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ARTICLE TYPE

# Synthesis of novel benzimidazole-carbazole-*N*-glycosylamines and their self-assembly into nanofibers

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Novel class of alkyl-benzimidazole-carbazole based *N*-glycosylamines were synthesised in good yield. The identities of the synthesised compounds were confirmed using <sup>1</sup>H and <sup>13</sup>C NMR. Molecular mass of representative samples were also confirmed using MALDI-TOF and EI-mass analysis. From the <sup>1</sup>H, NMR analysis of *N*-glycosylamines the existence of anomeric proton in β-configuration was identified and further supported with <sup>1</sup>H-<sup>1</sup>H COSY and 2D-ROESY NMR analysis of representative sample. All the *N*-glycosylamines were good gelators for aliphatic than aromatic solvents. Out of six gelators synthesised five were identified as super gelator, since they gelates at low CGC (<1%). Representative gel sample was characterized using SEM, HR-TEM, rheology and powder XRD. Microscopic analysis evidenced the self-assembly of *N*-glycosylamines into nanofibers.

## 15 Introduction

As a typical soft materials, gels are an intermediate between solid-liquid and present a particular interest in colloid chemistry and material science.<sup>1</sup> Supramolecular gels were obtained from low molecular weight organic molecules, self-assembled by non-bonding interaction (hydrogen bonding, π-π interaction, van der Waals force *etc.*) are representative class of gels.<sup>2</sup> Supramolecular gels can be functionalized by the introduction of electro- and/or photo-active functional moieties to the gelator.<sup>3</sup> Gels of multiple components forming charge transfer complexes, which arises from supramolecular interactions have also gained greater interest in recent years.<sup>4</sup> Self-assembly is a promising tool for the fabrication of functional molecular materials, which have application in tissue engineering,<sup>5</sup> optoelectronic devices,<sup>6</sup> water purifier,<sup>7</sup> drug delivery system,<sup>8</sup> *etc.* Great effort have been devoted for developing new chemical structures which can self-assemble to form gels with diverse functionality.<sup>9</sup>

Great number of organogelators have been designed and synthesised, which includes perylene, oligo-phenylene, porphyrin, tetrathiafulvalene, carbohydrates, amino acids, *etc.*,<sup>10</sup> and most of them bear long carbon chains or steroidal groups favouring balance between their solubility and crystallization.<sup>11</sup> Gelators without steroidal units or long alkyl chains were also reported, in which self-assembly takes place through π-π interactions and hydrogen bonding.<sup>12</sup> It is well known that carbazole derivatives are typical π-conjugated system which can

self-assembly through π-π interaction to form nano-fibers in the gels state.<sup>13</sup> Carbazoles were also a promising candidate for optoelectronic materials due to its intense luminescence and electron efficiency.<sup>14</sup>

Nano structures based on self-assembly of the organic molecules, such as carbazoles, benzimidazoles, thiophene *etc.*, have become the subject of ever-increasing attention, as a result of their unique optical and optoelectronic properties superior to those of their bulk counterpart.<sup>15</sup> One-dimensional (1D) nano organic materials are more promising building blocks for nano scale devices, such as organic field-effect transistors (OFETs),<sup>16</sup> solar cells<sup>17</sup> and memory devices.<sup>18</sup>

In general synthesis of hybrid organic molecules have greater attraction in recent years due to their enhanced biological and material application.<sup>19,20</sup> Among such hybrid molecules benzimidazoles-carbazoles have significant contribution for the development of novel materials and active pharmaceuticals.<sup>21</sup> Hole-transporting carbazole group and electron-transporting benzimidazole were connected for the construction of high efficient organic light-emitting materials.<sup>22</sup> Huang *et al.*, reported the rare class of benzimidazole-carbazole based blue phosphorescent organic light-emitting diodes (PhOLEDs).<sup>23</sup> Ionic form of benzimidazole-carbazoles were utilized as procarbenic species for the preparation of Ag(I), Au(II) and Au(III) *N*-heterocyclic carbene complexes.<sup>24</sup> Polymer made of benzimidazole and carbazole connected through the thiophene unit were reported for solar cell application.<sup>25</sup> Due to wide application of benzimidazole-carbazoles, they are conjugated with partially protected D-glucose into the designed structure with the view of attaining an efficient gelator material.

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† Electronic supplementary information (ESI) available. <sup>1</sup>H NMR, <sup>13</sup>C NMR, <sup>1</sup>H-<sup>1</sup>H COSY NMR, 2D ROESY NMR, MALDI-TOF and EI Mass spectra.

## Results and discussion

In the present report we have synthesised novel class of benzimidazole-carbazole-*N*-glycosylamines (**14-19**) in good yield, through the *N*-glycosylation protocol of benzimidazole-carbazole amines (**9, 10**) with 4,6-*O*-protected D-glucose derivatives (**11-13**). Benzimidazole-carbazole amines (**9, 10**) were synthesised from *o*-phenylene diamine (**1**) and 9-alkyl-9*H*-carbazole-3-carbaldehyde (**2, 3**) in three steps. All the *N*-glycosylamines (**14-19**) were characterized using <sup>1</sup>H and <sup>13</sup>C NMR. Molecular mass of the representative samples were confirmed using MALDI-TOF and EI mass analysis. Compound **14-19** were subjected to gelation with wide range of solvents and these compounds self-assembly to nanofibers in the gel state. Representative gel sample was studied using analytical techniques, viz., SEM, HR-TEM, rheology and powder XRD.

## Synthesis and characterization

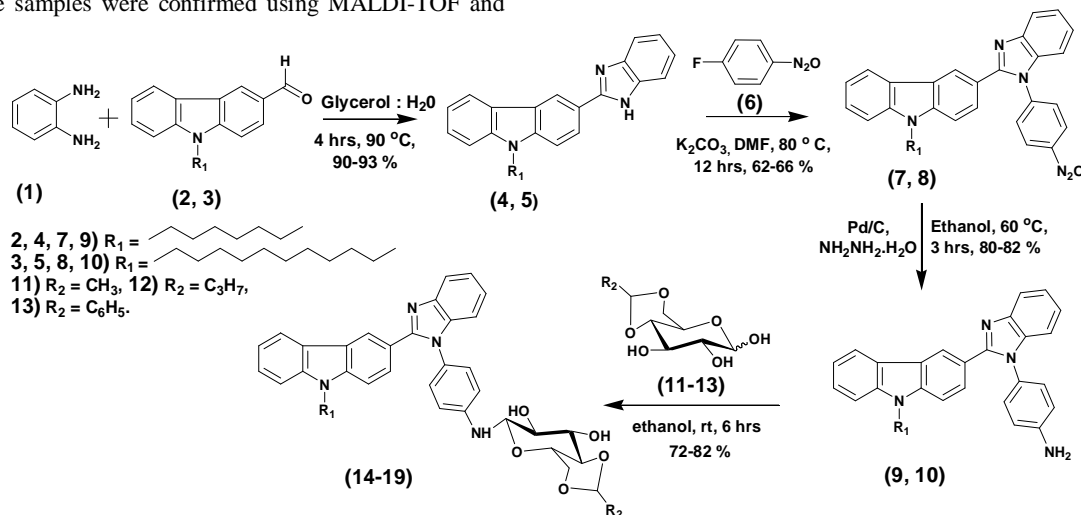
Cyclocondensation cum oxidation of 1,2-diaminobenzene (**1**) with 9-alkyl-9*H*-carbazole-3-carbaldehydes (**2, 3**) in glycerol:water with heating at 90°C for 4 hrs lead to the formation of benzimidazole-carbazoles (**4, 5**) in 90-93 % yield (Scheme 1).<sup>26</sup> Thus obtained benzimidazole-carbazoles (**4, 5**) were arylated with 1-fluoro-4-nitrobenzene (**6**) using K<sub>2</sub>CO<sub>3</sub> as base in DMF and heating the reaction mixture at 80 °C for 12 hrs afforded the 4-nitrophenyl-benzimidazole-carbazole (**7, 8**) in 62-66 % of yield.<sup>27</sup> The 4-nitrophenyl-benzimidazole-carbazole (**7, 8**) was further reduced using Pd/C and hydrazine hydrate to amino-benzimidazole-carbazole (**9, 10**) with yield 80-82 %.<sup>28</sup> The synthesised benzimidazole-carbazole amines (**9, 10**) were characterized using <sup>1</sup>H and <sup>13</sup>C NMR. The *N*-glycosylation of amino-benzimidazole-carbazole (**9, 10**) were carried successfully with three different 4,6-*O*-protected D-glucose derivatives (**11-13**) by conventional methodology (Scheme 1) as reported by Karthik Kumar *et al.*,<sup>29</sup> which resulted in formation of benzimidazole-carbazole-*N*-glycosylamines (**14-19**) with 72-82% of yield (Table 1).

