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Synthesis and Studies of Pyridoneimine-Functionalized PETIM Dendrimers

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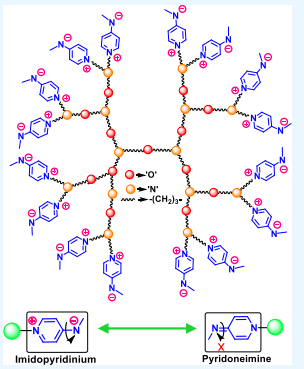
ABSTRACT: Pyridinoimine-functionalized poly(ether imine) (PETIM) dendrimers of 1−3 generations, possessing 4−16 moieties at the peripheries, are synthesized. Chloride-functionalized dendrimers are reacted with *N*-methylamino pyridine, under basic conditions, which led to functionalization of the peripheries of a dendrimer with pyridoneimine moieties. Variable-temperature ^{1}H NMR studies are performed to assess the contributing resonance forms of pyridoneimine in the dendrimers. Solvatochromism and ^{15}N NMR studies aid further the assessment of the contributing resonance forms. Comparison with derivatives that possess 1 and 2 pyridoneimines illustrates the contributing resonance forms between nonaromatic pyridoneimine and zwitter ionic aromatic imidopyridinium species.



INTRODUCTION

Fully branched, monodispersed macromolecules, namely, dendrimers, possess exo-structural features. Primary among them is the presence of multiple, uniformly distributed chain ends. The number of chain ends increases exponentially as the dendrimer generations increase. Several studies show the beneficial effects arising from the multiple chain ends.[1,2] Prominent examples of the studies are (i) the specific rotation neutrality of multiple, covalently attached chiral moieties at the peripheries of the dendrimers;[3] (ii) the formation of charge-transfer complexes in dendrimers functionalized with electron-rich moieties and their interaction with relevant acceptors;[4−6] and (iii) acceleration of the catalytic effects in metal catalysis.[7−9] Ligand clustering at the dendritic scaffolds provides an opportunity to identify the cluster effects on the ligand properties. This clustering enables to study (i) dendrimer effects in ligand−receptor interactions;[10−12] (ii) cluster effects in organometallic catalysis;[13−16] (iii) antenna effects in electron and energy transfer processes;[17−19] and (iv) macromolecular and supramolecular complexation properties.[20−23] Recent reports demonstrate (i) the convergent synthesis of hexaphenylbenzene core biphenyl-dendrimers and their surface modification with β-(1/6)-linked glucosamine as multivalent carbohydrate mimics to uncover biological activities[24] and (ii) facile synthesis of higher generation dendrimers, with dense peripheral functional surface groups, involving click and thiol-ene reactions under microwave conditions.[25] Studies of tautomerization behavior are also conducted, as demonstrated by Caminade, Majoral, Ouali and co-workers on β-diketone-functionalized phosphorus-based dendrimer and the resulting keto-enol tautomerism.[26] The efficacies of dendrimers as drug delivery nanocarriers at the interface of therapeutics and other biological applications are also well-established.[27−30] Magnetic nanodendrimers are an efficient vehicle for drug delivery. Encapsulated magnetic nanoparticles (NPs) act as a nanocarrier for drug molecules due to the presence of multiple functional groups.[31] Besides biological applications, magnetic nanodendrimers find immense utility in various organic catalysis.[32] Thus, applications of dendrimers in disparate studies illustrate the accrued benefits resulting from their highly branched structures.

We undertook a study to investigate the effect of clustering pyridoneimine moieties at the peripheries of poly(ether imine) (PETIM) dendrimers. Pyridoneimines represent an important class of compounds that possess intramolecular push-pull-type π-electron delocalizations. The delocalizations, leading to pyridoneimine and imidopyridinium resonance forms, are utilized to develop new organic materials, finding applications in nonlinear optical materials, organic light emitting diodes, fluorescence sensors, aggregation-induced emissions, solar energy conversions, and more.[33−42] Pyridoneimines also act as superbases, as a result of aromatization through electrophilic activation of the pyridyl nitrogen,[43,44] and the properties permit pyridoneimines as a base for site-selective reactions in

