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PAPER

Studies on a novel class of triaryl pyridine *N*-glycosylamine amphiphiles as super gelators†‡

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A novel class of six different triaryl pyridine *N*-glycosylamine amphiphiles was synthesised and characterized based on different spectral techniques, such as NMR and mass analysis. Gelation properties in different aromatic and aliphatic solvents were studied and gelation was observed predominantly in aliphatic solvents with CGC of 0.5% (w/v) and is attributed to the presence of long alkyl chain. All the gels thus obtained were studied using FE-SEM and powder XRD techniques which reveal fibrous entanglement of the molecules in the gel state with intermolecular spaces of 3.62 nm and 0.43 nm.

Introduction

Gels are viscoelastic materials consisting of low molecular weight gelator molecules and solvents. Depending upon the solvent in which the gel is obtained they are classified into hydrogelator and organogelator.[1–4] Multiple interactions, such as hydrogen bonding, π–π stacking, and hydrophobic interactions, are mainly responsible for the formation of gels.[5] Gelator molecules and their gels have a wide range of application in tissue engineering,[6] cosmetics,[7] as a vehicle for controlled drug delivery *etc.*[8] In addition, they are used in template syntheses of nanoparticles and inorganic nanostructures,[9] sensors,[10] and food processing.[11,12] Among the gelators, non-ionic amphiphilic gelators having carbohydrate head groups are reported to have growing applications in the areas of foods, pharmaceuticals, detergents[13] *etc.*, and this is due to their ready biodegradability, mildness to skin, non-toxicity and synergistic effects in combination with anionic amphiphiles.[14] Several non-ionic carbohydrate modified products are based on sorbitan,[15] glycosides,[16] sugar-esters,[17] including mannitol monoesters,[18] and amides,[19] *etc.*

In order to prepare gelators and gels with diverse functionality, we have incorporated the triaryl pyridine nucleus. In general the 3,4,5-triaryl pyridine nucleus is of special interest because of its close structural resemblance to the recommended photodynamic cell-specific symmetrical triaryl-telluropyrylium, selenopyrylium and thiopyrylium cancer therapeutic agents.[20] Triaryl pyridine derivatives also act as G-quadruplex binding ligands[21] and possess antimicrobial activity.[22] In addition, this class of derivatives is reported to have significance as novel materials in photosensitizers for the conversion of solar energy.[23]

The structural modification of carbohydrate molecules to obtain low molecular weight gelators has been an interesting field of research in recent years.[24] Since carbohydrate molecules are biocompatible, the gels derived from these molecules have wide application in biology and also as functional materials.[25] Moreover, the abundant availability of saccharides enhances research into the design of novel sugar based gelator molecules. The self-assembly of sugar based-amphiphilic systems is thus emerging as a particular powerful strategy to direct the self-assembly of relatively simple glycosyl amines into sophisticated materials possessing wide applications. Due to their dual affinity for polar and non-polar solvents these amphiphiles can self-assemble to minimize their free energy.[26] In addition the gels can be stabilized by intermolecular hydrogen bonds between sugar-OH groups as well as van der Waals interactions between alkyl groups. In the search of new molecular entities with potential gelation ability, we have recently reported pyridine based *N*-glycosylamine and 4,6-*O*-protected-β-C-glycosides[27] as potential gelators with diverse applications. In the present study we report a novel class of triaryl pyridine based *N*-glycosylamine amphiphiles as super gelators. Thus, the design was such that the hydrophilic head and hydrophobic tail are connected through a chromophoric planar base.

Results and discussion

Triaryl pyridine amine derivatives (**5–7**) were synthesised from long alkyl chain substituted benzaldehydes (**1–3**) and 4-aminoacetophenone (**4**) in the presence of NaOH and ammonium acetate in polyethylene glycol-300 [PEG-300] as reaction medium (Scheme 1). Three triaryl pyridine amines thus obtained were glycosylated according to the literature procedure[28] leading

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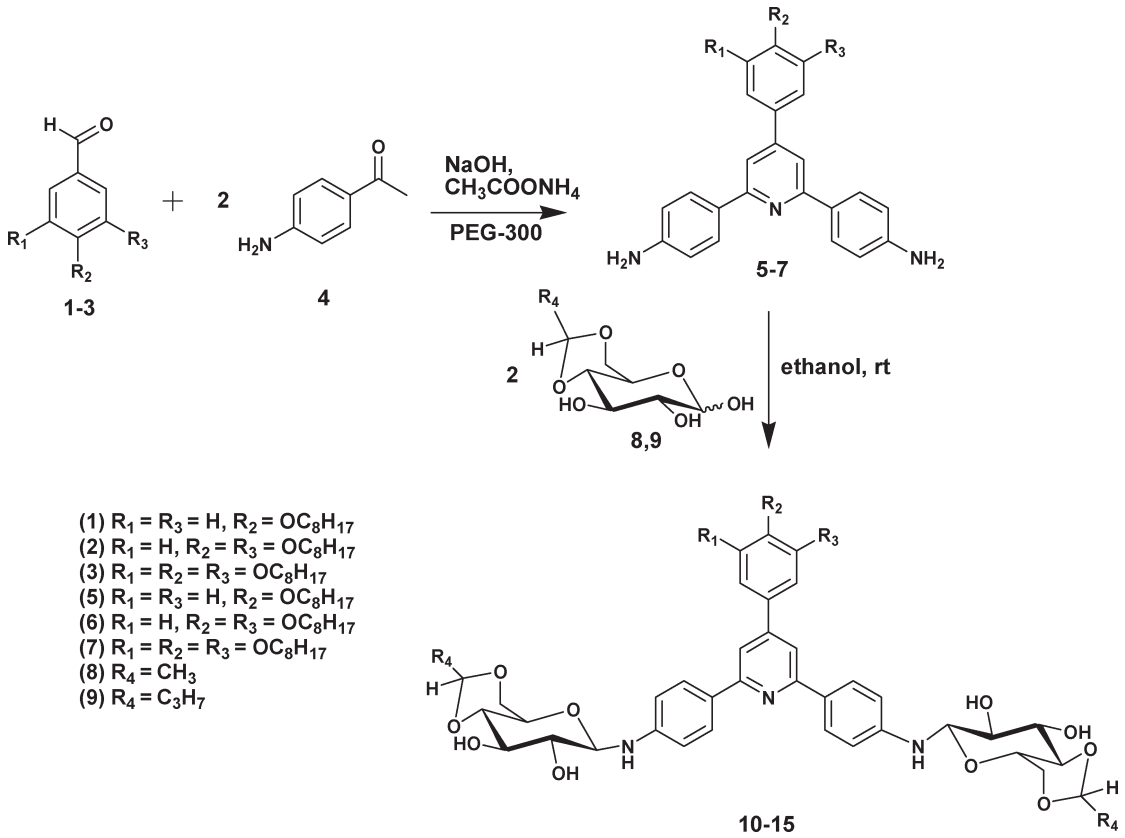
‡ Electronic supplementary information (ESI) available: ^{1}H and ^{13}C NMR, mass spectra, additional FE-SEM and TEM images. See DOI: 10.1039/c2ob06834f



