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Synthesis and characterisation of *N*-substituted bis-phenols as precursors for unsymmetrical triarylmethane cations

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Abstract

Bis-(4-hydroxy-3,5-dimethylphenyl)(4-aminophenyl)methane derivatives (**1–6**) are synthesised and characterised. Inclusion of acetonitrile by bis-(4-hydroxy-3,5-dimethylphenyl)(4-*N*,*N′*-dimethylaminophenyl)methane is observed in the crystal structure. Cations generated from these compounds have characteristic visible absorptions. An alternative method for generation of these cations from quinone methide namely 4-[(4′-hydroxy-3′,5′-dimethylphenyl)(4-*N*,*N′*-dimethylaminophenyl)methylene]-2,6-dimethylcyclohexa-2,5-dienone under very mild condition is described. The characteristic absorption peaks of the cationic species are used to distinguish different isomeric forms.

Keywords: Bis-phenol; Triarylmethane; Quinone-methide; Solvatochromicity; Isomeric cation

1. Introduction

The triarylmethane cations are relatively easy to generate and are stable [1–7]. These cations are generally prepared from the triphenylmethanes by using superacids [5–7]. Isomeric forms of a triarylmethyl cation can be proposed depending on the substituents present on the rings [8,9]. A phenyl substituted bis-phenol would provide precursors for generation of isomeric cations and complexity of such cations will be enhanced with incorporation of multiple units [10–12]. In the present investigation we have carried out spectroscopic study on bis-phenols which have substituted or unsubstituted aminophenyl units as well as phenolic groups. The presence of a nitrogen atom in one of the aromatic ring of these compounds would provide scope for the isomeric cations. With the objectives to differentiate such cations in solution we have synthesised several bis-phenolic compounds whose characterisation and properties of the cationic species are discussed.

2. Results and discussion

The nitrogen-containing bis-phenols **1–4** are synthesised and characterised (Fig. 1). The bis-phenol **1** is prepared from the bis-(4-hydroxy-3,5-dimethylphenyl)(4-nitrophenyl)methane. Reduction of the nitro group with NH_2NH_2–Pd/C gave the corresponding amino derivative namely bis-(4-hydroxy-3,5-dimethylphenyl)(4-aminophenyl)methane. Compounds **3–4** are synthesised by derivatising **1**. The bis-(4-hydroxy-3,5-dimethylphenyl)(4-*N*,*N′*-dimethylaminophenyl)methane **2** is synthesised by acid catalysed condensation of 2,6-dimethylphenol with 4-*N*,*N′*-dimethylaminobenzaldehyde. In general bis-phenolic compounds possess extensive H-bonded structure and these compounds are no exception to this. For example, in solution **2** has extensive H-bonding with solvents and is clearly reflected in the ^{1}H NMR spectra recorded in different solvents. The compound **2** has characteristic A_2B_2 pattern from the aromatic ring

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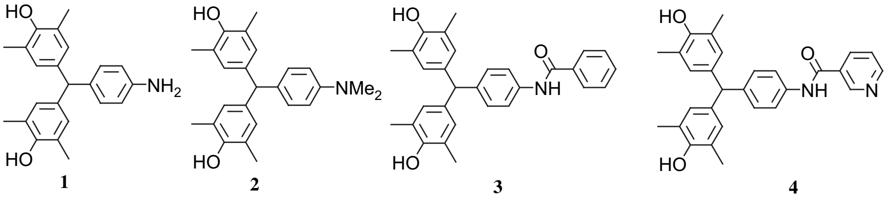


Fig. 1.