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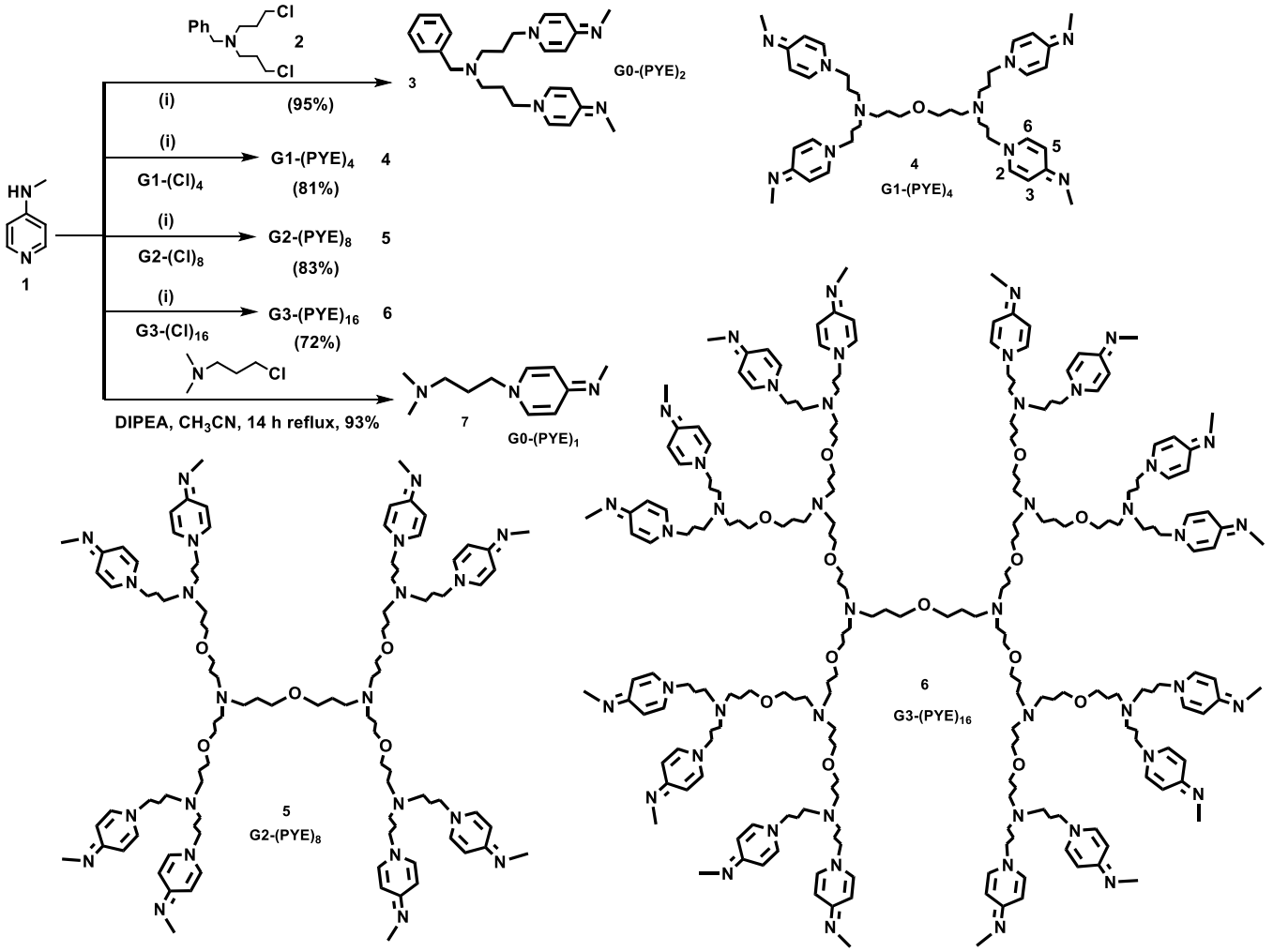
Scheme 1. Synthesis of Monomeric (7), Dimeric (3), First- (4), Second- (5), and Third (6)-Generations PYE-Functionalized Derivatives[a]



[a]Reaction condition: (i) DBU, THF, reflux, 24 h.

multifunctional compounds.[45,46] In the present study, the first-, second-, and third-generation PETIM dendrimers are functionalized with pyridoneimine moieties at their peripheries. The effects of clustering on the contributing resonance forms of pyridoneimine are studied. Details of the synthesis and studies of the clustered dendritic pyridoneimines are presented herein.

RESULTS AND DISCUSSION

Synthesis. Synthesis and molecular structures of the pyridoneimine-functionalized PETIM dendrimers **3**–**6** are presented in Scheme 1. The PETIM dendrimers are constituted with a tertiary amine as the branching juncture and an ether as a linking component that are interconnected by propylene spacers.[47−49] Zero to 3 generations of dendrimers, possessing 2, 4, 8, and 16 peripheral moieties, are chosen for functionalization with pyridoneimine, namely, *N*-[1-alkyl-4(1*H*)-pyridinylidene]methylamine (PYE). PYE-appended dendrimer 3 was prepared by mixing 1 molar equiv. of bis-chloride 2[50,51] to excess molar equivalents of 4-(*N*-methylamino)pyridine **1** and DBU in THF, at reflux for 24 h (Scheme 1).