All the synthesized *N*-glycosylamines (**14-19**) were characterized using <sup>1</sup>H and <sup>13</sup>C NMR, molecular mass of representative samples were confirmed using MALDI-TOF and

EI mass analysis. In the <sup>1</sup>H NMR of the benzimidazole-carbazole-*N*-glycosylamines (**14-19**) the signal of aromatic protons appear in the range of 8.49-6.63 ppm. The protons of the sugar unit appear in between 4.90-3.23 ppm and D-glucose unit in all the *N*-glycosylamines was found to exist as β anomers, which was identified by <sup>1</sup>H NMR. The chemical shift of the anomeric protons were found in the range of 4.61-3.76 ppm and their corresponding coupling constant was around 9 Hz, such a larger vicinal coupling constant is due to the trans diaxial orientation of H<sub>1</sub> and H<sub>2</sub> protons. From <sup>1</sup>H-<sup>1</sup>H COSY spectrum of compound **15** the cross peaks at 4.72, 4.60, 3.47 ppm indicates that the anomeric proton couple with H<sub>2</sub> and NH proton of glucose unit and this causes the anomeric proton's multiplicity as triplet. Further the β-configuration of the anomeric proton was confirmed by the NOE experiment (2D-ROESY). NOE cross peaks at 4.60, 3.76, 3.37 and 3.33 ppm shows the NOE contact of the anomeric proton with C<sub>2</sub>OH, H<sub>3</sub> and H<sub>5</sub>, which confirms the axial orientation (β-configuration) of the anomeric proton (See ESI for further details).<sup>30</sup> Alkyl protons of the *N*-glycosylamines (**14-19**) resonate at the range of 1.90-0.78 ppm. The <sup>13</sup>C NMR analysis of *N*-glycosylamines (**14-19**) showed signals in between 153.8-107.1 ppm, which corresponds to carbon atom of benzimidazole-carbazoles and phenyl ring attached to it. Acetal carbon of the 4,6-*O*-protecting unit showed signals in the range 99.7-101.9 ppm. The presence of the saccharide unit was confirmed by the peaks in the range of 86.2-66.2 ppm. The peaks from alkyl carbon occupy the region between 43.3-12.9 ppm. Further molecular mass of the synthesised compounds were confirmed by MALDI-TOF and EI mass analysis as part of study.

**Table 1** Synthesis of benzimidazole-carbazole-*N*-glycosylamines (**14-19**).

Compound	R <sub>1</sub>	R <sub>2</sub>	Yield %
<b>14</b>	C <sub>8</sub> H <sub>17</sub>	CH <sub>3</sub>	72
<b>15</b>	C <sub>8</sub> H <sub>17</sub>	C <sub>3</sub> H <sub>7</sub>	79
<b>16</b>	C <sub>8</sub> H <sub>17</sub>	C <sub>6</sub> H <sub>5</sub>	80
<b>17</b>	C <sub>12</sub> H <sub>25</sub>	CH <sub>3</sub>	79
<b>18</b>	C <sub>12</sub> H <sub>25</sub>	C <sub>3</sub> H <sub>7</sub>	82
<b>19</b>	C <sub>12</sub> H <sub>25</sub>	C <sub>6</sub> H <sub>5</sub>	76



**Scheme 1** Synthesis of benzimidazole-carbazole-*N*-glycosylamines (**14-19**).

### Gelation studies

All the synthesised benzimidazole-carbazole-*N*-glycosylamines (**14-19**) were tested for gelation in different aliphatic (hexane, chloroform, dichloroethane, ethylacetate, ethanol, methanol, *iso*-propyl alcohol) and aromatic solvents (benzene, toluene, dichlorobenzene). The gelation studies were carried out as per the reported procedure.<sup>31</sup> Measured quantity of the gelators (**14-19**) was added to 1 ml of solvent in a glass vial and warmed gently until homogenous solution of the gelator was obtained. 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. Critical gelator concentration (CGC) of benzimidazole-carbazole-*N*-glycosylamines (**14-19**) was determined from the minimum amount of gelator required for gel formation at room temperature. The gelator molecules self-assemble in the gel state to entrap of solvent molecules and make them immobilized. The results of gelation were summarized in Table 2.

Benzimidazole-carbazole-*N*-glycosylamines **15** and **16** were found to gelate both aromatic as well as aliphatic solvents, while other *N*-glycosylamines **14**, **17-19** showed gelation in aliphatic solvents and partial gelation or dissolve in aromatic solvents tested for gelation. Five gelators (**15-19**) can be assigned as super gelators, since they gelate with CGC less than 1%. Ethanol required the least quantity of gelator for its gelation, from these results ethanol was identified as best solvent among the ten solvents used for gelation. *N*-glycosylamine **18** was found to be the best gelator, since it gelates large number of solvents and even shows gelation with lowest CGC of 0.3% in ethanol. Photograph of gel derived from compound **18** in ethanol 0.3 % was shown in Figure 1.

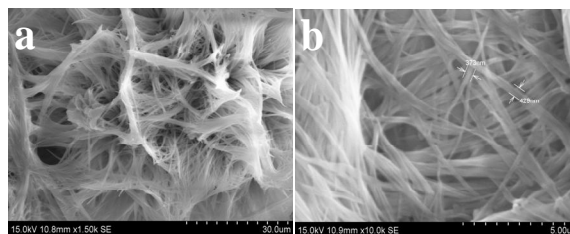
**Table 2** Gelation studies of benzimidazole-carbazole-*N*-glycosylamines (**14-19**).

Compound	Solvent (CGC* %)										
	Hexane	CHCl <sub>3</sub>	DCE	EtOAc	EtOH	MeOH	IPA	C <sub>6</sub> H <sub>6</sub>	C <sub>6</sub> H <sub>5</sub> CH <sub>3</sub>	C <sub>6</sub> H <sub>4</sub> Cl <sub>2</sub>	
<b>14</b>	I	2.5	2.5	PG	1.0	1.5	1.0	PG	PG	PG	
<b>15</b>	I	2.0	S	PG	0.8	1.0	1.5	1.5	PG	S	
<b>16</b>	I	PG	2.0	S	0.5	1.5	0.5	1.0	1.0	PG	
<b>17</b>	PG	1.0	1.0	2.0	0.8	1.0	1.5	PG	PG	S	
<b>18</b>	PG	0.8	1.5	1.0	0.3	0.5	0.5	PG	PG	S	
<b>19</b>	P	1.0	1.5	2.0	0.8	1.0	2.0	S	PG	S	

CGC- Critical gelator concentration, DCE-dichloroethane, EtOAc-ethylacetate, EtOH-ethanol, MeOH-methanol, IPA-*iso*-propyl alcohol, I-insoluble, PG-partial gelation, P-precipitation, S-soluble.

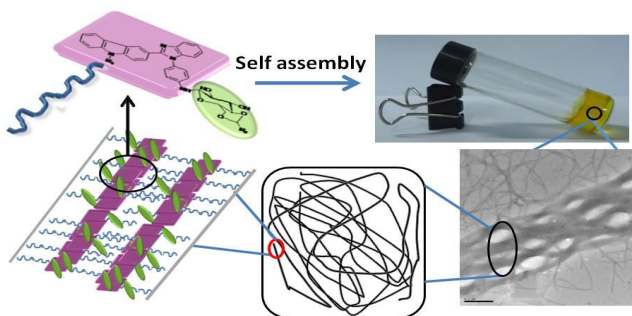
### Morphological studies

The self-assembly of the benzimidazole-carbazole-*N*-glycosylamines in the gel state was studied using microscopic analysis, such as scanning electron microscopic (SEM) and high resolution transmission electron microscopic (HR-TEM) analysis. 0.3 % gel of *N*-glycosylamines **18** in ethanol was prepared and allowed to dry at ambient temperature to obtain xerogel and subjected to SEM analysis.<sup>32</sup> SEM images shows, *N*-glycosylamine **18** self-assemble to fibrous network, thus the gelator trap the solvent molecules and make them immobilized (Figure 2).



**Figure 2** SEM images of 0.3 % gel **18** in ethanol. a) lower magnification (30  $\mu$ m) and b) higher magnification (5  $\mu$ m).

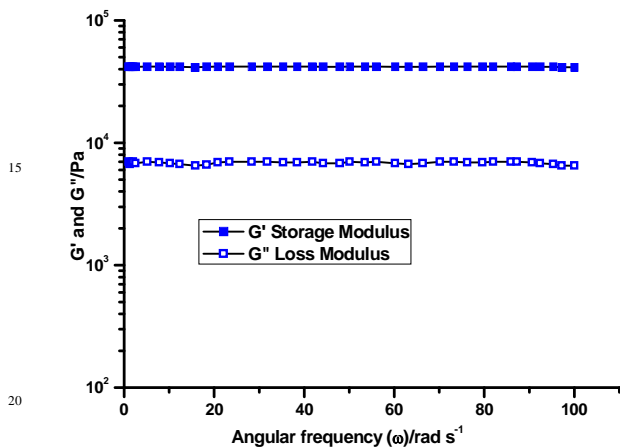
HR-TEM analysis was carried out at concentration of  $1 \times 10^{-4}$  M solution which was obtained by the dispersion of 0.3% ethanolic gel of *N*-glycosylamine **18**.<sup>33</sup> Such a low concentration was used for HR-TEM analysis to obtain good quality of images. HR-TEM analysis of *N*-glycosylamine **18** showed nanofibers at the self-assembled state (Figure 1). Thus SEM and TEM analysis clearly evidence the formation of nanofibers from the self-assembly of the gelator molecules.<sup>34</sup> Schematic representation for self-assembly of the gelator molecules was given in Figure 1.



**Figure 1** Schematic representation for self-assembly of benzimidazole-carbazole-*N*-glycosylamines, photograph of gel **18** (0.3% ethanol) and HR-TEM image of **18** ( $1 \times 10^{-4}$  M, ethanol, 500 nm).