Scheme 1 Synthesis of *N*-glycosylamines **10–15**.

Table 1 Synthesis of triaryl pyridine *N*-glycosylamines (**10–15**)

Compounds	R_1	R_2	R_3	R_4	Yield (%)
10	H	OC_8H_{17}	H	CH_3	65
11	H	OC_8H_{17}	H	C_3H_7	72
12	OC_8H_{17}	OC_8H_{17}	H	CH_3	68
13	OC_8H_{17}	OC_8H_{17}	H	C_3H_7	66
14	OC_8H_{17}	OC_8H_{17}	OC_8H_{17}	CH_3	80
15	OC_8H_{17}	OC_8H_{17}	OC_8H_{17}	C_3H_7	74

to the formation of glycosyl amines. The identities of all the synthesised *N*-glycosylamines were confirmed using NMR (^{1}H and ^{13}C), mass spectrometry and elemental analysis. All the synthesised compounds were subjected to gelation studies with a wide range of solvents and the gels thus obtained were characterized using microscopic techniques, *viz.*, FE-SEM, TEM analysis.

Synthesis and characterization

Attempts made to synthesise triaryl pyridine amines by adopting conventional methods[29–31] did not result in the formation of the expected product. However, by using the one-pot strategy reported by Smith *et al.*,[32] triaryl pyridine amines (**5–7**) were synthesised (Scheme 1) and were characterised based on NMR and elemental analysis. *N*-Glycosylation[28] of triaryl pyridine amines (**5–7**) using 4,6-*O*-protected-D-glucose derivatives (**8, 9**) resulted in the formation of the expected *N*-glycosylated products (**10–15**) in 65–80% yield (Table 1). *N*-Glycosylated products (**10–15**) were characterized based on NMR (^{1}H and ^{13}C) and mass spectral analysis. The ^{1}H NMR spectra of *N*-glycosylamines show peaks around 0.8–1.8 ppm, 3.3–4.5 ppm, 5–6 ppm, and 6.6–8.2 ppm corresponding to the alkyl chain, saccharide skeleton, glycosyl amine and aromatic groups respectively. Studies further show the existence of the β-anomeric form with chemical shifts around 4.7 ppm and coupling constants around 7.8 Hz. However ^{13}C NMR studies show peaks around 18–41 ppm, 72–106 ppm and 110–162 ppm corresponding to the alkyl chain, saccharide carbon, including acetal and aromatic carbons respectively (see ESI for details†).

Gelation studies

The gelation studies were carried out as per the reported procedure.[33] A known amount of triaryl pyridine amines (**5–7**)/*N*-glycosylamines (**10–15**) was added to 1 mL of solvent in a glass vial and heated to dissolve the gelator. After cooling to ambient temperature, the vial was turned upside down to verify the gel formation. The reversibility of the gelation was confirmed by repeated heating, and cooling. The critical gelation concentration (CGC) of triaryl pyridine amines (**5–7**) and *N*-glycosylamines (**10–15**) was determined from the minimum amount of gelator required for the formation of gel at room temperature and the study was carried out in ten different solvents. Studies further show that the triaryl pyridine amines do not form gels, whereas the corresponding *N*-glycosylated products do form gels, which is due to the entrapment of solvent molecules between the