4-(*N*-Methylamino)pyridine (**1**) is an ambident nucleophile with two nucleophilic nitrogen sites. In a neutral medium, the alkylation reaction proceeds through the azine site, in the presence of an alkyl halide. Deprotonation of the resulting iminium species, in the presence of DBU, results in the formation of a pyridoneimine derivative. On the other hand, in the presence of a strong base, such as NaH and *n*-BuLi, deprotonation occurs at the imine site to generate the corresponding anion and further alkylation leads to afford 4-(dialkylamino)pyridine derivative.[52,53]

A brown precipitate was obtained after evaporation of the solvents, which was further purified by column chromatography (neutral Al_2O_3, $CHCl_3$/MeOH, linear gradient). The PYE-functionalized **G0-(PYE)$_2$** (**3**), with two pyridoneimine moieties, was obtained in 95% yield, as a gum. A similar protocol was adopted for the synthesis of PYE-functionalized dendrimer **G1-(PYE)$_4$** (**4**), **G2-(PYE)$_8$** (**5**), and **G3-(PYE)$_{16}$** (**6**) (Scheme 1). The chloride-functionalized precursors for alkylation of **1** were prepared through chlorination of hydroxy-terminated dendrimers[48] with $SOCl_2$. The *N*-alkylation at the azine site occurred facile, and the high polarity of the resulting higher generation PYE-functionalized dendrimers **4**–**6** allowed purification of the reaction mixtures by trituration with solvents THF, Et_2O, PhMe, and hexane only. Excess reagents were removed, and evaporation of residual solvents and drying

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in vacuo afforded PYE-functionalized dendrimers **G1-(PYE)$_4$** (**4**), **G2-(PYE)$_8$** (**5**), and **G3-(PYE)$_{16}$** (**6**) (Scheme 1). Residual DBU is impervious to removal despite washing several times with THF, which was observed as minor peaks between 3 and 4 ppm in the ^{1}H NMR spectra, and between 30 and 40 ppm in the ^{13}C NMR spectra. Derivative **7** was synthesized by the reaction of **1** with 3-dimethylaminopropyl chloride, in the presence of DIPEA in MeCN under reflux for 14 h. The PYE-functionalized dendrimers are stable, yet hygroscopic when exposed to an ambient atmosphere, requiring it to be stored under an inert atmosphere. The materials are insoluble in common organic solvents, except in DMF, DMSO, MeOH, and aq. solutions. The newly synthesized compounds were characterized by ^{1}H and ^{13}C NMR spectroscopies. Characteristics of ^{1}H NMR spectra were the changes in the chemical shifts of the $-CH_2-$ moieties adjacent to the azine site upon alkylation of the chloride-functionalized dendrimer precursors. Mass spectrometry was secured for all compounds, except for the third-generation **G3-(PYE)$_{16}$** (**6**) dendrimer. Figure 1 depicts the resonance forms, namely, the nonaromatic pyridoneimine form and the aromatic imidopyridinium form.

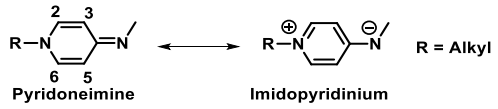

Figure 1. Resonance forms of pyridoneimine and imidopyridinium species.

In the contributing pyridoneimine form, each proton in the heterocycle appears as a distinct doublet, whereas in the contributing imidopyridinium form, the *ortho*- and *meta*-protons of the pyridinium species would appear as a set of merged protons, as a result of the bond rotation of the bond connecting the heterocycle with imido-substituent. When the bond rotations are faster than the frequency of the separation of the resonances, merging of the protons occurs. A slower rotation might, in principle, be expected to merge one set of protons, whereas a faster rotation would lead to merging of both the *ortho*- and *meta*-protons of the heterocycle. From merging of the protons, the activation energy for the rotational process might be evaluated through the Eyring equation. The ^{1}H NMR signals for the dendritic pyridoneimines and the monomer derivatives are given in Table 1, and the corresponding spectra are given in the Supporting Information.