## Rheological Studies

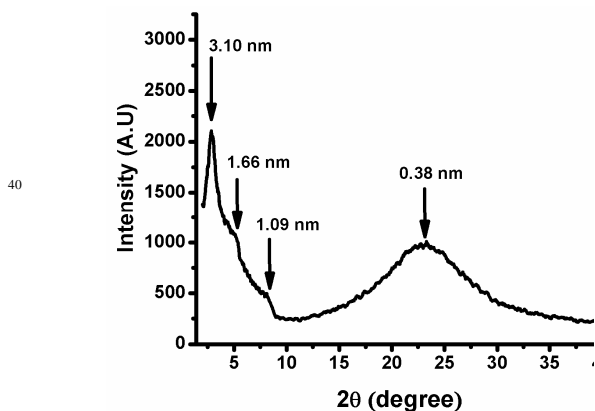
The viscoelastic property of the gel sample was characterized by rheological measurements. Rheological behaviour of gel **18** in ethanol at 0.3 % was shown in Figure 3. The storage modulus ( $G'$ ) and loss modulus ( $G''$ ) of gel **18** are shown as a function of angular frequency at a constant strain of 0.1%. Storage modulus ( $G'$ ) was higher than the loss modulus ( $G''$ ) over the entire measured frequency range (1-100 rad s<sup>-1</sup>). Storage ( $G'$ ) modulus was independent of the angular frequency, these rheological behaviour evidenced the viscoelastic nature of the gel.<sup>35</sup>



**Figure 3** Angular frequency sweep ( $\omega$ ) dependencies of dynamic storage ( $G'$ ) and loss modulus ( $G''$ ) of 0.3 % w/v **18** gel in ethanol.

## Powder XRD analysis

In order to study the molecular packing structures of the gel fibers, powder XRD (wide angle X-ray diffraction) study was performed on the xerogel of *N*-glycosylamine **18** obtained from ethanol at concentration of 1%. A sharp peak at low angle 2.85° ( $2\theta$ ) with interlayer distance of 3.10 nm (Figure 4) arises from the packing of the long alkyl chain due to van der Waals interactions.<sup>36</sup> The diffraction in the wide-angle region around 23.10° ( $2\theta$ ) gives a very broad peak with an interlayer distance of 0.38 nm which is due to the  $\pi$ - $\pi$  stacking of the benzimidazole-carbazole unit in the self-assembled state. In addition less intense diffraction pattern at  $2\theta = 5.32^\circ$ ,  $8.08^\circ$  with interlayer distance of

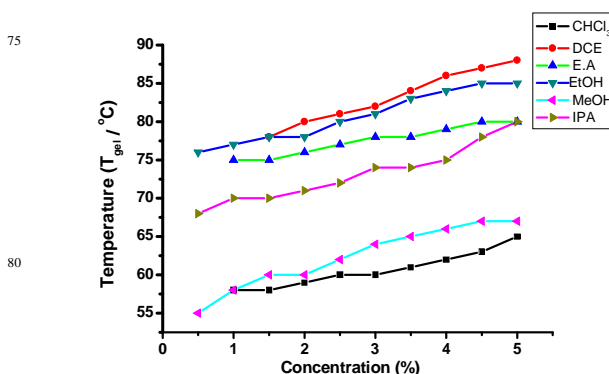


**Figure 4** Powder XRD graph of gel **18** in ethanol (1%).

1.66 nm and 1.09 nm were observed this pattern shows the crystalline nature of the *N*-glycosylamine **18** in the gel state. Thus the powder XRD analysis confirms the self-assembly of the molecules in the gel state arises also from  $\pi$ - $\pi$  stacking, van der Waals force.<sup>37</sup>

## Thermal Stability

The main characteristic property of supramolecular gels is thermo-reversible gel-to-sol and *vice versa* transition that occurs by self-assembly and dis-assembly processes. This thermo-reversibility made them as more compactable for wide range of applications. Depending on the application both responsiveness and stability towards heat are equally important. Gel-to-sol transition temperature ( $T_{gel}$ ) of the gels has been determined using “dropping ball method”.<sup>38</sup> Thermal stability of the gels were measured using the plot of  $T_{gel}$  Vs concentration. The thermal stability of benzimidazole-carbazole-*N*-glycosylamine **18** was studied in various solvents, such as CHCl<sub>3</sub>, dichloroethane, ethyl acetate, ethanol, methanol and *iso*-propyl alcohol. From the concentration dependent  $T_{gel}$  plot (Figure 5) it was concluded that gels of compound, **18** is thermally stable in all the solvents it studied. There was steady increase in the  $T_{gel}$  value as the concentration of the gelator increases. Gel to solution transition was observed even at temperature higher than their boiling point, while *iso*-propyl alcohol gels alone shows gel to solution transition nearer the boiling point. Such a good thermal stability for the gels was attained from the solvent-gelator and gelator-gelator non-bonding interactions.



**Figure 5** Concentration dependent  $T_{gel}$  plot of benzimidazole-carbazole-*N*-glycosylamines **18** in different solvents.

## Conclusion

Alkyl-benzimidazole-carbazole-*N*-glycosylamines were synthesized in good yield using *N*-glycosylation of 4,6-*O*-protected-D-glucose with benzimidazole-carbazole amines. All the synthesised compounds were characterized using <sup>1</sup>H and <sup>13</sup>C NMR and representative samples were also subjected to MALDI-TOF and EI mass analysis to confirm their molecular mass.  $\beta$ -anomeric form of the *N*-glycosylamines was identified with <sup>1</sup>H NMR, and supported with <sup>1</sup>H-<sup>1</sup>H COSY and NOE (2D-ROESY) NMR analysis. *N*-glycosylamines were identified as good gelators for aliphatic than aromatic solvents. Five *N*-glycosylamines were assigned as super gelator, since they gelate at low critical gelator concentration (<1%). Microscopic analysis

of representative showed that the synthesised compounds can self-assemble to nanofibers in the gel state.

## Experimental section

### 5 Materials

1,2-Diaminobenzene, carbazole, bromooctane, bromododecane, palladium/carbon 10%, 1-fluoro-4-nitrobenzene, paraldehyde, butyraldehyde, benzaldehyde-dimethylacetal were purchased from Sigma Aldrich chemicals  
 10 Pvt. Ltd. USA. Hydrazine hydrate, glycerol, con. hydrochloric acid, con. sulphuric acid, potassium carbonate, D-glucose, ethanol and other solvents for gelation were purchased from SRL India Ltd., were of high purity and used without further purification. Column chromatography was performed on silica gel (100-200  
 15 mesh). NMR spectra were recorded on a Bruker DRX 300 MHz instrument in CDCl<sub>3</sub> (with a few drops of DMSO-D<sub>6</sub>). Chemical shifts are referenced to internal TMS.

### General procedure for synthesis of 3-(1*H*-benzo[d]imidazol-2-yl)-9-octyl-9*H*-carbazoles (4).

20 To the stirred solution of 1,2-diaminobenzene **1** (1.08 g, 10 mmol) in water (10 ml), about 30 ml of glycerol was added and the temperature of the reaction mixture was slowly raised to 90°C followed by the addition of 9-octyl-9*H*-carbazole-3-aldehyde **2** (3.07 g, 10 mmol). The reaction mixture was stirred at 90 °C for  
 25 further 4 hrs. After confirming the completion of the reaction through thin layer chromatography (TLC). The reaction mixture was poured into the ice cold water and extracted with chloroform; the organic layer was separated, dried over anhydrous sodium sulfate and concentrated under reduced pressure to get the crude  
 30 product. Thus obtained crude product was further purified by silica gel column chromatography using hexane/ethyl acetate (70:30). 3-(1*H*-benzo[d]imidazol-2-yl)-9-octyl-9*H*-carbazoles (**4**) was obtained as a pale yellow solid in good yield (3.67 g, 93 %). Melting point: 135 °C. <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub> + DMSO-D<sub>6</sub>)  
 35 : δ<sub>H</sub> ppm 8.98(s, 1H, Ar-*H*), 8.33(d, *J* = 8.4 Hz, 1H, Ar-*H*), 8.15(d, *J* = 7.5 Hz, 1H, Ar-*H*), 7.68(m, 7.68-7.64, 2H, Ar-*H* & NH), 7.53(d, *J* = 8.7, 1H, Ar-*H*), 7.50(m, 7.50-7.45, 3H, Ar-*H*), 7.30(m, 7.30-7.24, 1H, Ar-*H*), 7.22(m, 7.22-7.19, 2H, Ar-*H*), 4.35 (t, *J* = 6.9 Hz, 2H, NCH<sub>2</sub>), 1.89(t, *J* = 6.6 Hz, 2H, CH<sub>2</sub>),  
 40 1.45(m, 1.45-1.40, 2H, CH<sub>2</sub>), 1.36(m, 1.36-1.25, 8H, CH<sub>2</sub>), 0.86(t, *J* = 6.6 Hz, 3H, CH<sub>3</sub>). <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub> + DMSO-D<sub>6</sub>) : δ<sub>C</sub> 152.3(1C, Ar-C), 140.3(2C, Ar-C), 140.0(2C, Ar-C), 125.2(2C, Ar-C), 123.8(2C, Ar-C), 122.1(1C, Ar-C), 121.9(1C, Ar-C), 121.0(2C, Ar-C), 120.1(1C, Ar-C), 119.6(1C,  
 45 Ar-C), 118.5(1C, Ar-C), 118.4(1C, Ar-C), 108.2(1C, Ar-C), 108.0(2C, Ar-C), 42.3(1C, N-CH<sub>2</sub>), 30.7(1C, CH<sub>2</sub>), 28.3(1C, CH<sub>2</sub>), 28.1(1C, CH<sub>2</sub>), 28.0(1C, CH<sub>2</sub>), 26.2(1C, CH<sub>2</sub>), 21.6(1C, CH<sub>2</sub>), 13.1(1C, CH<sub>3</sub>).