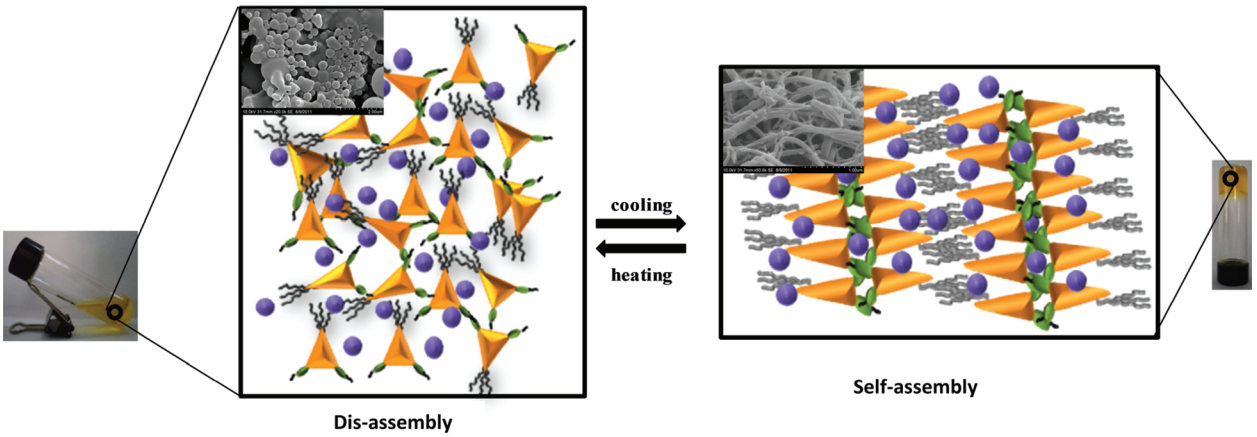


Fig. 1 Schematic representation of solution to gel transition.

Table 2 Gelation studies of triaryl pyridine *N*-glycosylamines (**10–15**)

	Status of compound (CGC[a] %)					
Solvent	**10**	**11**	**12**	**13**	**14**	**15**
$CHCl_3$	G (1.5)	G (1.5)	G (1.5)	G (1)	G (0.5)	G (0.5)
EtOH	G (1.5)	G (1.5)	G (1.5)	G (1)	G (0.5)	G (0.5)
THF	PG	G (1.5)	PG	G (1)	G (0.5)	G (0.5)
DCM	G (1.5)	S	S	G (1)	G (0.5)	G (0.5)
EtOAc	G (2)	G (1.5)	G (1.5)	G (1.5)	G (0.5)	G (0.5)
Acetone	S	S	S	G (1.5)	G (0.5)	G (0.5)
IPA	I	I	PG	PG	G (1)	G (1.5)
Benzene	P	P	P	PG	G (1)	G (1)
Toluene	P	P	PG	PG	G (1)	G (1)
Hexane	I	I	P	P	PG	PG

[a] G – gelation, PG – partial gelation, S – soluble, I – insoluble, P – precipitation. CGC – critical gelation concentration.

gelators. The results of gelation are summarised in Table 2. Polar (ethanol, tetrahydrofuran, ethyl acetate, isopropyl alcohol, acetone, dichloromethane) and non-polar solvents (hexane, chloroform, benzene,toluenee) were used for gelation. Among these, the aliphatic solvents *viz.*, chloroform, dichloromethane, tetrahydrofuran, ethanol, ethyl acetate, acetone and isopropyl alcohol were found to be the best for gelation, which is due to the presence of long alkyl chains. However, among the different aromatic solvents studied benzene and toluene were found to form gels. A schematic representation of the sol to gel transition upon cooling and heating due to self-assembly and dis-assembly of *N*-glycosylamines is shown in Fig. 1.

Morphological studies

The morphology of *N*-glycosylamines in solution and gel state were studied with FE-SEM and TEM analysis using 1% w/v of *N*-glycosylamine **13** in ethanol. FE-SEM images (Fig. 2a) of *N*-glycosylamine **13**, recorded immediately after heating the compound **13** (1% w/v) in ethanol, show a spherical structure which is due to the identical state of the *N*-glycosylamine molecules in solution. However cooling the solution to room temperature for a period of 1 h leads to the formation of a gel, which shows a

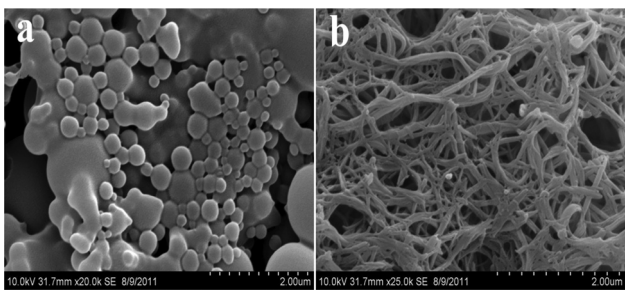


Fig. 2 FE-SEM images of gel **13** (1% w/v ethanol): a) solution and b) gel.

fibrous network (Fig. 2b). Thus the FE-SEM analysis reveals the conversion of spherical particles into fibres upon self-assembly in the gel state,[34] and TEM images of *N*-glycosylamine **13** also show nanofibres (see ESI for further details†). Thus FE-SEM and TEM analysis clearly evidence the formation of gels due to self-assembly of molecules from the dis-assembled solution state (Fig. 1).

Thermal stability

The main characteristic property of gels obtained from low molecular weight gelators (LMWG) is the thermo-reversible gel to solution and *vice versa* transitions that occur by self-assembly and dis-assembly of the molecules. The gel to solution transition temperatures (T_{gel}) of the gelators have been determined using the dropping ball method.[35] T_{gel} values for *N*-glycosylamine **13** in tetrahydrofuran, ethanol and chloroform as a function of concentration are shown in Fig. 3. As the concentration increases the T_{gel} increases and attains stability near the boiling point. Tetrahydrofuran and ethanol also show similar trends in gel melting temperature, while chloroform has same T_{gel} of 58 °C from a concentration of 35 mg mL^{-1} to 50 mg mL^{-1}. The studies further reveal that the gels of compound **13** are thermally more stable even at temperatures nearer to the boiling point of the solvent, which is due to the self-assembly of the molecules and is further evidenced from the morphological studies.