containing dimethylamine group and it has also signals arising from proton on the ring at *meta* to the hydroxyl groups. This signal is very sensitive to the solvent. In methanol-d_4 this signal appears at 6.58 ppm, whereas in acetonitrile-d_4 it appears at 6.69 ppm. The ^{1}H NMR spectrum of the compound **2** in a mixture of two solvents ($CD_3OD + CD_3CN$) shows that this peak appears at 6.67 ppm. Thus, protic solvents interact with the −OH group of the bis-phenol causing shifts in the ^{1}H NMR signals of the ring protons. The effect of hydrogen bonding with solvent molecules is reflected in solid-state structure of the compound also. The compound **2** was crystallised from acetonitrile as 1:1 adduct with the solvent. In the crystal structure it is clear that **2** has a propeller-like conformation (Fig. 2) and the molecules are held together through O−H···O hydrogen-bonding interaction along crystallographic *c*-axis. The acetonitrile molecules are held in between two bis-phenolic units and the C≡N of the acetonitrile unit is coordinated to one the phenolic −OH group. Interestingly the O−H···O hydrogen bonds between the phenolic OH-groups in the molecules of **2** are not disrupted by the interaction with the acetonitrile. The arrangement of the acetonitrile in the crystal lattice has very organized features. Looking at the perpendicular view on the longitudinal arrangement of acetonitrile it is very clear that the alternative molecules are arranged in same disposition. But the acetonitrile next to each other has projection such that if the −C≡N unit is projecting upward in one case the next −C≡N unit is projected downward.

The di-bis-phenols (**5**–**6**) are synthesised by functionalisation of bis-(4-hydroxy-3,5-dimethylphenyl)(4-aminophenyl)methane **1** (Scheme 1). The parent bis-phenol **1** is linked with amide linker by treating it with acid chloride of the corresponding dicarboxylic acid (Scheme 1). The important feature of the two molecules **5** and **6** is that the bis-phenol units are separated by a rigid amide spacer. These two molecules in solution do not self-assemble and is confirmed by mass spectroscopy.

A triarylmethane cation may be symmetric or non-symmetric based on the nature of the aryl units anchored to the central carbon atom. To look at such possibilities arising from the presence of a nitrogen-containing functional group; four monomeric substrates **1**–**4** were treated with trifluoroacetic acid to generate their corresponding cations. Formation of the cation from **2** is relatively easy, compared to either **3** or **4**. However, the same cation of **2** can be alternatively generated by treatment of the quinone methide, namely 4-[(4′-hydroxy-3′,5′-dimethylphenyl)(4-*N*,*N*′-dimethylaminophenyl)methylene]-2,6-dimethylcyclohexa-2,5-dienone with mineral acid, the quinone methide in turn can be prepared by oxidation of the corresponding bis-phenol **2** by ammonium persulphate. The generation of cation from the quinone methide involves protonation of the quinone methide with a mineral acid, as shown in Scheme 2 for **7**. Similar cation