### 3-(1*H*-benzo[d]imidazol-2-yl)-9-dodecyl-9*H*-carbazoles (5).

50 By following the synthetic procedure for compound **4**, compound **5** was synthesised from the reaction of 1,2-diaminobenzene **1** (1.08 g, 10 mmol) with 9-dodecyl-9*H*-carbazole-3-aldehyde **3** (3.63 g, 10 mmol) as a pale yellow solid in good yield (4.06 g, 90 %). Melting point: 153 °C. <sup>1</sup>H NMR  
 55 (300 MHz, CDCl<sub>3</sub>+ DMSO-D<sub>6</sub>) : δ<sub>H</sub> 8.91(s, 1H, Ar-*H*),

8.31(d, *J* = 8.7 Hz, 1H, Ar-*H*), 8.15(d, *J* = 7.8 Hz, 1H, Ar-*H*), 7.65(m, 7.65-7.62, 2H, Ar-*H*), 7.59(s, 1H, NH), 7.53(m, 7.53-7.47, 3H, Ar-*H*), 7.28(t, *J* = 6.6 Hz, 1H, Ar-*H*), 7.23(m, 7.23-7.19, 2H, Ar-*H*), 4.34(t, *J* = 7.2 Hz, 2H, NCH<sub>2</sub>), 1.90(m, 1.90-1.86, 2H, CH<sub>2</sub>), 1.43(m, 1.43-1.35, 2H, CH<sub>2</sub>), 1.30(m, 1.30-1.22, 16H, CH<sub>2</sub>), 0.85(t, *J* = 6.3 Hz, 3H, CH<sub>3</sub>). <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub> + DMSO-D<sub>6</sub>) : δ<sub>C</sub> 152.5(1C, Ar-C), 140.5(1C, Ar-C), 140.1(1C, Ar-C), 125.4(1C, Ar-C), 123.9(1C, Ar-C), 122.2(1C, Ar-C), 121.9(1C, Ar-C), 121.1(2C, Ar-C), 120.2(1C, Ar-C),  
 65 119.7(2C, Ar-C), 118.6(2C, Ar-C), 118.5(2C, Ar-C), 108.4(1C, Ar-C), 108.2(2C, Ar-C), 42.4(1C, N-CH<sub>2</sub>), 31.0(2C, CH<sub>2</sub>), 28.6(1C, CH<sub>2</sub>), 28.7(2C, CH<sub>2</sub>), 28.5(1C, CH<sub>2</sub>), 28.4(1C, CH<sub>2</sub>), 28.1(1C, CH<sub>2</sub>), 26.4(1C, CH<sub>2</sub>), 21.8(1C, CH<sub>2</sub>), 13.4(1C, CH<sub>3</sub>).

### General procedure for synthesis of 3-(1-(4-nitrophenyl)-1*H*-benzo[d]imidazol-2-yl)-9-octyl-9*H*-carbazoles (7).

3-(1*H*-benzo[d]imidazol-2-yl)-9-octyl-9*H*-carbazoles **4** (3.16 g, 8 mmol) and potassium carbonate (2.21 g, 16 mmol) were stirred at room temperature in 30 ml of dry DMF for 0.5 hrs, to which 1-fluoro-4-nitrobenzene **6** (1.25 ml, 12 mmol) was added  
 75 and the temperature of the reaction mixture was slowly raised to 80 °C and heating was continued for further 12 hrs. After completion of the reaction the DMF was removed through evaporation at reduced pressure. To the concentrated reaction mixture ice cold water was added and extracted with ethyl acetate  
 80 thrice. Organic phase was separated and collected together, then dried over anhydrous sodium sulfate and concentrated at reduced pressure. The crude product thus obtained was purified using silica gel chromatography in Hexane/ ethylacetate (90:10) to obtain the pure 3-(1-(4-nitrophenyl)-1*H*-benzo[d]imidazol-2-yl)-  
 85 9-octyl-9*H*-carbazole (**7**) as yellow solid with the yield of 2.56 g (62%). Melting Point : 124 °C. <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>) : δ<sub>H</sub> 8.43(s, 1H, Ar-*H*), 8.35(d, *J* = 9 Hz, 2H, Ar-*H*), 7.99(d, *J* = 7.8 Hz, 1H, Ar-*H*), 7.94(d, *J* = 7.8 Hz, 1H, Ar-*H*), 7.55(d, *J* = 9 Hz, 2H, Ar-*H*), 7.51(d, *J* = 8.7, 1H, Ar-*H*), 7.48(m, 7.47-7.39, 3H, Ar-*H*), 7.36(m, 7.36-7.31, 2H, Ar-*H*), 7.28(m, 7.28-7.22, 2H, Ar-*H*), 4.27(t, *J* = 7.2 Hz, 2H, NCH<sub>2</sub>), 1.86(t, *J* = 6.6 Hz, 2H, CH<sub>2</sub>),  
 90 1.33(m, 1.33-1.24, 10H, CH<sub>2</sub>), 0.86(t, *J* = 6.9 Hz, 3H, CH<sub>3</sub>). <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>) : δ<sub>C</sub> 153.8(1C, Ar-C), 146.6(1C, Ar-C), 142.9(1C, Ar-C), 140.9(2C, Ar-C), 128.7(1C, Ar-C), 128.2(2C, Ar-C), 127.0(2C, Ar-C), 126.0(1C, Ar-C), 123.0(2C, Ar-C),  
 95 122.6(1C, Ar-C), 122.1(1C, Ar-C), 120.6(2C, Ar-C), 119.4(1C, Ar-C), 119.3(1C, Ar-C), 119.2(1C, Ar-C), 115.8(2C, Ar-C), 110.4(1C, Ar-C), 108.9(1C, Ar-C), 108.3(1C, Ar-C), 43.2(1C, N-CH<sub>2</sub>), 31.8(2C, CH<sub>2</sub>), 29.3(1C, CH<sub>2</sub>), 29.2(1C, CH<sub>2</sub>), 29.0(1C,  
 100 CH<sub>2</sub>), 27.3(1C, CH<sub>2</sub>), 22.6(1C, CH<sub>2</sub>), 14.0(1C, CH<sub>3</sub>).

### 3-(1-(4-nitrophenyl)-1*H*-benzo[d]imidazol-2-yl)-9-dodecyl-9*H*-carbazoles (8).

Compound **8** was synthesised using the similar procedure of compound **7** from the reaction of 3-(1*H*-benzo[d]imidazol-2-yl)-  
 105 9-dodecyl-9*H*-carbazoles, **5** (3.61 g, 8 mmol) with 4-fluoro nitrobenzene, **6** (1.25 ml, 12 mmol) using potassium carbonate (2.21 g, 16 mmol) as base in DMF as yellow solid with the yield of 3.01 g (66 %), Melting point: 146 °C. <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>) : δ<sub>H</sub> 8.43(s, 1H, Ar-*H*), 8.33(d, *J* = 8.7 Hz, 2H, Ar-*H*),  
 110 7.99(d, *J* = 7.8 Hz, 1H, Ar-*H*), 7.93(d, *J* = 7.8 Hz, 1H, Ar-*H*), 7.53(d, *J* = 8.7 Hz, 2H, Ar-*H*), 7.47(d, *J* = 7.2 Hz, 1H, Ar-*H*), 7.42(m, 7.42-7.39, 3H, Ar-*H*), 7.32(m, 7.32-7.30, 2H, Ar-*H*),

7.29(m, 7.29-7.26, 1H, Ar-H), 7.25(m, 7.24-7.21, 1H, Ar-H), 4.25(t,  $J = 7.5$  Hz, 2H,  $NCH_2$ ), 1.87(m, 1.87-1.82, 2H,  $CH_2$ ), 1.33(m, 1.33-1.24, 18H,  $CH_2$ ), 0.86(t,  $J = 6.0$  Hz, 3H,  $CH_3$ ).  $^{13}C$  NMR (75 MHz,  $CDCl_3$ ):  $\delta_C$  153.6(1C, Ar-C), 146.8(1C, Ar-C), 143.2(1C, Ar-C), 141.1(1C, Ar-C), 140.9(1C, Ar-C), 136.3(1C, Ar-C), 128.1(2C, Ar-C), 126.8(1C, Ar-C), 126.4(1C, Ar-C), 125.3(2C, Ar-C), 123.6(1C, Ar-C), 123.1(1C, Ar-C), 122.6(1C, Ar-C), 122.3(1C, Ar-C), 120.0(1C, Ar-C), 119.7(2C, Ar-C), 119.4(1C, Ar-C), 109.8(1C, Ar-C), 109.1(1C, Ar-C), 108.6(1C, Ar-C), 43.3(1C, N- $CH_2$ ), 31.8(1C,  $CH_2$ ), 29.3(2C,  $CH_2$ ), 29.2(1C,  $CH_2$ ), 29.0(2C,  $CH_2$ ), 27.3(1C,  $CH_2$ ), 22.6(2C,  $CH_2$ ), 22.4(1C,  $CH_2$ ), 14.1(1C,  $CH_3$ ).