In **G0-(PYE)$_2$** (**3**), distinct resonances occur for the protons, H-2, H-3, H-5, and H-6 of the heterocycle, as doublets. As the dendrimer generations grow, the resonances of protons merge progressively. In **G1-(PYE)$_4$** (**4**), H-2 and H-6 protons are seen as a set of doublets, whereas the remaining two protons merge to a broad peak. In the case of **G2-(PYE)$_8$** (**5**) and **G3-(PYE)$_{16}$** (**6**), the resonances of H-2 and H-6 are seen as broad peaks, and H-3 and H-5 proton resonances merge to a broad peak. The merging of the resonances might indicate the contributing imidopyridinium form as the dendrimer generations increase. With this indication of the contributing resonance forms, it was desired to estimate the free energy of activation for the rotational process and the assessment was performed with the aid of variable-temperature ^{1}H NMR studies.

At room temperature, signals of H-2 and H-6 *ortho* to azine appeared as a set of signals, even when H-3 and H-5 *meta* to azine appeared as a merged signal. These protons are sensitive to temperature, as a result of the ground state energy between the resonating forms. An effect of clustering the pyridoneimine moieties at the peripheries of dendrimers is the transformation of the distinct sets of resonances for each proton of the heterocycle in pyridoneimine to only a set of signals for the H-2, H-6 and H-3, H-5 protons, as the dendrimer generation advances.

Such a transition is also observed as a function of temperature. ^{1}H NMR of **G1-(PYE)$_4$** (**4**) in D_2O as a function of temperature (Figure 2) shows four sets of protons for the

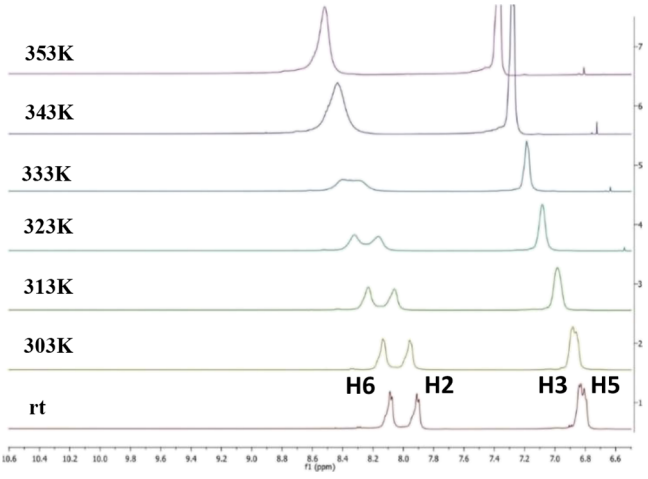

Figure 2. Variable-temperature ^{1}H NMR spectra of the heterocycle portion of **G1-(PYE)$_4$** (**4**) in D_2O.

heterocycle at room temperature, and at increasing temperature, only a set of protons is seen as broad resonances, with coalescence (T_C) occurring at 343 K. The experiments were performed for dendrimers **5** and **6**. The ^{1}H NMR spectra were recorded at 10 K intervals in a D_2O solution. In the case of derivative **3**, signals for H-2 and H-6 are well-resolved at room

Table 1. ^{1}H NMR Chemical Shifts Corresponding to the Heterocycle of Monomers and the Dendritic Pyridoneimines in D_2O

derivative	H-6 and H-2	H-5 and H-3	-NMe
3 (**G0-(PYE)$_2$**)	7.92 (d, J = 6.8 Hz)	6.73 (d, J = 6.8 Hz)	2.93 (s)
	7.75 (d, J = 6.8 Hz)	6.69 (d, J = 6.8 Hz)	
4 (**G1-(PYE)$_4$**)	8.05 (d, J = 6.0 Hz)	6.82–6.80 (br)	2.93 (s)
	7.88 (d, J = 6.4 Hz)		
5 (**G2-(PYE)$_8$**)	8.01 (br), 7.83 (br)	6.76 (br)	2.88 (s)
6 (**G3-(PYE)$_{16}$**)	8.12 (br), 7.94 (br)	6.86 (br)	2.98 (s)
7 (**G0-(PYE)$_1$**)	8.05 (d, J = 6.4 Hz)	6.77 (br)	2.93 (s)
	7.88 (d, J = 6.4 Hz)	6.81 (br)	

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temperature and appeared as two separate doublets, whereas signals for H-3 and H-5 appeared as two nearby doublets. Upon increasing the temperature, signals for H-3 and H-5 merged to a single broad peak at 313 K, whereas H-2 and H-6 coalesced at 333 K. For dendrimers **G2-(PYE)$_8$** (**5**) and **G3-(PYE)$_{16}$** (**6**), signals for H-2 and H-6 appeared as two broad peaks, whereas signals for H-3 and H-5 merged into a single broad peak at room temperature. T_C was 333 and 323 K for **5** and **6**, respectively.