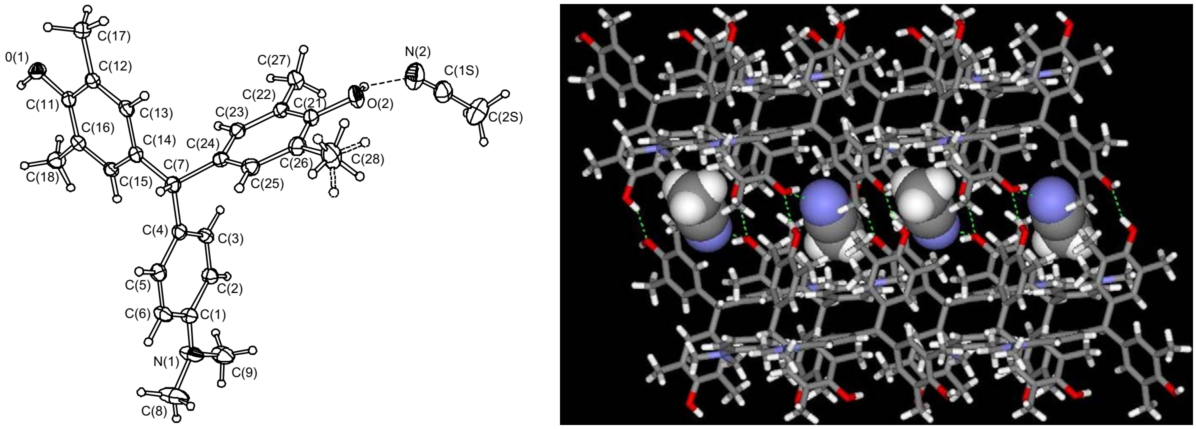
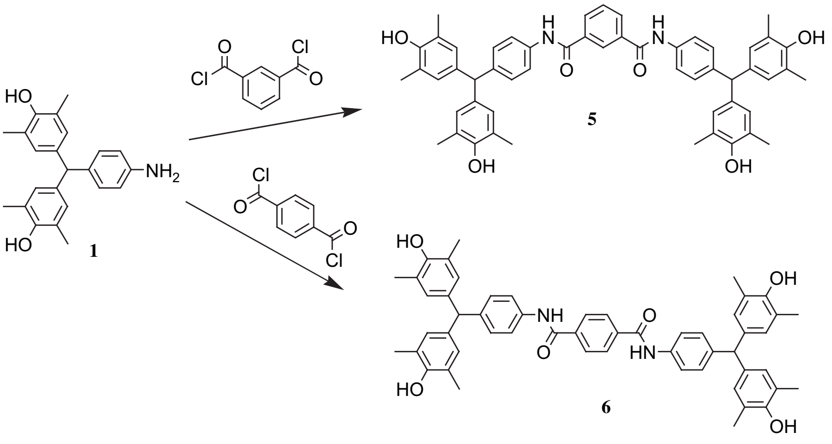


Fig. 2. Crystal structure of 1:1 adduct of **2** with acetonitrile and the packing of the solvent molecules in the crystal lattice showing the hydrogen-bonding interactions [monoclinic, P2(1)/*c*; *a*, 12.146(3); *b*, 15.584(4); *c*, 13.294(3); *β*, 107.61(1); selected bond distances (Å) and bond angles (°): N2−C1S 1.140(3); N2−C1S···C2S 178.5(2); O2−H02···N2 2.845(2) 147(2); O1−H01···O2 2.751(17) 150(2); O1−H01 0.89(3); N1−C1 1.384(2); O2−H02 0.92(3); N1−C1 1.384(2); C1−N1···C8 119.03 (15); C1−N1···C9 119.16 (14); C8−N1···C9 118.75 (15)].

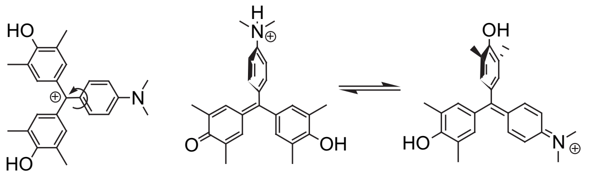


Scheme 1. Synthesis of **5**–**6**.

generation from simple quinone methides was demonstrated earlier [13]. The visible spectral properties of each isomeric cation can be assigned distinctly in the absorption spectra, however, solvent has a role in deciding the position of the absorption. Thus, the advantage of the chromophoric properties of the cations is taken to distinguish isomeric forms. Due to the non-coplanar conformation of the three aromatic rings in the related quinone methides whose crystal structures are studied [13], a cation generated from **7** would have a disposition of the aromatic rings in different planes. This would also be obvious that the steric effect of the methyl groups present at the *ortho*-position would make the system non-planar and enable one to identify different isomers arising from the delocalisation effect (Scheme 2). Two different forms of cations are thus expected, as out of three possible forms two of them will be equivalent.