#### General procedure for synthesis of 3-(1-(4-aminophenyl)-1H-benzo[d]imidazol-2-yl)-9-octyl-9H-carbazoles (**9**).

Nitro derivative of benzimidazole-carbazoles (**7**) was reduced to its corresponding amino derivative (**9**) using Pd/C, hydrazine hydrate in ethanol. To the stirred solution of nitro benzimidazole-carbazole, **7** (2.31 g, 4.5 mmol) at room temperature in 20 ml ethanol 0.2 g of palladium carbon (10 %) was added and temperature was raised to 50 °C. To this solution 6 ml of hydrazine hydrate 80 % dissolved in 12 ml of ethanol was added slowly and the reaction mixture was refluxed for 3 hrs and its was filtered over celite at hot condition to remove Pd/C catalyst. The filtrate was evaporated under reduced pressure to dryness and purified by silica gel column chromatography in Hexane/ethylacetate (80:20). Alkyl benzimidazole-carbazole amine, **9** was obtained as milky white solid with yield of 1.90 g (82 %). Melting point: 186 °C.  $^1H$  NMR (300 MHz,  $CDCl_3$ ):  $\delta_H$  8.48(s, 1H, Ar-H), 7.99(d,  $J = 7.8$  Hz, 1H, Ar-H), 7.89(d,  $J = 7.8$  Hz, 1H, Ar-H), 7.68(d,  $J = 6.9$  Hz, 1H, Ar-H), 7.49(m, 7.49-7.44, 1H, Ar-H), 7.40(m, 7.40-7.35, 1H, Ar-H), 7.32(m, 7.32-7.30, 2H, Ar-H), 7.27(m, 7.27-7.23, 3H, Ar-H), 7.15(d,  $J = 8.4$  Hz, 2H, Ar-H), 6.77(d,  $J = 8.4$  Hz, 2H, Ar-H), 4.26(t,  $J = 7.2$  Hz, 2H,  $NCH_2$ ), 3.88(s, 2H,  $NH_2$ ), 1.85(t,  $J = 6.6$  Hz, 2H,  $CH_2$ ), 1.34(m, 1.34-1.24, 10H,  $CH_2$ ), 0.86(t,  $J = 6.6$  Hz, 3H,  $CH_3$ ).  $^{13}C$  NMR (75 MHz,  $CDCl_3$ ):  $\delta_C$  153.8(1C, Ar-C), 146.6(1C, Ar-C), 143.0(1C, Ar-C), 140.8(2C, Ar-C), 138.0(1C, Ar-C), 128.6(1C, Ar-C), 128.0(2C, Ar-C), 127.0(1C, Ar-C), 126.0(1C, Ar-C), 123.0(2C, Ar-C), 122.7(1C, Ar-C), 122.5(1C, Ar-C), 122.1(1C, Ar-C), 120.7(1C, Ar-C), 120.6(1C, Ar-C), 119.3(2C, Ar-C), 115.7(2C, Ar-C), 110.4(1C, Ar-C), 108.9(1C, Ar-C), 108.3(1C, Ar-C), 43.2(1C, N- $CH_2$ ), 31.8(1C,  $CH_2$ ), 29.3(1C,  $CH_2$ ), 29.2(1C,  $CH_2$ ), 29.0(1C,  $CH_2$ ), 27.3(1C,  $CH_2$ ), 22.6(1C,  $CH_2$ ), 14.0(1C,  $CH_3$ ).

#### 3-(1-(4-aminophenyl)-1H-benzo[d]imidazol-2-yl)-9-dodecyl-9H-carbazoles (**10**).

Compound **10** was synthesised using the similar procedure of compound **9** from the reduction of 3-(1-(4-nitrophenyl)-1H-benzo[d]imidazol-2-yl)-9-dodecyl-9H-carbazoles, **8** (2.57 g, 4.5 mmol) using 0.2 g palladium carbon 10 % and 6 ml of hydrazine hydrate 80 % resulted in the formation of amino dodecyl derivative **10** as milky white solid with yield of 1.95 g (80 %). Melting point : 192 °C.  $^1H$  NMR (300 MHz,  $CDCl_3$ ):  $\delta_H$  8.40(s, 1H, Ar-H), 7.90(d,  $J = 7.8$  Hz, 1H, Ar-H), 7.81(d,  $J = 7.8$  Hz, 1H, Ar-H), 7.58(d,  $J = 8.1$  Hz, 1H, Ar-H), 7.39(m, 7.39-7.36, 1H, Ar-H), 7.34(m, 7.34-7.20, 3H, Ar-H), 7.17(m, 7.17-7.10, 3H, Ar-H), 7.03(d,  $J = 8.4$  Hz, 2H, Ar-H), 6.65(d,  $J = 8.4$  Hz, 2H, Ar-H), 4.14(t,  $J = 7.2$  Hz, 2H,  $NCH_2$ ), 3.78(s, 2H,  $NH_2$ ), 1.76(m, 1.76-

1.72, 2H,  $CH_2$ ), 1.39(m, 1.39-1.15, 18H,  $CH_2$ ), 0.78(t,  $J = 6.3$  Hz, 3H,  $CH_3$ ).  $^{13}C$  NMR (75 MHz,  $CDCl_3$ ):  $\delta_C$  153.8(1C, Ar-C), 146.7(1C, Ar-C), 143.0(1C, Ar-C), 140.8(2C, Ar-C), 138.0(1C, Ar-C), 128.6(1C, Ar-C), 128.0(1C, Ar-C), 127.0(1C, Ar-C), 126.0(1C, Ar-C), 122.9(1C, Ar-C), 122.7(2C, Ar-C), 122.6(1C, Ar-C), 122.1(1C, Ar-C), 120.6(1C, Ar-C), 119.3(3C, Ar-C), 115.7(2C, Ar-C), 110.5(1C, Ar-C), 108.9(1C, Ar-C), 108.3(1C, Ar-C), 43.2(1C, N- $CH_2$ ), 31.9(1C,  $CH_2$ ), 29.6(2C,  $CH_2$ ), 29.5(2C,  $CH_2$ ), 29.4(2C,  $CH_2$ ), 29.3(1C,  $CH_2$ ), 29.0(1C,  $CH_2$ ), 27.3(1C,  $CH_2$ ), 22.7(1C,  $CH_2$ ), 14.2(1C,  $CH_3$ ).

#### General procedure for synthesis of 1(2(9-octyl-carbazol-3-yl)-benzimidazol-1-yl)phenylamino-4(4,6-O-ethylidene-D-glucose) (**14**).

To the stirred solution of 1 mmol (0.21 g) of 4,6-O-ethylidene-D-glucose, **11** in 5 ml of ethanol, 1 mmol (0.49 g) of octyl-benzimidazole-carbazole amines, **9** was added. The reaction mixture was stirred at 50 °C for 10 min and at room temperature for 6 hrs. The reaction was monitored through TLC. The solid *N*-glycosylamine (**14**) which separated was filtered off, washed with ethanol and dried with ether. Thus octyl-benzimidazole-carbazole-ethylidene-*N*-glycosylamine, **14** was obtained as a pale yellow solid with the yield of 0.49 g (72 %). *N*-glycosylamine **14** was of satisfactory purity and characterized using  $^1H$  and  $^{13}C$  NMR. Melting point: 188 °C.  $^1H$  NMR (300 MHz,  $CDCl_3$ ):  $\delta_H$  8.48(s, 1H, Ar-H), 7.99(d,  $J = 7.8$  Hz, 1H, Ar-H), 7.88(d,  $J = 7.8$  Hz, 1H, Ar-H), 7.55(d,  $J = 8.1$  Hz, 1H, Ar-H), 7.45(m, 7.45-7.42, 1H, Ar-H), 7.38(m, 7.38-7.36, 1H, Ar-H), 7.33(m, 7.33-7.31, 1H, Ar-H), 7.28(m, 7.28-7.26, 2H, Ar-H & Sacc-OH), 7.23(m, 7.23-7.20, 3H, Ar-H), 7.15(d,  $J = 8.7$  Hz, 2H, Ar-H), 6.77(d,  $J = 8.7$  Hz, 2H, Ar-H), 4.73(s, 1H, Gly-NH), 4.71(s, 1H, Sacc-OH), 4.24(m, 4.24-4.15, 4H,  $NCH_2$ , Ace-H & Sacc-H), 3.82(t,  $J = 9$  Hz, 1H, Ano-H), 3.55(m, 3.55-3.49, 3H, Sacc-H), 3.44(m, 3.44-3.43, 1H, Sacc-H), 3.37(m, 3.37-3.34, 1H, Sacc-H), 1.82(m, 1.82-1.80, 2H,  $CH_2$ ), 1.39(m, 1.39-1.36, 5H,  $CH_2$  &  $CH_3$ ), 1.28(m, 1.28-1.23, 8H,  $CH_2$ ), 0.85(t,  $J = 6.6$  Hz, 3H,  $CH_3$ ).  $^{13}C$  NMR (75 MHz,  $CDCl_3$ ):  $\delta_C$  153.8(1C, Ar-C), 145.6(1C, Ar-C), 142.6(1C, Ar-C), 140.9(2C, Ar-C), 137.6(1C, Ar-C), 128.7(1C, Ar-C), 128.4(2C, Ar-C), 126.9(1C, Ar-C), 126.2(1C, Ar-C), 122.9(2C, Ar-C), 122.8(1C, Ar-C), 122.1(1C, Ar-C), 120.6(1C, Ar-C), 120.0(1C, Ar-C), 119.5(2C, Ar-C), 119.0(1C, Ar-C), 115.2(1C, Ar-C), 110.5(1C, Ar-C), 108.9(1C, Ar-C), 108.4(1C, Ar-C), 99.7(1C, Ace-C), 86.0(1C, Ano-C), 74.3(1C, Sacc-C), 74.2(1C, Sacc-C), 68.3(1C, Sacc-C), 67.3(1C, Sacc-C), 43.2(1C, N- $CH_2$ ), 31.8(1C,  $CH_2$ ), 29.3(1C,  $CH_2$ ), 29.2(1C,  $CH_2$ ), 28.9(1C,  $CH_2$ ), 27.3(1C,  $CH_2$ ), 22.6(1C,  $CH_2$ ), 20.3(1C,  $CH_3$ ), 14.1(1C,  $CH_3$ ).