For compound **7** with pyridoneimine and distal tertiary nitrogen connected with a propyl linker, H-3 and H-5 signals merged at rt, whereas H-2 and H-6 peak signals appeared as two doublets. Observed T_C for this compound is 353 K.

From the T_C values and peak separations $\Delta\nu$ (in Hertz) of nonequivalent H-2 and H-6 protons, the activation energies $\Delta G^{\ddagger}$ of the rotational process along the C-4 bridge bond and the rate of rotation (k_c) at T_C were calculated by applying eqs 1 and 2.[54] Pertinent data related to the VT-^{1}H NMR experiment and the activation parameters are given in Table 2.

$$\Delta G^{\ddagger}\ (\text{kcal/mol}) = (4.575 \times 10^{-3})\ T_C\ [9.97 + \log(T_C/\Delta\nu)] \quad (1)$$

$$kc = \pi(\Delta\nu)/\sqrt{2} \quad (2)$$

Table 2. Variable-Temperature Data and Experimental Activation Parameters for Derivatives 3−7 in D_2O

compound	T_C (K)[a]	$\Delta\nu$ (Hz)[b]	k_c (Hz)[c]	$\Delta G^{\ddagger}$ (kJ/mol)
3(**G0-(PYE)$_2$**)	333	50.8	112.8	68.69
4 (**G1-(PYE)$_4$**)	343	52	115.5	70.84
5 (**G2-(PYE)$_8$**)	333	54.4	120.8	68.53
6 (**G3-(PYE)$_{16}$**)	323	56.4	125.3	65.81
7 (**G0-(PYE)$_1$**)	353	48	106	73.18

[a]T_C of H-2 and H-6 NMR shifts of the pyridine ring. [b]Peak separation of anisochronous H-2 and H-6 of the pyridine ring. [c]Rate of rotation along *ipso*-carbon and imine nitrogen bond.

$\Delta\nu$ is the frequency difference of nuclei with differing magnetic environments, and is found to increase for the pyridoneimine moiety as dendrimer generations increase periodically, indicating the dependence of $\Delta\nu$ on the dendrimer generation.

A perceptible increase in the rate of rotation (k_c) is seen for the higher-generation dendrimers, implying a tendency toward the contributing imidopyridinium form. A consequence of this trend is the decrease in the activation energy ($\Delta G^{\ddagger}$) for higher generation dendrimers than lower generations. The contribution of imidopyridinium form in higher generation dendrimers might be due to the coordination of the lone pairs of electrons on imine and ether moieties with the positive charge on pyridinium species. An earlier study on the PETIM dendrimers showed that anomalous fluorescence of this series of dendrimers increases upon protonation of the tertiary amines constituting the molecular structures.[55]

Further studies of solvatochromism and ^{15}N NMR studies[56] were performed in order to ascertain the above observations. As the compounds are soluble only in polar solvents, the solvatochromism studies are conducted only in water, MeOH, and DMSO solutions. Table 3 summarizes changes in λ_{max} in the UV−vis spectra of the compounds in these solvents. The corresponding UV−vis spectra are given in Figure S16 (Supporting Information).

Decreasing solvent polarities from water to DMSO led to a red shift of the charge-transfer band in all the cases. For the higher-generation dendrimer compounds, a clear red shift of 4 to 7 nm is observed with decreasing solvent polarity, whereas in the case of lower-generation compounds, the shift was less. The polarity differences among solvents used in the studies are less, due to which a significant change in the charge transfer band does not result.

^{15}N NMR studies were performed in D_2O solutions, referenced to external CH_3NO_2 and expressed with respect to NH_3(l) at 0 ppm. Table 4 presents the results obtained from the study for the pyridoneimine moiety. In **G0-(PYE)$_1$** (**7**) and **G0-(PYE)$_2$** (**3**), the observed values appeared to correspond to the contributing pyridoneimine resonance form. In the case of **G3-(PYE)$_{16}$** (**6**), the presence of resonances at 171.26 and 168.36 ppm, and the absence of ∼138 and 226 ppm resonances suggested that the contributing imidopyridinium resonance form in this derivative. With **G1-(PYE)$_4$** (**4**) and **G2-(PYE)$_8$** (**5**), resonances that would correspond to both pyridoneimine and imidopyridium contributing forms are observed.