Compound **7** has absorption bands at 522 nm ($\varepsilon = 2.04 \times 10^4\ \mathrm{M^{-1}\,cm^{-1}}$) in methanol; upon acidification two absorption bands (Fig. 3) at 453 nm ($\varepsilon = 1.58 \times 10^4\ \mathrm{M^{-1}\,cm^{-1}}$) and 551 nm ($\varepsilon = 2.4 \times 10^4\ \mathrm{M^{-1}\,cm^{-1}}$) are observed due to the formation of the corresponding cations. The presence of $-\mathrm{NMe_2}$ group in the cations (as shown in Scheme 2) would make it possible to distinguish two conformational states, *B* and *C*. The absorption at 453 nm is assigned to the cation having conformation *B*. In the conformation *C*, the N-atom is in conjugation with the phenolic group and in this state *C* absorbs at 551 nm. This suggests that two types of cations have different absorptions. Stability of the conformations of the cation in this molecule may be explained by invoking participation of the lone pair on nitrogen in the resonance as shown in *C*. Alternatively, the phenolic −OH group can participate in resonance so that the cationic charge now extends over two oxygen atoms at two ends, there is only one way leading to structure *B*. Because the N-atom can interact with both the phenolic and the quinonoid groups following protonation, there are two possibilities that could lead to resonance stabilisation in the cationic state. This explains the observed 1:2 intensity ratio between the two absorption peaks.

Visible spectroscopy also discerns the extent of delocalisation of the π-electrons over the rings in the 4-[(4′-hydroxy-3′,5′-dimethylphenyl)(4-*N*,*N*′-dimethylaminophenyl)methylene]-2,6-dimethylcyclohexa-2,5-dienone **7** and it is reflected in the solvatochromicity shown by the compound. The 4-[(4′-hydroxy-3′,5′-dimethylphenyl)(4-*N*,*N*′-dimethylaminophenyl)methylene]-2,6-dimethylcyclohexa-2,5-dienone has absorption maxima in methanol, acetonitrile, dimethylformamide, dichloromethane at 522 nm, 486 nm, 501 nm, 482 nm, respectively. Since in each solvent the absorption peaks



Single conformation (**B**)
λ_{max} 445nm

2 equivalent conformations (**C**)
λ_{max} 547nm

Scheme 2. Isomeric cations from **7**.

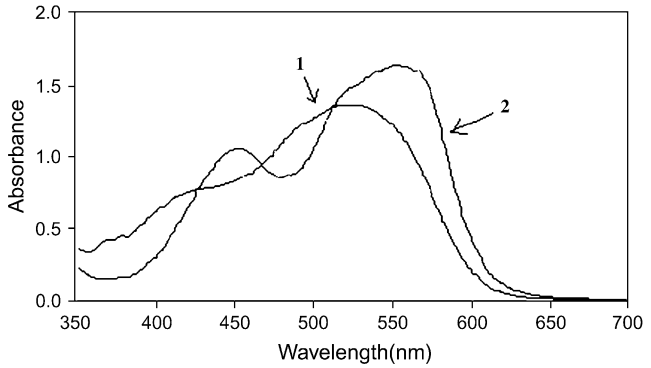


Fig. 3. Absorbance of **7** in (1) methanol (6.7×10^{-5} M); (2) on addition of HCl (4 μl of 0.1 M) to (1).

occur at different wavelength we have studied the possibility of obtaining isosbestic points in the visible spectra from different compositions of the solvents with constant concentration of **7**.

The solvatochromicity study was performed with mixed solvents such as methanol/dichloromethane, methanol/acetonitrile and methanol/dimethylformamide. In the case of methanol/dimethylformamide system, protonation led to the formation of isosbestic point (Fig. 4); while in the other two systems there were none. Occurrence of an isosbestic point clearly indicates that there is a conversion of one state to another. This is attributed to the disruption of the hydrogen bonds among the quinone methides. Since DMF is a much polar solvent than either of the dichloromethane or acetonitrile, the former can lead to disruption of intermolecular hydrogen-bonding interactions in solution.

