solution of sodium ascorbate (0.1677 g, 0.85 mmol) and $CuSO_4{\cdot}H_2O$ (0.1057 g, 0.42 mmol) in H_2O (5 mL) was added. The mixture was stirred at ambient temperature for 48 h. After evaporation of the organic solvent, the crude product was purified by the general procedure for repeated anion exchange to give **23** as a pale yellow viscous gum (1.4721 g, 86 %). ^{1}H NMR (400 MHz, D_2O): δ = 8.70 (s, 9H, NCHN in imidazole), 7.95 (s, 6H, *m*-NCHC in triazole), 7.75 (s, 3H, *p*-NCHC in triazole), 7.41 (s, 18H, imidazole), 6.75 (br, 12H, *o*-Ar and *m*-Ar), 6.58 (br, 6H, *o*-Ph), 4.92 (br, 24H, $ArCH_2O$ and triazole-CH_2), 4.29–4.21 (br, 18H, imidazole-CH_2), 4.11–4.07 (m, 18H, triazole-CH_2), 3.86 (s, 27H, NCH_3), 1.72–1.18 ppm (br, 72H, CCH_3 and CH_2 in hexyl); ^{13}C NMR (100 MHz, D_2O): δ = 25.5, 29.8, 36.4, 49.9, 62.7, 70.2, 107.5, 122.7, 124.2, 125.7, 134.2, 136.2, 136.5, 142.6, 152.4, 156.9 ppm; IR (KBr pellet): $\tilde{\nu}_{max}$ = 3430, 3065, 2940, 2860, 1605, 1565, 1500, 1455, 1360, 840 cm^{-1}; MS (MALDI-TOF): *m/z*: calcd for $C_{158}H_{208}N_{45}O_{12}$: 2927.7 $[M-9Br^--8H^+]^+$; found: 2928.6.

IL-Br-G1 (**24**): Prepared from acetylene-terminated dendrimer **15** and $[N{-}C{-}Min]^+Br^-$ (**22**, 36 equiv.) according to the general procedure for the click reaction. Purification by the general procedure for anion exchange gave **24** as a viscous gum (85 %). ^{1}H NMR (400 MHz, D_2O): δ = 8.72 (s, 18H, NCHN in imidazole), 8.00 (s, 12H, *m*-NCHC in triazole), 7.76 (s, 6H, *p*-NCHC in triazole), 7.41 (s, 36H, imidazole), 6.77 (br, 12H, *o*-Ar and *m*-Ar), 6.41–6.55 (br, 21H, PhH), 4.93 (br, 44H, $ArCH_2O$ and triazole-CH_2), 4.21–4.27 (m, 36H, imidazole-CH_2), 4.08 (s, 36H, triazole-CH_2), 3.85 (s, 54H, NCH_3), 1.71 (s, 75H, CCH_3 and CH_2 in hexyl), 1.17 ppm (s, 72H, CH_2 in hexyl); ^{13}C NMR (100 MHz, D_2O): δ = 25.5, 29.8, 36.4, 49.8, 50.8, 58.8, 62.7, 70.1, 107.6, 122.7, 124.1, 125.5, 134.0, 136.2, 136.4, 143.4, 152.4, 160.3 ppm; IR (KBr pellet): $\tilde{\nu}_{max}$ = 3440, 3075, 2935, 2860, 1635, 1560, 1510, 1450, 1360, 1165, 835 cm^{-1}; MS (MALDI-TOF): *m/z*: calcd for $C_{317}H_{415}N_{90}O_{27}$: 5914.4 $[M-18Br^--17H^+]^+$; found: 5924.8.

IL-Br-G2 (**25**): Prepared from acetylene-terminated dendrimer **16** and $[N\text{-}C\text{-}Min]^+Br^-$ (**22**, 72 equiv.) according to the general procedure for the click reaction. Purification by the general procedure for anion exchange gave **25** as a viscous gum (70.4 %). ^{1}H NMR (400 MHz, D_2O): δ = 8.72 (s, 36H, NCHN in imidazole), 7.98 (s, 24H, *m*-NCHC in triazole), 7.76 (s, 12H, *p*-NCHC in triazole), 7.41 (s, 72H, imidazole), 6.80–6.42 (m, 63H, ArH and PhH), 4.92 (br, 114H, $ArCH_2O$ and triazole-CH_2), 4.27–4.21 (m, 72H, imidazole-CH_2), 4.08 (s, 72H, triazole-CH_2), 3.85 (s, 108H, NCH_3), 1.71 (br, 144H, CCH_3 and CH_2 in hexyl), 1.17 ppm (br, 144H, CH_2 in hexyl); ^{13}C NMR(100 MHz, D_2O): δ = 25.5, 25.7, 29.8, 30.0, 36.4, 49.8, 50.8, 62.6, 70.2, 107.6, 122.7, 124.1, 125.5, 134.1, 136.4, 143.5, 152.5, 160.2 ppm; IR (KBr pellet): $\tilde{\nu}_{max}$ = 3435, 3075, 2940, 2860, 1630, 1560, 1510, 1460, 1365, 1170, 835 cm^{-1}; MS (ESI-TOF): *m/z*: calcd for $C_{635}H_{864}Br_{19}N_{180}O_{57}$: 789.6 $[M-17Br^-]^{17+}$; found 792.5.