Table 4. ^{15}N NMR Chemical Shift Values for Derivatives 3−7

compound	azine	imine	azinium	imido
7 (**G0-(PYE)$_1$**)	137.8	226.66		
3 (**G0-(PYE)$_2$**)	137.77	226.65		
4 (**G1-(PYE)$_4$**)	138.8	227.7	168.49	151.89
5 (**G2-(PYE)$_8$**)		226.7	168.35	151.33
6 (**G3-(PYE)$_{16}$**)			171.26	168.36

The above observations suggest a generation-driven effect on the pyridoneimines functionalized at the peripheries of the dendrimers. Relatively increasing rates of rotation (k_c), accompanied by reduced activation energies, imply that pyridoneimines encounter a higher propensity toward the imidopyridinium contributing resonance form, as the generation increases. Solvatochromism and ^{15}N NMR provide further indication of this contributing resonance form. The required stabilization of the imidopyridinium species might emerge through stabilization of the positive charge aided by an electron-rich dendrimer scaffold, as suggested earlier for the stabilizations of electron-deficient moieties in the PETIM

Table 3. Solvent-Dependent λ_{max} in UV−Vis Spectra of PYE-Functionalized Compounds[a]

solvent	*ET*[b]	G0-(PYE)$_1$	G0-(PYE)$_2$	G1-(PYE)$_4$	G2-(PYE)$_8$	G3-(PYE)$_{16}$
water	63.1	277	280	277	277	278
MeOH	55.4	280	280	280	280	280
DMSO	45.1	282	284	282	284	283

[a]c = 4 μM for compounds **3**−**7**, at 298 K. [b]Reichardt's solvent polarity.

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dendrimer matrix.[57] The bond rotation through imido-nitrogen and *ipso*-carbon is a primary requirement for the merging of the resonances that characterize the protons of the heterocyclic moiety. The study shows the relative rates of rotation and the activation energies as required for the process in each dendrimer generation and, in comparison to a monomer. The comparisons show the effect of the dendrimer scaffolds distinctly on the contributing resonance forms of the functional moiety when presented in multiples at the peripheries, in comparison to the monomer.

CONCLUSIONS

The work herein illustrates the multivalent presentation of pyridoneimine moieties at the peripheries of dendrimers. The query of clustering the pyridonimine moieties at the PETIM dendrimer peripheries and the attendant alternations between the contributing resonance forms are investigated in this work. NMR studies of the dendritic pyridoneimine in D_2O show a gradation in the imido-nitrogen and *ipso*-carbon bond rotation and the associated activation energies. The effect of the dendrimer scaffold is seen not only in the increased rates of rotation but also in concomitant reduction in the activation energies, as the dendrimer generations increase. Important findings of the work are (i) the contributing resonance structures between pyridoneimine and imidopyridinium are observed to be dependent on the clustering of the moieties; and (ii) although monomers and lower-generation dendrimer prefer pyridoneimine as the contributing resonance form at the room temperature, the contributing resonance form for the higher generations is the imidopyridinium form. The clustering on to dendrimer peripheries appears to impact directly on the contributing resonance forms of pyridoneimine. Although the origin of the alternation in the contributing resonance structure is unclear, electron-rich PETIM dendrimers are likely to play a role. In summary, this work accomplishes the synthesis of pyridoneimine-functionalized PETIM dendrimers of generations 1−3 and a study of the resonating forms of the pyridoneimine moieties.

EXPERIMENTAL SECTION

General Methods. Unless otherwise noted, all reagents were purchased commercially and used as received. Solvents were dried and distilled according to literature procedures. Analytical TLC was performed on commercial Merck plates coated with silica gel or neutral aluminum oxide 60 F254 (type E, 0.2 mm). Visualization of the spots on the TLC plates was achieved by UV radiation or by using I_2 as a staining agent. Silica gel (100−200 and 230−400 mesh size) and neutral alumina were used for column chromatography. IR spectra were recorded as neat samples. Mass spectral characterizations were performed on an ESI-QTOF instrument, operating in the positive ion mode, on samples in either MeCN/water or MeOH/water solution. ^{1}H and ^{13}C NMR spectral analyses were performed on a spectrometer operating at 400 and 100 MHz, respectively. Processing of the FID data was performed on Bruker TopSpin and Mnova software, with default settings. Coupling constants (J) are reported in Hertz. Standard abbreviations s, d, t, dd, br s, m, and app refer to singlet, doublet, triplet, doublet of doublet, broad singlet, multiplet, and apparent, respectively. Variable-temperature NMR studies were recorded at varying concentrations in D_2O (0.5 mL), due to exponentially varying molecular weights of dendrimers and the attendant quantities required for the analysis. The exact concentration is given in each variable-temperature NMR spectrum. ^{15}N NMR studies were performed on a 500 MHz NMR spectrometer, operating at 50.7 MHz for the ^{15}N nucleus, in D_2O solutions. The resonances were referenced to external CH_3NO_2 and expressed with respect to NH_3(l) at 0 ppm.