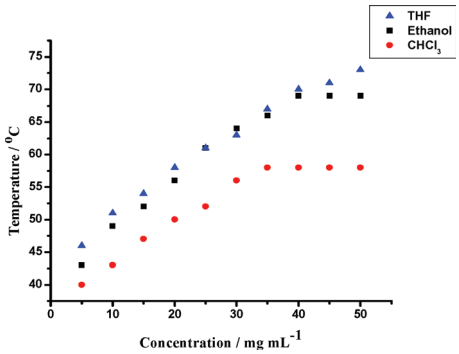


Fig. 3 Concentration dependent melting temperature of gels of compound **13** in THF, EtOH and $CHCl_3$.

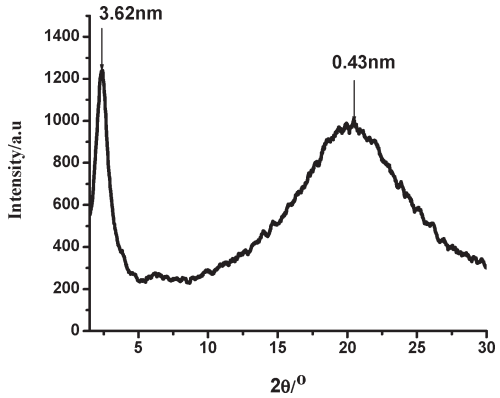


Fig. 4 Powder XRD pattern of xerogel **13**.

XRD analysis of the gels

In order to study the molecular packing in the gel, WAXD (wide angle X-ray diffraction) studies was carried out on the xerogel of *N*-glycosylamine **13**. The XRD pattern of xerogel **13** is shown in Fig. 4. The X-ray diffractogram reveals a lamellar structure,[36] which is due to the ordered packing of molecules in the gel state. A sharp peak at low angle 2.48° (2θ) with an interlayer distance of 3.62 nm arises from the packing of the long alkyl chain due to van der Waals interactions. The diffraction in the wide-angle region around 20.55° (2θ) gives a very broad peak with an interlayer distance of 0.43 nm attributable to the π–π stacking[37] of the triaryl pyridine unit in the self-assembled state. Thus the XRD analysis confirms the self-assembly of the molecules in the gel state.

Photophysical studies

The chromophoric nature of the *N*-glycosylamines **10–15** was investigated using absorption and emission spectroscopy. The absorption spectra of the *N*- glycosylamines have been recorded at a concentration of 1×10^{-5} M in ethanol. *N*-Glycosylamines **10–15** show characteristic absorption bands in the range of 300–320 nm and 340–360 nm (Fig. 5). On excitation of the *N*-glycosylamines at their absorption maxima of 300–320 nm they show corresponding emission in the range of 450–500 nm (Fig. 6).

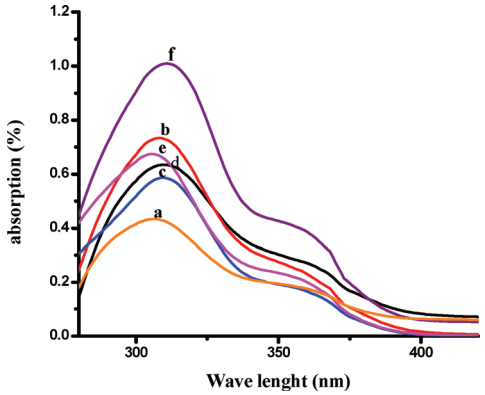


Fig. 5 Absorption spectra of a) **10**, b) **11**, c) **12**, d) **13**, e) **14** and f) **15** in ethanol at 1×10^{-5} M concentration.

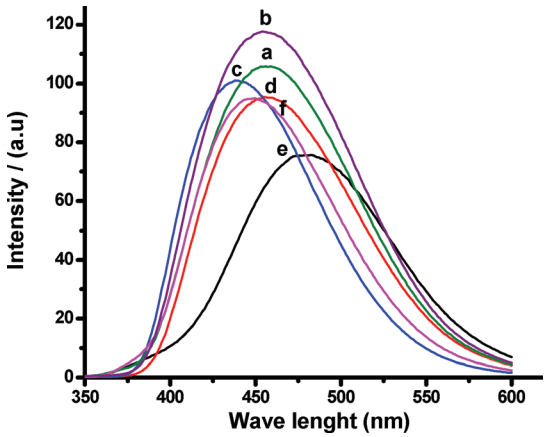


Fig. 6 Emission spectra of a) **10**, b) **11**, c) **12**, d) **13**, e) **14** and f) **15** in ethanol at 1×10^{-5} M concentration.

Conclusion

A one-pot facile modified literature procedure has been adopted to synthesise triaryl pyridine amines and their corresponding glycosylated products in good yield. Identities of all the synthesised compounds were confirmed using NMR and mass spectral techniques. Gelation studies reveal that the *N*-glycosylamines are super gelators. Morphological studies using FE-SEM and TEM show fibrous networks of the *N*-glycosylamines in the gel state. Thus triaryl pyridine *N*-glycosylamines act as amphiphilic gelators due to the hydrophobic tail and hydrophilic head that are linked through a chromophoric triaryl pyridine moiety.

Experimental section

Materials

Polyethylene glycol-300 (PEG-300), 4-aminoacetophenone, and butyraldehyde were purchased from Sigma Aldrich chemicals Pvt. Ltd. USA. Hydrochloric acid, NaOH, D-glucose, ethanol were purchased from SRL India Ltd., were of high purity and were used without further purification. Column chromatography was performed on silica gel (100–200 mesh). NMR spectra were recorded on a Bruker DRX 300 MHz instrument in $CDCl_3$ (with a few drops of DMSO-d_6). Chemical shifts are referenced to

internal TMS. FE-SEM images were recorded on a Hitachi SU-6600 instrument. Mass spectra were recorded using a Thermo Finnigan-ESI mass spectrometer, and optical rotation was performed using a Rudolph-Autopol II digital polarimeter. Elemental analyses were carried out on a Thermoquest microanalyser.