IL-Br-G3 (**26**): Prepared from acetylene-terminated dendrimer **17** and $[N\text{-}C\text{-}Min]^+Br^-$ (**22**, 144 equiv.) according to the general procedure for the click reaction. Purification by the general procedure for anion exchange gave **26** as a viscous gum (68 %). ^{1}H NMR (400 MHz, D_2O): δ = 8.71 (s, 72H, NCHN in imidazole), 7.98 (br, 48H, *m*-NCHC in triazole), 7.73 (br, 24H, *p*-NCHC in triazole), 7.38 (s, 144H, imidazole), 6.76 (m, 6H, *o*-Ar; 6H, *m*-Ar; 90H, *o*-Ph; 21H, *p*-Ph), 4.90 (br, 90H, $ArCH_2O$; 144H, triazole-CH_2), 4.20–4.06 (m, 144H, imidazole-CH_2; 144H, triazole-CH_2), 3.83–3.82 (d, *J* = 4.8 Hz, 216H, NCH_3), 1.66 (br, 288H, CH_2 in hexyl), 1.13 ppm (br, 288H, CH_2 in hexyl); ^{13}C NMR (100 MHz, D_2O): δ = 25.5, 25.7, 29.8, 30.0, 36.5, 49.8, 50.7, 58.8, 63.2, 70.2, 107.6, 122.7, 124.1, 125.5, 134.2, 136.2, 136.4, 136.7, 143.5, 144.4, 152.4, 160.3 ppm; IR (KBr pellet): $\tilde{\nu}_{max}$ = 3435, 3080, 2935, 2960, 1635, 1560, 1510, 1450, 1360, 1165, 835 cm^{-1}; MS (MALDI-TOF): molecular ion peak could not be obtained.

IL-NTf_2-G0 (**27**): Prepared from dendrimer IL-Br-G0 (**23**) according to the general procedure for anion exchange to give **27** as a viscous gum (89 %). ^{1}H NMR (400 MHz, CD_3CN): δ = 8.39 (s, 9H, NCHN in imidazole), 7.88 (s, 6H, *m*-NCHC in triazole), 7.77 (s, 3H, *p*-NCHC in triazole), 7.34–7.31 (d, *J* = 9.5 Hz, 18H, NCHCHN in imidazole), 7.06–7.04 (d, *J* = 8.7 Hz, 6H, *o*-Ar), 6.93 (s, 6H, *o*-Ph; 6H, *m*-Ar), 5.14 (s, 12H, *m*-triazole-CH_2), 5.02 (s, 6H, *p*-triazole-CH_2), 4.98 (s, 6H, $ArCH_2O$), 4.36–4.27 (m, 18H, imidazole-CH_2), 4.08–4.04 (t, *J* = 7.3 Hz, 18H, triazole-CH_2), 3.80 (s, 27H, NCH_3), 2.09 (s, 3H, CCH_3), 1.88–1.74 (m, 36H, CH_2 in hexyl), 1.29 ppm (s, 36H, CH_2 in hexyl); ^{13}C NMR (100 MHz, CD_3CN): δ = 26.1, 30.4, 37.0, 50.6, 63.9, 66.9, 70.9, 108.9, 119.6 (CF_3SO), 122.7, 123.4, 124.8, 130.7, 134.7, 137.0, 138.3, 143.3, 153.5, 158.1 ppm; IR (KBr pellet): $\tilde{\nu}_{max}$ = 3155, 2945, 1629, 1605, 1352, 1193, 1055 cm^{-1}; MS (MALDI-TOF): *m/z*: calcd for $C_{174}H_{216}F_{48}N_{53}O_{44}S_{16}$: 5175.1 $[M-NTf_2^-]^+$; found: 5176.9.