General Procedure for the Synthesis of PYE Functionalized Compounds. A solution of chloride-functionalized PETIM dendrimer[48,50] (1 mol. equiv.) in THF (10 mL) was added with 4-(*N*-methylamino)pyridine **1** (2.5 mol. equiv. per halide moiety) and DBU as a base (2 mol. equiv. per halide moiety), under N_2 blanket and the reaction mixture refluxed for a defined time period. The precipitate formed in the reaction was filtered, washed several times with solvents (THF, Et_2O, PhMe, and hexane), and the residual solvents were removed in vacuo and dried to afford the required PYE-functionalized dendrimers **4**−**6**, in good yields. In the case of derivatives **3** and **7**, the crude reaction mixture obtained after the evaporation of the solvent was purified by column chromatography (neutral Al_2O_3) (eluant: $CHCl_3$/MeOH, linear gradient) to afford the desired products in good yields.

Characterization of the PYE Functionalized Products. *G0-(PYE)$_2$ (**3**).* A mixture of bis-chloride **2** (0.21 g, 0.81 mmol), **1** (0.44 g, 4.05 mmol), and DBU (0.48 mL, 3.24 mmol) in THF (10 mL) was stirred at reflux and under an inert atmosphere for 24 h, and worked-up as given in the general procedure. **G0-(PYE)$_2$** (**3**) was secured after purification by column chromatography (neutral Al_2O_3) (eluant: $CHCl_3$/MeOH = 92:8) as a colorless gum (0.31 g, 95%). FT-IR (neat) ν 3140, 3067, 2954, 1650, 1592, 1562, 1520, 1460, 1438, 1370, 1326, 1219, 1189, 1106, 1032, 839; ^{1}H NMR (400 MHz, D_2O) δ 7.92 (d, J = 6.8 Hz, 2 H), 7.75 (d, J = 6.8 Hz, 2 H), 7.29−7.27 (m, 3 H), 7.17−7.15 (m, 2 H), 6.73 (d, J = 6.8 Hz, 2 H), 6.69 (d, J = 6.8 Hz, 2 H), 4.06 (t, J = 6.6 Hz, 4 H), 3.52 (s, 2 H), 2.93 (s, 6 H), 2.41 (t, J = 7.6 Hz, 4 H), 2.01−1.95 (m, 4 H). ^{13}C NMR (100 MHz, D_2O) δ 157.7, 143.0, 140.5, 137.1, 129.7, 128.6, 127.4, 110.7, 105.0, 57.3, 55.7, 48.8, 28.8, 26.3. ESI-MS m/z: $[M + H]^+$ calcd for $C_{25}H_{33}N_5H$, 404.2814; found 404.2811.

*G1-(PYE)$_4$ (**4**).* A mixture of dendrimer tetrakis-chloride G1-$(Cl)_4$ (0.15 g, 0.35 mmol), **1** (0.38 g, 3.5 mmol), and DBU (0.42 mL, 2.8 mmol) in THF (10 mL) was stirred at reflux and under an inert atmosphere for 24 h and worked-up as given in the general procedure. **G1-(PYE)$_4$** (**4**) (brown gum, 0.21 g, 81%). FT-IR (neat) ν 3140, 3067, 2954, 1650, 1592, 1562, 1520, 1460, 1438, 1370, 1326, 1219, 1189, 1106, 1032, 839; ^{1}H NMR (400 MHz, D_2O) δ 8.05 (d, J = 6.0 Hz, 4 H), 7.88 (d, J = 6.4 Hz, 4 H), 6.82−6.80 (br, 8 H), 4.09 (t, J = 6.4 Hz, 8 H), 3.44 (t, J = 6.2 Hz, 4 H), 2.93 (s, 12 H), 2.49−2.45 (m, 12 H), 2.01−1.93 (m, 4 H), 1.71−1.61 (m, 8 H). ^{13}C NMR (100 MHz, D_2O) δ 157.7, 143.0, 140.6, 110.7, 105.1, 68.7. 55.8, 49.6, 49.0, 28.8, 26.6, 25.3. ESI-MS m/z: $[M + H]^+$ calcd for $C_{42}H_{64}N_{10}OH$, 725.5343; found 725.5341.