Synthesis of 2,6-bis(4-aminophenyl)-4-(alkyloxyphenyl) pyridine (5–7)[31]

To a stirred solution of 4-aminoacetophenone, **4** (4 mmol), and NaOH (4 mmol) in PEG-300, 2 mmol of benzaldehyde derivative (**1–3**) was added and heated to 100 °C. After stirring for 3 h the temperature was reduced to 70 °C and ammonium acetate (2 g) was added, then the temperature was increased to 100 °C and stirring continued for a further 3 h. After completion of the reaction, the reaction mixture was poured on to crushed ice, and the precipitate thus obtained was filtered and further purified by crystallization to obtain 2,6-bis(4-aminophenyl)-4-(alkyloxyphenyl)pyridines, **5–7**, in 73–85% yield.

General procedure for the synthesis of 2,6-bis-(4(4,6-*O*-protected-β-D-glycopyranosy-amino)-phenyl)-4-(alkoxy-phenyl) pyridines (10–15)

To a stirred solution of 2 mmol of 4,6-*O*-protected-D-glucose derivatives (**8**) in 5 ml of ethanol, 1 mmol of alkyl substituted triaryl pyridine amine (**5**) was added. The reaction mixture was stirred at 50 °C for 10 min and at room temperature for 24 h. The reaction was monitored through TLC. The solid *N*-glycosylamine (**10**) which separated was filtered off, washed with ethanol and dried with ether. These *N*-glycosyl amines are of satisfactory purity and have been characterized using ^{1}H and ^{13}C NMR and mass analysis. A similar procedure was adopted for the synthesis of compounds **11–15**.

2,6-Bis-(4(4,6-*O*-ethylidene-β-D-glucopyranosyl-amino) phenyl)-4-(4-*O*-octyl-phenyl)pyridine (10). Orange yellow solid; 0.55 g (yield, 65%); mp: 160–163 °C; $[\alpha]_D$ −22 (*c* 0.1% in ethanol); **^{1}H NMR** (300 MHz, $CDCl_3$ + DMSO-d_6, ppm): δ_H 7.98 (d, *J* = 8.1 Hz, 4H, Ar-*H*); 7.64–7.59 (m, 4H, Ar-*H*); 6.96 (d, *J* = 8.4 Hz, 2H, Ar-*H*); 6.79 (d, *J* = 8.4 Hz, 4H, Ar-*H*); 5.97 (d, 2H, *J* = 6.6 Hz, Gly-N*H*); 5.11 (s, 2H, Sacc-O*H*), 5.06 (s, 2H, Sacc-O*H*); 4.69 (d, *J* = 4.8 Hz, 2H, Ace-*H*); 4.59 (t, *J* = 7.8 Hz, 2H, Ano-*H*); 4.08 (d, *J* = 6 Hz, 2H, Sacc-*H*); 3.96 (t, *J* = 6.6 Hz, 4H, O*CH*$_2$, Sacc-*H*); 3.76–3.61 (m, 2H, Sacc-*H*); 3.44–3.20 (m, 6H, Sacc-*H*); 1.77–1.70 (m, 2H, C*H*$_2$); 1.31–1.23 (m, 16H, C*H*$_2$ & C*H*$_3$); 0.82–0.80 (m, 6H, C*H*$_3$). **^{13}C NMR** (75 MHz, $CDCl_3$ + DMSO-d_6, ppm): δ_C 164.1 (2C, Ar-*C*); 161.1 (1C, Ar-*C*); 153.8 (2C, Ar-*C*); 151.7 (1C, Ar-*C*); 135.7 (2C, Ar-*C*); 134.6 (2C, Ar-*C*); 132.4 (4C, Ar-*C*); 132.2 (4C, Ar-*C*); 119.3 (2C, Ar-*C*); 118.1 (3C, Ar-*C*); 103.7 (2C, Ace-*C*); 90.7 (2C, Ano-*C*); 84.9 (2C, Sacc-*C*); 78.5 (2C, Sacc-*C*); 78.2 (2C, Sacc-*C*); 72.6 (1C, O*CH*$_2$); 72.4 (2C, Sacc-*C*); 71.4 (2C, Sacc-*C*); 36.0 (1C, *CH*$_2$); 33.6 (1C, *CH*$_2$); 33.4 (1C, *CH*$_2$) 30.3 (2C, *CH*$_2$); 26.9 (1C, *CH*$_2$); 25.8 (2C, *CH*$_3$); 18.5 (1C, *CH*$_3$). Anal. Calcd for $C_{47}H_{59}N_3O_{11}$: C, 67.04; H, 7.06; N, 4.99. Found: C, 67.20; H,7.16, N, 4.94%. EI-MS: *m*/*z* calcd for $C_{47}H_{59}N_3O_{11}$. 841.41, found 842.47.