IL-NTf_2-G1 (**28**): Prepared from dendrimer IL-Br-G1 (**24**) according to the general procedure for anion exchange to give **28** as a viscous gum (87 %). ^{1}H NMR (400 MHz, CD_3CN): δ = 8.39 (s, 18H, NCHN in imidazole), 7.87 (s, 12H, *m*-NCHC in triazole), 7.75 (s, 6H, *p*-NCHC in triazole), 7.33–7.30 (d, *J* = 9.5 Hz, 36H, NCHCHN in imidazole), 7.03–7.01 (d, *J* = 8.0 Hz, 6H, *o*-Ar), 6.93–6.90 (d, *J* = 13.6 Hz, 6H, *m*-Ar; 12H, *o*-Ph), 6.76 (s, 6H, *o*-Ph), 6.62 (s, 3H, *p*-Ph), 5.13 (s, 18H, $ArCH_2O$), 5.01 (s, 36H, triazole-CH_2), 4.34–4.25 (m, 36H, imidazole-CH_2), 4.08–4.03 (m, 36H, triazole-CH_2), 3.79 (s, 54H, NCH_3), 2.05 (s, 3H, CCH_3), 1.85–1.76 (m, 72H, CH_2 in hexyl), 1.27 ppm (s, 72H, CH_2 in hexyl); ^{13}C NMR (100 MHz, CD_3CN): δ = 25.9, 30.2, 36.8, 50.2, 63.4, 66.5, 70.7, 108.2, 119.3 (CF_3SO), 122.4, 123.2, 124.6, 134.3, 136.8, 137.6, 143.0, 153.2, 161.0 ppm; IR (KBr pellet): $\tilde{\nu}_{max}$ = 3150, 2941, 1639, 1597, 1352, 1192, 1055 cm^{-1}; MS (MALDI-TOF): *m/z*: calcd for $C_{351}H_{432}F_{102}N_{107}O_{95}S_{34}$: 10690.1 $[M-NTf_2^-]^+$; found: 10694.6.

IL-NTf_2-G2 (**29**): Prepared from dendrimer IL-Br-G2 (**25**) according to the general procedure for anion exchange to give **29** as a viscous gum (85 %). ^{1}H NMR (400 MHz, CD_3CN): δ = 8.40 (s, 36H, NCHN in imidazole), 7.86 (s, 24H, *m*-NCHC in triazole), 7.73 (s, 12H, *p*-NCHC in triazole), 7.32–7.29 (d, *J* = 11.3 Hz, 72H, NCHCHN in imidazole), 7.01–6.96 (m, 6H, *o*-Ar), 6.92–6.88 (d, *J* = 15.6 Hz, 6H, *m*-Ar; 24H, *o*-Ph), 6.75 (s, 18H, *o*-Ph), 6.61 (s, 9H, *p*-Ph), 5.10 (s, 42H, $ArCH_2O$), 4.98 (s, 72H, triazole-CH_2), 4.30–4.23 (m, 72H, imidazole-CH_2), 4.07–4.01 (m, 72H, triazole-CH_2), 3.78 (s, 108H, NCH_3), 2.00 (s, 3H, CCH_3), 1.81–1.74 (m, 144H, CH_2 in hexyl), 1.25 ppm (s, 144H, CH_2 in hexyl); ^{13}C NMR (100 MHz, CD_3CN): δ = 25.9, 26.3, 30.2, 30.5, 36.8, 50.2, 63.5, 66.8, 70.8, 108.3, 119.3(CF_3SO), 122.4, 123.2, 124.6, 134.2, 136.8, 137.8, 144.1, 153.3, 161.0 ppm; IR (KBr pellet): $\tilde{\nu}_{max}$ = 3153, 2947, 1639, 1597, 1352, 1192, 1055 cm^{-1}; MS (ESI-TOF): *m/z*: calcd for $C_{693}H_{864}F_{174}N_{209}O_{173}S_{58}$: 2862.9 $[M-7NTf_2^-]^{7+}$; found:2867.5.

IL-NTf_2-G3 (**30**): Prepared from dendrimer IL-Br-G3 (**26**) according to the general procedure for anion exchange to give **30** as a viscous gum (81 %). ^{1}H NMR (400 MHz, CD_3CN): δ = 8.40 (s, 72H, NCHN in imidazole), 7.84 (s, 48H, *m*-NCHC in triazole), 7.71 (s, 24H, *p*-NCHC in triazole), 7.31–7.27 (d, *J* = 12.5 Hz, 144H, NCHCHN in imidazole), 6.89 (s, 6H, *o*-Ar; 48H, *o*-Ph), 6.73 (s, 6H, *m*-Ar; 18H, *o*-Ph; 21H, *p*-Ph), 6.58 (s, 24H, *o*-Ph), 5.06–4.96 (m, 90H, $ArCH_2O$; 144H, triazole-CH_2), 4.30–4.19 (m, 144H, imidazole-CH_2), 4.05–3.99 (m, 144H, triazole-CH_2), 3.78–3.76 (m, 216H, NCH_3), 2.13 (s, 3H, CCH_3), 1.73 (m, 288H, CH_2 in hexyl), 1.23 ppm (s, 288H, CH_2 in hexyl); ^{13}C NMR (100 MHz, CD_3CN): δ = 25.9, 26.3, 30.3, 30.5, 36.8, 50.3, 50.7, 63.5, 66.7, 70.8, 108.3, 119.3 (CF_3SO), 122.4, 123.1, 124.6, 134.2, 136.8, 137.8, 144.0, 153.3, 161.0 ppm; IR (KBr pellet): $\tilde{\nu}_{max}$ = 3152, 2947, 1629, 1602, 1350, 1195, 1053 cm^{-1}; MS (MALDI-TOF): molecular ion peak could not be obtained.

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