#### 1(2(9-octyl-carbazol-3-yl)-benzimidazol-1-yl)phenylamino-4(4,6-O-butylidene-D-glucose) (**15**).

Octyl-benzimidazole-carbazole-butylidene-*N*-glycosylamine, **15** was synthesised by adopting the same procedure of compound **14**. The reaction of 4,6-O-butylidene D-glucose, **12** (1 mmol, 0.23 g) with octyl-benzimidazole-carbazole amine, **9** (1 mmol, 0.49 g) resulted in the formation of compound **15** as a pale yellow solid. Yield: 79 % (0.56 g). Melting point: 197 °C.  $^1H$  NMR (300 MHz,  $CDCl_3$ ):  $\delta_H$  8.41(s, 1H, Ar-H), 7.91(d,  $J = 7.5$  Hz, 1H, Ar-H), 7.81(d,  $J = 7.2$  Hz, 1H, Ar-H), 7.46(d,  $J = 8.4$  Hz, 1H, Ar-H), 7.36(t,  $J = 7.2$  Hz, 1H, Ar-H), 7.30(s, 1H, Ar-H), 7.26(d,  $J = 5.7$

Hz, 1H, Ar-H), 7.23(m, 7.23-7.20, 1H, Ar-H), 7.18(m, 7.18-7.10, 3H, Ar-H & Sacc-OH), 7.04(d,  $J = 8.1$  Hz, 2H, Ar-H), 6.65(d,  $J = 8.1$  Hz, 2H, Ar-H), 4.72(d,  $J = 5.1$  Hz, 1H, Gly-NH), 4.60(t,  $J = 9$  Hz, 1H, Ano-H), 4.45(t,  $J = 4.8$  Hz, 1H, Ace-H), 4.15(m, 4.15-4.05, 4H, NCH<sub>2</sub> & Sacc-H), 3.76(t,  $J = 6.6$  Hz, 1H, Sacc-H), 3.47(t,  $J = 6.6$  Hz, 1H, Sacc-H), 3.37(m, 3.37-3.23, 3H, Sacc-H & OH), 1.73(m, 1.73-1.71, 2H, CH<sub>2</sub>), 1.57(m, 1.57-1.54, 2H, CH<sub>2</sub>), 1.35(m, 1.35-1.30, 2H, CH<sub>2</sub>), 1.23(m, 1.23-1.15, 10H, CH<sub>2</sub>), 0.86(m, 0.86-0.81, 3H, CH<sub>3</sub>), 0.80(m, 0.80-0.75, 3H, CH<sub>3</sub>).

<sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>):  $\delta_C$  152.8(1C, Ar-C), 144.5(1C, Ar-C), 141.6(1C, Ar-C), 139.8(2C, Ar-C), 136.7(1C, Ar-C), 127.9(1C, Ar-C), 127.5(3C, Ar-C), 125.9(1C, Ar-C), 125.1(1C, Ar-C), 121.8(3C, Ar-C), 121.1(1C, Ar-C), 119.6(1C, Ar-C), 119.2(1C, Ar-C), 118.4(2C, Ar-C), 118.1(1C, Ar-C), 114.2(1C, Ar-C), 109.5(1C, Ar-C), 107.9(1C, Ar-C), 107.4(1C, Ar-C), 101.5(1C, Ace-C), 85.0(1C, Ano-C), 79.1(1C, Sacc-C), 73.4(1C, Sacc-C), 73.1(1C, Sacc-C), 67.3(1C, Sacc-C), 66.5(1C, Sacc-C), 42.2(1C, N-CH<sub>2</sub>), 35.2(1C, CH<sub>2</sub>), 30.7(1C, CH<sub>2</sub>), 28.3(1C, CH<sub>2</sub>), 28.1(1C, CH<sub>2</sub>), 27.9(1C, CH<sub>2</sub>), 26.3(1C, CH<sub>2</sub>), 21.6(1C, CH<sub>2</sub>), 16.4(1C, CH<sub>2</sub>), 13.0(1C, CH<sub>3</sub>), 12.9(1C, CH<sub>3</sub>). MALDI-TOF:  $m/z$  calcd for C<sub>43</sub>H<sub>50</sub>N<sub>4</sub>O<sub>5</sub> **702.87**, found **703.91** (M+H).

**1(2(9-octyl-carbazol-3-yl)-benzimidazol-1-yl)phenylamino-4(4,6-O-benzylidene-D-glucose) (16).**

Octyl-benzimidazole-carbazole-benzylidene-*N*-glycosylamine, **16** was synthesised by adopting the same procedure of compound **14**. The reaction of 4,6-*O*-benzylidene D-glucose, **13** (1 mmol, 0.29 g) with octyl-benzimidazole-carbazole amine, **9** (1 mmol, 0.49 g) resulted in the formation of compound **16** as pale yellow solid. Yield: 80 % (0.60 g). Melting point: 205 °C. <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>):  $\delta_H$  8.49(s, 1H, Sacc-OH), 8.45(s, 1H, Ar-H), 8.34(d,  $J = 8.7$  Hz, 1H, Ar-H), 8.00(m, 8.00-7.96, 1H, Ar-H), 7.92(m, 7.92-7.87, 1H, Ar-H), 7.56(m, 7.56-7.51, 3H, Ar-H), 7.49(m, 7.49-7.45, 3H, Ar-H), 7.42(m, 7.42-7.38, 2H, Ar-H), 7.35(m, 7.35-7.20, 4H, Ar-H), 7.14(d,  $J = 8.7$  Hz, 2H, Ar-H), 6.75(d,  $J = 8.7$  Hz, 2H, Ar-H), 4.72(s, 1H, Gly-NH), 4.70(s, 1H, Sacc-OH), 4.24(m, 4.24-4.19, 4H, NCH<sub>2</sub>, Ace-H & Sacc-H), 3.85(t,  $J = 8.7$  Hz, 1H, Ano-H), 3.58(m, 3.58-3.48, 2H, Sacc-H), 3.45(m, 3.45-3.40, 1H, Sacc-H), 3.37(m, 3.37-3.31, 1H, Sacc-H), 1.84(m, 1.84-1.82, 2H, CH<sub>2</sub>), 1.37(m, 1.37-1.35, 4H, CH<sub>2</sub>), 1.29(m, 1.29-1.25, 6H, CH<sub>2</sub>), 0.84(t,  $J = 5.4$  Hz, 3H, CH<sub>3</sub>).

<sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>):  $\delta_C$  153.7(1C, Ar-C), 146.7(1C, Ar-C), 142.4(1C, Ar-C), 140.9(1C, Ar-C), 137.6(1C, Ar-C), 137.0(1C, Ar-C), 129.6(2C, Ar-C), 128.6(1C, Ar-C), 128.3(1C, Ar-C), 126.9(1C, Ar-C), 126.3(1C, Ar-C), 126.2(1C, Ar-C), 122.9(1C, Ar-C), 122.8(2C, Ar-C), 122.1(2C, Ar-C), 120.6(1C, Ar-C), 120.0(1C, Ar-C), 119.5(2C, Ar-C), 119.0(1C, Ar-C), 115.7(1C, Ar-C), 115.1(2C, Ar-C), 110.6(1C, Ar-C), 109.0(1C, Ar-C), 108.5(1C, Ar-C), 101.9(1C, Ace-C), 86.1(1C, Ano-C), 80.7(1C, Sacc-C), 74.3(1C, Sacc-C), 74.0(1C, Sacc-C), 67.3(2C, Sacc-C), 43.2(1C, N-CH<sub>2</sub>), 31.8(1C, CH<sub>2</sub>), 29.3(1C, CH<sub>2</sub>), 29.2(1C, CH<sub>2</sub>), 28.9(1C, CH<sub>2</sub>), 27.3(1C, CH<sub>2</sub>), 22.6(1C, CH<sub>2</sub>), 14.1(1C, CH<sub>3</sub>).

EI-MS:  $m/z$  calcd for C<sub>46</sub>H<sub>48</sub>N<sub>4</sub>O<sub>5</sub> **736.36**, found **735.88** (M<sup>+</sup>).