2,6-Bis-(4(4,6-*O*-butylidene-β-D-glucopyranosyl-amino)phenyl)-4-(4-*O*-octyl-phenyl)pyridine (11). Compound, **11** was obtained by the reaction of the mono-octyl derivative of triaryl pyridine amine, **5**, with 4,6-*O*-butylidene-D-glucopyranose, **9** as an orange yellow solid; 0.65 g (yield, 72%); mp: 170–172 °C; $[\alpha]_D$ −30 (*c* 0.1% in ethanol); **^{1}H NMR** (300 MHz, $CDCl_3$ + DMSO-d_6, ppm): δ_H 7.98 (d, *J* = 8.4 Hz, 4H, Ar-*H*); 7.70–7.59 (m, 4H, Ar-*H*); 6.96 (d, *J* = 8.7 Hz, 2H, Ar-*H*); 6.79 (d, *J* = 8.4 Hz, 4H, Ar-*H*); 6.04 (d, *J* = 6.6 Hz, 2H, Gly-N*H*); 5.21 (s, 2H, Sacc-O*H*); 5.01 (s, 2H, Sacc-O*H*); 4.58 (t, *J* = 7.5 Hz,2H, Ano-*H*); 4.51 (t, *J* = 4.8 Hz, 2H, Ace-*H*); 4.10 (d, *J* = 6 Hz, 2H, Sacc-*H*); 3.97 (t, *J* = 6.6 Hz, 2H, O*CH*$_2$); 3.60 (t, *J* = 4.5 Hz, 2H, Sacc-*H*); 3.42–3.32 (m, 8H, Sacc-*H*); 1.77–1.72 (m, 4H, C*H*$_2$); 1.58–1.53 (m, 4H, C*H*$_2$); 1.41–1.23 (m, 12H, C*H*$_2$); 0.78–0.88 (m, 9H, C*H*$_3$). **^{13}C NMR** (75 MHz, $CDCl_3$ + DMSO-d_6, ppm): δ_C 164.6 (2C, Ar-*C*); 161.5 (1C, Ar-*C*); 153.8 (2C, Ar-*C*); 152.3 (1C, Ar-*C*); 135.8 (2C, Ar-*C*); 134.3 (2C, Ar-*C*); 132.9 (4C, Ar-*C*); 132.6 (4C, Ar-*C*); 119.8 (2C, Ar-*C*); 119.3 (1C, Ar-*C*); 118.5 (2C, Ar-*C*); 106.9 (2C, Ace-*C*); 91.1 (2C, Ano-*C*); 85.5 (2C, Sacc-*C*); 78.9 (2C, Sacc-*C*); 78.7 (2C, Sacc-*C*); 78.1 (1C, O*CH*$_2$); 72.8 (2C, Sacc-*C*); 72.1 (2C, Sacc-*C*); 41.1 (2C, *CH*$_2$); 36.5 (1C, *CH*$_2$); 34.0 (1C, *CH*$_2$); 33.9(2C, *CH*$_2$); 30.7 (2C, *CH*$_2$); 27.3 (1C, *CH*$_2$); 22.2 (2C, *CH*$_2$); 18.9 (2C, *CH*$_3$); 18.8 (1C, *CH*$_3$). Anal. Calcd for $C_{51}H_{67}N_3O_{11}$: C,68.21; H, 7.52; N, 4.68. Found: C, 68.11; H,7.46; N, 4.71%. EI-MS: *m*/*z* calcd for $C_{51}H_{67}N_3O_{11}$. 897.47, found 898.67.

2,6-Bis-(4(4,6-*O*-ethylidene-β-D-glucopyranosyl-amino)phenyl)-4-(3,4 di-*O*-octyl-phenyl)pyridine (12). Compound **12** was obtained by the reaction of the di-*O*-octyl derivative of triaryl pyridine amine **6** with 4,6-*O*-ethylidene-D-glucopyranose **8** as an orange yellow solid; 0.66 g (yield, 68%); mp: 165–168 °C; $[\alpha]_D$ −32 (*c* 0.1% in ethanol); **^{1}H NMR** (300 MHz, $CDCl_3$ + DMSO-d_6, ppm): δ_H 7.98 (d, *J* = 7.8 Hz, 2H, Ar-*H*); 7.91 (d, *J* = 7.5 Hz, 2H, Ar-*H*); 7.64 (s, 2H, Ar-*H*); 7.25–7.20 (m, 2H, Ar-*H*); 6.95 (d, *J* = 8.4 Hz, 1H, Ar-*H*); 6.80 (d, *J* = 8.4 Hz, 2H, Ar-*H*); 6.71 (d, *J* = 8.1 Hz, 2H, Ar-*H*); 6.00 (s, 1H, Gly-N*H*); 4.69 (d, 2H, *J* = 4.8 Hz, Ace-*H*); 4.59 (d, 2H, *J* = 6 Hz, Ano-*H*); 4.09-3.97 (m, 8H, O*CH*$_2$, Sacc-O*H*, *H*); 3.73–3.61 (m, 13H, O*CH*$_2$, Sacc-*H*); 1.78 (s, 6H, C*H*$_2$); 1.45 (d, *J* = 3.6 Hz, 6H, C*H*$_2$); 1.31–1.23 (m, 18H, C*H*$_2$, C*H*$_3$); 0.82 (s, 6H, C*H*$_3$). **^{13}C NMR** (75 MHz, $CDCl_3$ + DMSO-d_6, ppm): δ_C 161.6 (1C, Ar-*C*); 154.8(1C, Ar-*C*); 154.2 (1C, Ar-*C*); 153.5 (2C, Ar-*C*); 152.2 (1C, Ar-*C*); 136.8 (1C, Ar-*C*); 134.5 (1C, Ar-*C*); 133.3 (1C, Ar-*C*); 132.8 (2C, Ar-*C*); 132.6 (2C, Ar-*C*); 124.8 (1C, Ar-*C*); 119.4 (2C, Ar-*C*); 118.9 (2C, Ar-*C*), 118.5 (2C, Ar-*C*); 117.8 (1C, Ar-*C*); 104.1 (2C, Ace-*C*); 91.2 (2C, Ano-*C*); 85.4 (2C, Sacc-*C*); 78.9 (2C, Sacc-*C*); 78.7 (2C, Sacc-*C*); 74.4 (1C, O*CH*$_2$); 74.0 (1C, O*CH*$_2$); 73.3 (2C, Sacc-*C*); 71.9 (2C, Sacc-*C*); 36.5 (2C, *CH*$_2$); 34.1 (2C, *CH*$_2$); 34.0 (2C, *CH*$_2$); 33.9 (2C, *CH*$_2$); 30.8 (2C, *CH*$_2$); 30.8 (2C, *CH*$_2$); 27.3 (2C, *CH*$_2$); 25.3 (2C, *CH*$_3$); 18.9 (2C, *CH*$_3$). Anal. Calcd for $C_{55}H_{75}N_3O_{12}$: C, 68.09; H, 7.79; N, 4.33. found: C, 68.15; H, 7.75; N, 4.29%.