*G2-(PYE)$_8$ (**5**).* A mixture of dendrimer octakis-chloride G2-$(Cl)_8$ (0.12 g, 0.10 mmol), **1** (0.22 g, 2.0 mmol), and DBU (0.24 mL, 1.6 mmol) in THF (10 mL) was stirred at reflux and under an inert atmosphere for 24 h, and worked-up as given in the general procedure. **G2-(PYE)$_8$** (**5**) (brown gum, 0.15 g, 83%). FT-IR (neat) ν 3140, 3067, 2954, 1650, 1592, 1562, 1520, 1460, 1438, 1370, 1326, 1219, 1189, 1106, 1032, 839; ^{1}H NMR (400 MHz, D_2O) δ 8.01 (d, J = 6.4 Hz, 8 H), 7.83 (d, J = 6.4 Hz, 8 H), 6.76 (br, 16 H), 4.11 (t, J = 6.8 Hz, 16

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H), 3.48 (b-t, J = 7.6 Hz, 20 H), 2.88 (s, 24 H), 2.53−2.48 (m, 36 H), 2.04−1.95 (m, 16 H), 1.73−1.64 (m, 20 H). ^{13}C NMR (100 MHz, D_2O) δ 157.7, 143.1, 140.6, 110.7, 105.1, 68.8, 55.8, 50.0, 49.7, 49.1, 28.8, 26.6, 25.3, 25.2. HRMS (ESI) m/z: $[M + H]^+$ calcd for $C_{102}H_{165}N_{22}O_5$, 1778.3333; found 222.1959 $[M/8]^+$.

*G3-(PYE)$_{16}$ (**6**).* A mixture of dendrimer G3-$(Cl)_{16}$ (83 mg, 0.03 mmol), 4-(*N*-methylamino) pyridine **1** (0.13 g, 1.2 mmol), and DBU (0.14 mL, 0.96 mmol) in THF (10 mL) was stirred at reflux and under an inert atmosphere for 24 h, and worked-up as given in the general procedure. **G3-(PYE)$_{16}$** (**6**) (brown gum, 85 mg, 72%). FT-IR (neat) ν 3140, 3067, 2954, 1650, 1592, 1562, 1520, 1460, 1438, 1370, 1326, 1219, 1189, 1106, 1032, 839. ^{1}H NMR (400 MHz, D_2O) δ 8.12 (br, 16 H), 7.94 (br, 16 H), 6.86 (br, 32 H), 4.15 (br, 32 H), 3.52 (br, 52 H), 2.98 (s, 48 H), 2.54 (br, 84 H), 2.01 (br, 32 H), 1.75 (br, 52 H). ^{13}C NMR (100 MHz, D_2O) δ 157.8, 143.1, 140.7, 110.8, 105.2, 69.0, 55.9, 50.0, 49.8, 49.7, 49.2, 28.9, 26.7, 25.4, 22.7.

*G0-(PYE)$_1$ (**7**).* A solution of 3-dimethylaminopropyl chloride hydrochloride (0.10 g, 0.63 mmol) in MeCN (10 mL) was added with **1** (0.17 g, 1.6 mmol) and *N, N*-diisopropyl ethylamine (0.2 mL, 1.3 mmol) under an inert atmosphere and refluxed for 14 h. The white precipitate formed was filtered and the crude residue purified by column chromatography (neutral Al_2O_3, eluent: MeOH/$CHCl_3$ 1:9) to afford the **G0-(PYE)$_1$** (7) (0.15 g, 93%) as a white solid. FT-IR (neat) ν 3138, 3061, 2951, 1647, 1587, 1457, 1372, 1185, 1036, 836; ^{1}H NMR (400 MHz, D_2O) δ 8.05 (d, J = 6.4 Hz, 1 H), 7.88 (d, J = 6.4 Hz, 1 H), 6.81−6.77 (br, 2 H), 4.12 (t, J = 7.2 Hz, 2 H), 2.93 (s, 3 H), 2.34 (t, J = 7.2 Hz, 2 H), 2.18 (s, 6 H), 2.01 (q, J = 7.2 Hz, 2 H). ^{13}C NMR (100 MHz, D_2O) δ 157.8, 143.0, 140.5, 110.7, 105.1, 55.9, 54.7, 43.7, 28.7, 27.6. HRMS (ESI) m/z: $[M + H]^+$ calcd for $C_{11}H_{19}N_3H$, 194.1657; found 194.1658.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acsomega.3c03720.

^{1}H, ^{13}C, and ^{15}N NMR of the compounds, variable-temperature NMR spectra, and solvatochromism spectra (PDF)

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The manuscript was written through the contributions of all authors. All authors have given approval to the final version of the manuscript.

Notes

The authors declare no competing financial interest.

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■ ABBREVIATIONS

PETIM, poly(ether imine); PYE, *N*-[1-alkyl-4(1*H*)-pyridinylidene]methylamine; DBU, 1,8-diazabicyclo[5.4.0]-undec-7-ene; TLC, thin-layer chromatography; VT, variable temperature

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