**1(2(9-dodecyl-carbazol-3-yl)-benzimidazol-1-yl)phenylamino-4(4,6-O-ethylidene-D-glucose) (17).**

Dodecyl-benzimidazole-carbazole-ethylidene-*N*-glycosylamine, **17** was synthesised by adopting the same procedure of compound **14**. The reaction of 4,6-*O*-ethylidene D-

glucose, **11** (1 mmol, 0.21 g) with dodecyl-benzimidazole-carbazole amine, **10** (1 mmol, 0.54 g) resulted in the formation of compound **17** as pale yellow solid. Yield: 79 % (0.58 g). Melting point: 172 °C. <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>):  $\delta_H$  8.48(s, 1H, Ar-H), 7.99(d,  $J = 7.5$  Hz, 1H, Ar-H), 7.89(d,  $J = 7.8$  Hz, 1H, Ar-H), 7.55(d,  $J = 8.7$  Hz, 1H, Ar-H), 7.43(d,  $J = 7.5$  Hz, 1H, Ar-H), 7.38(m, 7.38-7.35, 1H, Ar-H), 7.33(m, 7.33-7.28, 1H, Ar-H), 7.26(s, 2H, Ar-H), 7.22(m, 7.22-7.20, 3H, Ar-H & Sacc-OH), 7.14(d,  $J = 8.4$  Hz, 2H, Ar-H), 6.75(d,  $J = 8.4$  Hz, 2H, Ar-H), 4.78(m, 4.78-4.77, 1H, Sacc-H), 4.72(m, 4.72-4.70, 2H, Gly-NH & Sacc-H), 4.23(m, 4.23-4.16, 3H, NCH<sub>2</sub> & Ace-H), 3.85(t,  $J = 9$  Hz, 1H, Ano-H), 3.58(m, 3.58-3.48, 2H, Sacc-H), 3.46(m, 3.46-3.34, 3H, Sacc-H & OH), 1.90(m, 1.90-1.81, 4H, CH<sub>2</sub>), 1.37(m, 1.37-1.33, 5H, CH<sub>2</sub> & CH<sub>3</sub>), 1.31(m, 1.31-1.23, 14H, CH<sub>2</sub>), 0.87(t,  $J = 6.6$  Hz, 3H, CH<sub>3</sub>).

<sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>):  $\delta_C$  153.8(1C, Ar-C), 145.4(1C, Ar-C), 142.7(1C, Ar-C), 140.9(2C, Ar-C), 137.8(1C, Sacc-C), 129.1(1C, Ar-C), 128.5(2C, Ar-C), 126.9(1C, Ar-C), 126.1(1C, Ar-C), 122.8(3C, Ar-C), 122.1(1C, Ar-C), 120.6(2C, Ar-C), 120.3(1C, Ar-C), 119.4(2C, Ar-C), 119.1(1C, Ar-C), 115.3(2C, Ar-C), 110.5(1C, Ar-C), 108.9(1C, Ar-C), 108.4(1C, Ar-C), 99.7(1C, Ace-C), 85.9(1C, Ano-C), 80.1(1C, Sacc-C), 74.4(1C, Sacc-C), 74.2(1C, Sacc-C), 68.3(1C, Sacc-C), 67.4(1C, Sacc-C), 43.3(1C, N-CH<sub>2</sub>), 31.9(1C, CH<sub>2</sub>), 29.6(2C, CH<sub>2</sub>), 29.5(1C, CH<sub>2</sub>), 29.4(1C, CH<sub>2</sub>), 29.3(1C, CH<sub>2</sub>), 29.0(2C, CH<sub>2</sub>), 27.3(1C, CH<sub>2</sub>), 22.7(1C, CH<sub>2</sub>), 20.3(1C, CH<sub>3</sub>), 14.1(1C, CH<sub>3</sub>).

**1(2(9-dodecyl-carbazol-3-yl)-benzimidazol-1-yl)phenylamino-4(4,6-O-butyldene-D-glucose) (18).**

Dodecyl-benzimidazole-carbazole-butyldene-*N*-glycosylamine, **18** was synthesised by adopting the same procedure of compound **14**. The reaction of 4,6-*O*-butyldene D-glucose, **12** (1 mmol, 0.23 g) with dodecyl-benzimidazole-carbazole amine, **10** (1 mmol, 0.54 g) resulted in the formation of compound **18** as pale yellow solid. Yield: 82 % (0.62 g). Melting point: 175 °C. <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>):  $\delta_H$  8.42(s, 1H, Ar-H), 7.92(d,  $J = 7.5$  Hz, 1H, Ar-H), 7.81(d,  $J = 7.5$  Hz, 1H, Ar-H), 7.45(d,  $J = 8.4$  Hz, 1H, Ar-H), 7.37(d,  $J = 7.8$  Hz, 1H, Ar-H), 7.34(m, 7.34-7.27, 2H, Ar-H), 7.25(m, 7.25-7.16, 3H, Ar-H & Sacc-OH), 7.14(m, 7.14-7.07, 3H, Ar-H & Sacc-OH), 7.03(d,  $J = 7.8$  Hz, 2H, Ar-H), 6.63(d,  $J = 8.1$  Hz, 2H, Ar-H), 4.69(d,  $J = 5.4$  Hz, 1H, Ace-H), 4.61(t,  $J = 9$  Hz, 1H, Ano-H), 4.45(s, 1H, Gly-NH), 4.12(m, 4.12-4.07, 3H, NCH<sub>2</sub> & Sacc-H), 3.77(t,  $J = 5.1$  Hz, 1H, Sacc-H), 3.50(m, 3.50-3.44, 1H, Sacc-H), 3.40(m, 3.40-3.32, 2H, Sacc-H), 3.29(m, 3.29-3.23, 1H, Sacc-H), 1.80(m, 1.80-1.72, 2H, CH<sub>2</sub>), 1.55(m, 1.55-1.51, 2H, CH<sub>2</sub>), 1.37(m, 1.37-1.15, 20H, CH<sub>2</sub>), 0.85(m, 0.85-0.77, 6H, CH<sub>3</sub>).

<sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>):  $\delta_C$  152.5(1C, Ar-C), 144.3(1C, Ar-C), 141.2(1C, Ar-C), 139.5(2C, Ar-C), 136.3(1C, Ar-C), 127.4(1C, Ar-C), 127.1(2C, Ar-C), 125.6(1C, Ar-C), 124.8(1C, Ar-C), 121.5(3C, Ar-C), 120.8(1C, Ar-C), 119.3(2C, Ar-C), 118.8(1C, Ar-C), 118.1(1C, Ar-C), 117.7(2C, Ar-C), 113.8(2C, Ar-C), 109.2(1C, Ar-C), 107.6(1C, Ar-C), 107.1(1C, Ar-C), 101.2(1C, Ace-C), 84.7(1C, Ano-C), 78.8(1C, Sacc-C), 73.1(1C, Sacc-C), 72.8(1C, Sacc-C), 67.0(1C, Sacc-C), 66.2(1C, Sacc-C), 41.9(1C, N-CH<sub>2</sub>), 34.9(1C, CH<sub>2</sub>), 30.6(2C, CH<sub>2</sub>), 28.3(3C, CH<sub>2</sub>), 28.0(2C, CH<sub>2</sub>), 27.6(1C, CH<sub>2</sub>), 26.0(1C, CH<sub>2</sub>), 21.3(1C, CH<sub>2</sub>), 16.1(1C, CH<sub>2</sub>), 12.8(1C, CH<sub>3</sub>), 12.6(1C, CH<sub>3</sub>).

MALDI-TOF:  $m/z$  calcd for C<sub>47</sub>H<sub>58</sub>N<sub>4</sub>O<sub>5</sub> **758.44**, found **759.87**



(M<sup>+</sup>).

**1(2(9-dodecyl-carbazol-3-yl)-benzimidazol-1-yl)phenylamino-4(4,6-O-benzylidene-D-glucose) (19).**

Dodecyl-benzimidazole-carbazole-bezylidene-N-glycosylamine, **19** was synthesised by adopting the same procedure of compound **14**. The reaction of 4,6-O-benzylidene D-glucose, **13** (1 mmol, 0.29 g) with dodecyl-benzimidazole-carbazole amine, **10** (1 mmol, 0.54 g) resulted in the formation of compound **19** as pale yellow solid. Yield: 76 % (0.601 g). Melting point: 183 °C. <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>): δ<sub>H</sub> 8.38(s, 1H, Ar-H), 8.34(s, 1H, Gly-NH), 7.89(d, J = 7.2 Hz, 1H, Ar-H), 7.80(d, J = 7.8 Hz, 1H, Ar-H), 7.44(d, J = 8.4 Hz, 1H, Ar-H), 7.37(m, 7.37-7.30, 2H, Ar-H), 7.25(m, 7.25-7.15, 3H, Ar-H), 7.13(m, 7.13-7.10, 3H, Ar-H), 7.09(m, 7.10-7.04, 4H, Ar-H), 6.99(d, J = 8.7 Hz, 2H, Ar-H), 6.65(d, J = 8.7 Hz, 2H, Ar-H), 4.90(s, 1H, Sacc-OH), 4.61(s, 1H, Sacc-OH), 4.19(t, J = 8.7 Hz, 1H, Ano-H), 4.08(m, 4.08-4.00, 3H, NCH<sub>2</sub> & Ace-H), 3.81(m, 3.81-3.79, 2H, Sacc-H), 3.61(m, 3.61-3.44, 4H, Sacc-H), 1.80(m, 1.80-1.70, 2H, CH<sub>2</sub>), 1.32(m, 1.32-1.14, 18H, CH<sub>2</sub>), 0.78(t, J = 6.6 Hz, 3H, CH<sub>3</sub>). <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>): δ<sub>C</sub> 153.4(1C, Ar-C), 146.1(1C, Ar-C), 141.5(1C, Ar-C), 140.9(2C, Ar-C), 137.4(1C, Ar-C), 137.1(1C, Ar-C), 129.2(1C, Ar-C), 128.5(2C, Ar-C), 128.3(3C, Ar-C), 126.8(1C, Ar-C), 126.3(3C, Ar-C), 123.1(1C, Ar-C), 122.8(1C, Ar-C), 122.1(1C, Ar-C), 120.6(1C, Ar-C), 119.6(1C, Ar-C), 118.8(1C, Ar-C), 118.6(1C, Ar-C), 115.7(1C, Ar-C), 115.0(1C, Ar-C), 110.8(1C, Ar-C), 109.0(1C, Ar-C), 108.5(1C, Ar-C), 101.8(1C, Ace-C), 86.2(1C, Ano-C), 80.7(1C, Sacc-C), 74.3(1C, Sacc-C), 74.0(1C, Sacc-C), 68.8(1C, Sacc-C), 67.2(1C, Sacc-C), 43.2(1C, N-CH<sub>2</sub>), 31.9(2C, CH<sub>2</sub>), 29.6(2C, CH<sub>2</sub>), 29.4(2C, CH<sub>2</sub>), 28.9(1C, CH<sub>2</sub>), 27.3(1C, CH<sub>2</sub>), 22.7(2C, CH<sub>2</sub>), 14.1(1C, CH<sub>3</sub>).