2,6-Bis-(4(4,6-*O*-butylidene-β-D-glucopyranosyl-amino)phenyl)-4-(3,4 di-*O*-octyl-phenyl)pyridine (13). Compound **13** was obtained by the reaction of the di-*O*-octyl derivative of triaryl pyridine amine **6** with 4,6-*O*-butylidene-D-glucopyranose, **8** as an orange yellow solid; 0.68 g (yield, 66%); mp: 175–178 °C;

$[\alpha]_D$ −13 (*c* 0.1% in ethanol); **^{1}H NMR** (300 MHz, $CDCl_3$ + DMSO-d_6, ppm): δ_H 7.97 (d, *J* = 8.4 Hz, 2H, Ar-*H*); 7.91 (d, *J* = 8.4 Hz, 2H, Ar-*H*); 7.55 (s, 2H, Ar-*H*); 7.22-7.17 (m, 2H, Ar-*H*); 6.92 (d, *J* = 8.1 Hz, 1H, Ar-*H*); 6.78 (d, *J* = 8.4 Hz, 2H, Ar-*H*); 6.70 (d, *J* = 8.4 Hz, 2H, Ar-*H*); 5.80 (s, 1H, GlyN*H*); 4.60 (t, *J* = 7.8 Hz, 2H, Ano-*H*); 4.51 (d, *J* = 4.8 Hz, 2H, Ace-*H*); 4.12–4.10 (s, 2H, Sacc-O*H*); 4.03–3.91 (m, 7H, OCH_2, Sacc-*H*, Gly-N*H*); 3.67 (t, *J* = 9 Hz, 2H, OCH_2); 3.44–3.37 (m, 9H, Sacc-*H*); 1.77 (s, 6H, CH_2); 1.59–1.56 (m, 4H, CH_2); 1.43–1.22 (m, 22H, CH_2); 0.87–0.83 (m, 12H, CH_3). **^{13}C NMR** (75 MHz, $CDCl_3$ + DMSO-d_6, ppm): δ_C 161.6 (1C, Ar-*C*); 154.8 (2C, Ar-*C*); 154.2 (2C, Ar-*C*); 153.1 (2C, Ar-*C*); 151.0 (1C, Ar-*C*); 136.8 (1C, Ar-*C*); 133.7 (1C, Ar-*C*); 132.8 (2C, Ar-*C*); 132.7 (2C, Ar-*C*); 124.7 (2C, Ar-*C*); 119.5 (2C, Ar-*C*); 118.8 (2C, Ar-*C*); 118.6 (2C, Ar-*C*); 117.8 (1C, Ar-*C*); 107.0 (2C, Ace-*C*); 91.1 (2C, Ano-*C*); 85.3 (2C, Sacc-*C*); 78.9 (2C, Sacc-*C*); 78.7 (2C, Sacc-*C*); 74.4 (1C, OCH_2); 73.9 (1C, OCH_2); 73.2 (2C, Sacc-*C*); 72.0 (2C, Sacc-*C*); 41.0 (2C, CH_2); 36.5 (2C, CH_2); 34.1 (2C, CH_2); 34.1 (2C,CH_2); 33.9 (2C, CH_2); 30.8 (2C, CH_2); 27.3 (2C, CH_2); 22.1 (2C, CH_2); 18.8 (2C, CH_3); 18.7 (2C, CH_3). Anal. Calcd for $C_{59}H_{83}N_3O_{12}$: C,69.05; H, 8.15; N, 4.09. found: C, 69.20; H, 8.05; N, 4.06%.