**EI-MS:** m/z calcd for C<sub>50</sub>H<sub>56</sub>N<sub>4</sub>O<sub>5</sub> **792.43**, found **792.53** (M+H).

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**Reference**

- (a) P. Terech and R. G. Weiss, *Chem. Rev.*, 1997, **97**, 3133; (b) S. Banerjee, R. K. Das, P. Terech, A. Geyer, C. Aymonier, A. Loppinet-Serani, G. Raffy, U. Maitra, A. Guerso and J. P. Desvergne, *J. Mater. Chem. C*, 2013, **1**, 3305.
- C. Tomasini and N. Castellucci, *Chem. Soc. Rev.*, 2013, **42**, 156.
- (a) S. Prasanthkumar, A. Gopal and A. Ajayaghosh, *J. Am. Chem. Soc.*, 2010, **132**, 13206; (b) M. D. Segarra-Maset, V.J. Nebot, J. F. Miravet and B. Escuder, *Chem. Soc. Rev.*, 2013, **42**, 7086.
- (a) S. Basak, S. Bhattacharya, A. Datta and A. Banerjee, *Chem. Eur. J.*, 2014, **20**, 5721. (b) H. Kar and S. Ghosh, *Chem. Commun.*, 2014, **50**, 1064.
- A. R. Hirst, B. Escuder, J. F. Miravet and D. K. Smith, *Angew. Chem., Int. Ed.* 2008, **47**, 8002

- (a) K. Sugiyasu, S. Kawano, N. Fujita and S. Shinkai, *Chem. Mater.*, 2008, **20**, 2863; (b) P. Xue, R. Lu, J. Jia, M. Takafuji and I. Hamachi, *Chem., Eur. J.* 2012, **18**, 3549.
- (a) S. R. Jadhav, P. K. Vemula, R. Kumar, S. R. Raghavan, G. John, *Angew. Chem. Int. Ed.*, 2010, **49**, 7695; (b) X. Dou, P. Li, D. Zhang and C. L. Feng, *Soft Matter*, 2012, **8**, 3231.
- (a) F. Zhao, M. L. Mab and B. Xu, *Chem. Soc. Rev.*, 2009, **38**, 883; (b) J. Majumder, J. Deb, M. Rani Das, S. Sankar Jana and P. Dastidar *Chem. Commun.*, 2014, **50**, 1671.
- M. Oliver, M. Piepenbrock, G. O. Lloyd, N. Clarke and J. W. Steed, *Chem. Rev.*, 2010, **110**, 1960.
- S. Santhosh Babu, V. K. Praveen and A. Ajayaghosh. *Chem. Rev.*, 2014, **114**, 1973.
- N. M. Sangeetha and U. Maitra, *Chem. Soc. Rev.*, 2005, **34**, 821.
- (a) S. Ghosh, X. Q. Li, V. Stepanenko and F. Wuethner, *Chem. Eur. J.* 2008, **14**, 11343; (b) Y. Qian, S. Li, Q. Wang, X. Sheng, S. Wu, S. Wang, J. Lia and G. Yang, *Soft Matter*, 2012, **8**, 757.
- (a) X. Liu, X. Zhang, R. Lu, P. Xue, D. Xu and H. Zhou, *J. Mater. Chem.*, 2011, **21**, 8756; (b) P. Xue, Q. Xu, P. Gong, C. Qian, Z. Zhang, J. Jia, X. Zhao, R. Lu, A. Renb and T. Zhang, *RSC Adv.*, 2013, **3**, 26403.
- (a) S. Zhang, R. Chen, J. Yin, F. Liu, H. Jiang, N. Shi, Z. An, C. Ma, B. Liu and W. Huang, *Org. Lett.*, 2010, **12**, 3438; (b) H. Shi, J. Dai, L. Xu, L. Shi, L. Fang, S. Shuanga and C. Dong, *Org. Biomol. Chem.*, 2012, **10**, 3852.
- Y. Che, H. Huang, M. Xu, C. Zhang, B. R. Bunes, X. Yang, and L. Zang, *J. Am. Chem. Soc.*, 2011, **133**, 1087.
- (a) B. K. An, S. K. Kwon and S. Y. Park, *Angew. Chem. Int. Ed.*, 2007, **46**, 1978; (b) C. Wang, Y. Liu, Z. Ji, E. Wang, R. Li, H. Jiang, Q. Tang, H. Li and W. Hu, *Chem. Mater.*, 2009, **21**, 2840.
- W. W. H. Wong, T. Birendra Singh, D. Vak, W. Pisula, C. Yan, X. Feng, E. L. Williams, K. L. Chan, Q. Mao, D. J. Jones, C. Ma, K. Müllen, P. Bäuerle and A. B. Holmes, *Adv. Funct. Mater.*, 2010, **20**, 927.
- H. Zhuang, Q. Zhou, Y. Li, Q. Zhang, H. Li, Q. Xu, N. Li, J. Lu and L. Wang, *ACS Appl. Mater. Interfaces*, 2014, **6**, 94.
- (a) C. Nitsche, V. N. Schreier, M. A. M. Behnam, A. Kumar, R. Bartschlagler and C. D. Klein, *J. Med. Chem.*, 2013, **56**, 8389; (b) S. Ponnuchamy, S. Kanchithalaivan, R. Ranjith Kumar, M. Ashraf Ali and T. S. Choon, *Bioorg. Med. Chem. Lett.*, 2014, **24**, 1089.
- (a) M. Liu, S. J. Su, M. C. Jung, Y. Qi, W. M. Zhao and J. Kido, *Chem. Mater.*, 2012, **24**, 3817; (b) V. K. Praveen, C. Ranjith, E. Bandini, A. Ajayaghosh and N. Armaroli, *Chem. Soc. Rev.*, Doi: 10.1039/c3cs60406c.
- (a) S. Takizawa, V. A. Montes and P. Anzenbacher, Jr. *Chem. Mater.*, 2009, **21**, 2452; (b) H. Z. Zhang, G. L.V. Damu, G. X. Cai and C. H. Zhou, *Eur. J. Med. Chem.*, 2013, **64**, 329.
- H. C. Ting, Y. M. Chen, H. W. You, W. Y. Hung, S. H. Lin, A. Chaskar, S. H. Chou, Y. Chi, R. H. Liu and K. T. Wong, *J. Mater. Chem.*, 2012, **22**, 8399.
- H. Huang, X. Yang, B. Pan, L. Wang, J. Chen, D. Mab and C. Yang, *J. Mater. Chem.*, 2012, **22**, 13223.
- J. Dinda, S. D. Adhikary, S. K. Seth and A. Mahapatra, *New J. Chem.*, 2013, **37**, 431.
- S. Song, S. H. Park, Y. Jin, I. Kim, K. Lee and H. Suh, *Sol. Energy Mater. Sol. Cells*, 2011, **95**, 521.
- H. M. Bachhav, S. B. Bhagat and V. N. Telvekar, *Tetrahedron Lett.*, 2011, **52**, 5697.
- W. K. Huang, H. P. Wu, P. L. Lin, Y. P. Lee and E. W. G. Diau, *J. Phys. Chem. Lett.*, 2012, **3**, 1830.
- G. S. Liou, S. H. Hsiao and H. W. Chen, *J. Mater. Chem.*, 2006, **16**, 1831.
- K. Karthik Kumar, M. Elango, V. Subramanian and T. Mohan Das, *New J. Chem.*, 2009, **33**, 1570.
- K. Duskova, L. Gude and M. S. Arias-Pérez, *Tetrahedron*, 2014, **70**, 1071.
- H. Svobodová, Nonappa, M. Lahtinen, Z. Wimmer and E. Kolehmainen, *Soft Matter*, 2012, **8**, 7840.
- K. Rameshbabu, L. Zou, C. Kim, A. Urbas and Q. Li, *J. Mater. Chem.*, 2011, **21**, 15673.

- 
33. R. Rajaganesh, A. Gopal, T. Mohan Das and A. Ajayaghosh, *Org. Lett.*, 2102, **14**, 748.
34. P. Rajamalli and E. Prasad, *Soft Matter*, 2012, **8**, 8896.
35. (a) J. W. Steed, *Chem. Soc. Rev.*, 2010, **39**, 3686; (b) T. Yang, R. Ji, X. X. Deng, F. S. Du and Z. C. Li, *Soft Matter*, 2014, **10**, 2671.
- 5 36. A. Pal, R. Mahapatra and J. Dey, *RSC Adv.*, 2014, **4**, 7760.
37. K. K. Kartha, S. S. Babu, S. Srinivasan and A. Ajayaghosh, *J. Am. Chem. Soc.* 2012, **134**, 4834.
38. (a) D. J. Abdallah and R. G. Weiss, *Langmuir*, 2000, **16**, 352; (b) Y. Yu and Y. Ma, *Soft Matter*, 2011, **7**, 884.
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