2,6-Bis-(4(4,6-*O*-ethylidene-β-D-glucopyranosyl-amino)phenyl)-4-(3,4,5 tri-*O*-octyl-phenyl)pyridine (14). Compound, **14** was obtained by the reaction of the tri-*O*-octyl derivative of triaryl pyridine amine **7** with 4,6-*O*-ethylidene-D-glucopyranose, **8** as a yellow orange solid; 0.88 g (yield, 80%); mp: 178–182 °C; $[\alpha]_D$ −48 (*c* 0.1% in ethanol); **^{1}H NMR** (300 MHz. $CDCl_3$ + DMSO-d_6, ppm): δ_H 7.99 (d, *J* = 8.4 Hz, 4H, Ar-*H*); 7.58 (s, 2H, Ar-*H*); 6.84 (s, 2H, Ar-*H*); 6.79 (d, *J* = 8.7 Hz, 4H, Ar-*H*); 6.05 (s, 2H, Gly-N*H*); 5.09 (s, 4H, Sacc-O*H*); 4.68 (d, *J* = 4.8 Hz, 2H, Ace-*H*); 4.56 (t, *J* = 7.8 Hz, 2H, Ano-*H*); 4.03 (t, *J* = 6 Hz, 6H, -OCH_2); 3.92 (t, *J* = 6.3 Hz, 4H, Sacc-*H*); 3.61–3.54 (m, 2H, Sacc-*H*); 3.47–3.33 (m, 6H, Sacc-*H*); 1.80–1.66 (m, 8H, CH_2); 1.45 (d, *J* = 6.9 Hz, 6H, CH_2); 1.30–1.23 (m, 31H, CH_2 & CH_3); 0.82 (s, 9H, CH_3). **^{13}C NMR** (75 MHz, $CDCl_3$ + DMSO-d_6, ppm): δ_C 161.5 (1C, Ar-*C*), 158.2 (4C, Ar-*C*); 154.6 (1C, Ar-*C*); 152.8 (2C, Ar-*C*); 143.4 (2C, Ar-*C*); 139.5 (2C, Ar-*C*); 133.8 (2C, Ar-*C*); 132.6 (4C, Ar-*C*); 119.2 (2C, Ar-*C*); 118.5 (2C, Ar-*C*); 110.5 (1C, Ar-*C*); 101.6 (2C, Ace-*C*); 97.2 (2C, Ano-*C*); 90.3 (2C, Sacc-*C*); 81.3 (1C, OCH_2); 79.5 (2C, Sacc-*C*); 77.8 (2C, OCH_2); 75.1 (2C, Sacc-*C*); 73.9 (2C, Sacc-C); 66.1 (2C, Sacc-C); 36.6 (2C, CH_2); 36.5 (2C, CH_2); 35.1 (2C, CH_2); 34.2 (2C, CH_2); 34.1 (2C, CH_2); 33.9 (2C, CH_2); 30.9 (2C, CH_2); 28.4 (2C, CH_3); 27.3 (3C, CH_2); 22.5 (3C, $CH3$); 18.9 (3C, CH_3). Anal. Calcd for $C_{63}H_{91}N_3O_{13}$: C,68.89; H, 8.35; N, 3.83%. Found: C, 68.65; H, 8.52; N, 3.81. EI-MS: *m*/*z* calcd for $C_{63}H_{91}N_3O_{13}$ 1097.65, found 1098.73.

2,6-Bis-(4(4,6-*O*-butylidene-β-D-glucopyranosyl-amino)phenyl)-4-(3,4,5 tri-*O*-octyl-phenyl)pyridine (15). Compound **15** was obtained by the reaction of the tri-*O*-octyl derivative of triaryl pyridine amine **7** with 4,6-*O*-butylidene-D-glucopyranose, **9** as an orange yellow solid; 0.85 g (yield, 72%); mp: 190–195 °C; $[\alpha]_D$ −41 (*c* 0.1% in ethanol); **^{1}H NMR** (300 MHz, $CDCl_3$ + DMSO-d_6, ppm): δ_H 7.99 (d, *J* = 8.4 Hz, 4H, Ar-*H*); 7.65 (s, 2H, Ar-*H*); 6.93 (s, 2H, Ar-*H*); 6.88 (d, *J* = 8.7 Hz, 4H, Ar-*H*); 5.95 (s, 2H, GlyN*H*); 5.10 (s, 2H, Sacc-O*H*); 4.92 (s, 2H, sacc-O*H*); 4.58 (t, *J* = 7.2 Hz, 2H, Ano-*H*); 4.50 (d, *J* = 4.8 Hz, 2H, Ace-*H*); 4.12-4.08 (m, 6H, OCH_2); 3.93 (t, *J* = 6.3 Hz, 4H, Sacc-*H*); 3.72 (d, *J* = 6.6 Hz, 2H, Sacc-*H*); 3.63–3.43 (m, 6H, Sacc-*H*); 1.78–1.68 (m, 8H, CH_2); 1.56–1.54 (m, 8H, CH_2); 1.40(s, 30H, CH_2); 0.88 (s, 15H, CH_3). **^{13}C NMR** (75 MHz, $CDCl_3$ + DMSO-d_6, ppm): δ_C 161.4 (1C, Ar-*C*); 158.2 (4C, Ar-*C*); 154.7 (2C, Ar-*C*); 152.3 (2C, Ar-*C*); 143.4 (2C, Ar-*C*); 139.5 (2C, Ar-*C*); 134.3 (2C, Ar-*C*), 132.7 (4C, Ar-*C*); 118.8 (1C, Ar-*C*); 118.5 (2C, Ar-*C*); 110.4 (1C, Ar-*C*); 106.9 (2C, Ace-*C*); 91.1 (2C, Ano -*C*); 85.5 (2C, Sacc-*C*); 78.9 (1C, O*C*H2); 78.7 (2C, Sacc-*C*); 78.1 (2C, OCH_2); 73.9 (2C, Sacc-*C*); 73.1 (2C, Sacc-*C*); 72.1 (2C, Sacc-*C*); 41.1 (2C, CH_2); 36.6 (2C, CH_2); 36.5 (2C, CH_2); 35.1 (2C, CH_2); 34.2 (2C, CH_2); 34.1 (2C, CH_2); 34.0 (2C, CH_2); 30.9 (2C, CH_2); 27.4 (2C, CH_2); 27 (2C, CH_2); 22.2 (2C, CH_2); 18.9 (2C, CH_3); 18.8 (3C, CH_3). Anal. Calcd for $C_{67}H_{99}N_3O_{13}$: C, 69.70; H, 8.64; N, 3.64. Found: C, 69.82; H, 8.81; N, 3.68%. EI-MS: *m*/*z* calcd for $C_{67}H_{99}N_3O_{13}$ 1153.71, found 1154.80

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