When the two triarylmethane cations are separated by a spacer, the issue of delocalisation through space becomes relevant. For example, assuming *A* as a bisphenol unit separated by a spacer, we may imagine three distinct states A—A, A—A^+ and A^+—A^+ as shown in Scheme 3. If the property associated with A^+ is independent of another A or A^+ then we shall be able to see only one type of feature in visible spectroscopy when a monocation or dications are generated from A—A. Thus, for an N-substituted aryl containing compound there will be only two characteristic states associated with A^+ from the isomers. However, in the case when A^+ interacts with A there will be more numbers of states having characteristic spectral properties. So, an interacting system should show characteristic of three different species A—A, A—A^+ and A^+—A^+, whereas a non-interacting case will lead to two possibilities one corresponding to A and other to A^+. With this background the visible spectra of **5** and **6** were recorded by adding trifluoroacetic acid. It is found that **5** has two new absorptions in each case due to the generation of cations. The cations of **5** are characterised by an absorption at 473 nm and 518 nm. The intensities of the two peaks have a ratio 1:2 which corresponds to the generation of two types of cations one in twofold excess similar to the one explained by Scheme 2.

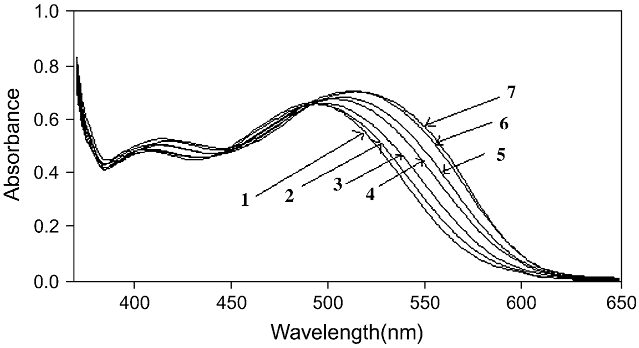
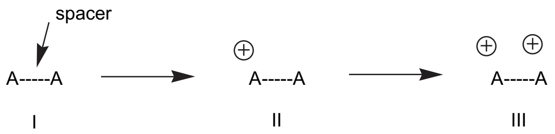


Fig. 4. Visible spectra of 4-[(4′-hydroxy-3′,5′-dimethylphenyl)(4-*N*,*N*′-dimethylaminophenyl)methylene]-2,6-dimethylcyclohexa-2,5-dienone (3.4×10^{-5} mM): methanol and dimethylformamide in the ratio: (1) [2:0]; (2) [1.5:0.5]; (3) [1.2:0.8]; (4) [1:1]; (5) [0.8:1.2]; (6) [0.5:1.5]; (7) [2:0].



Scheme 3.

In conclusion we have demonstrated that the non-symmetric nature of the triphenylmethyl cations is revealed in the visible spectroscopy. The ease of generation of these cations by mineral acid makes quinone methides to be perspective candidates for proton sensor.

3. Experimental section

Preparation of bis-(4-hydroxy-3,5-dimethylphenyl)(4-nitrophenyl)methane: 2,6-dimethylphenol (0.5 g, 4.1 mmol) and 4-nitrobenzaldehyde (0.303 g, 2 mmol) were dissolved in glacial acetic acid (7 ml) and the solution was cooled in ice (0 °C). To this a mixture of H_2SO_4—AcOH (1:4, 10 ml) was added dropwise over a period of 30 min. The reaction mixture was kept under ice-cold condition for 3 days. Then cold water (10 ml) was added to the reaction mixture and the solids were filtered, washed thoroughly with water to remove all the acids and dried in air. The bis-phenol bis-(4-hydroxy-3,5-dimethylphenyl)(4-nitrophenyl)methane was obtained as pale yellow solid (84%) after recrystallisation from dichloromethane. *m*/*e* 377; IR (KBr, cm^{-1}) 3432 (b), 2930 (s), 1598 (s), 1527 (s). ^1H NMR ($CDCl_3$, 400 MHz): δ (ppm) 8.13 (2H, dd, $J = 8.0$ Hz), 7.28 (2H, d, $J = 6.8$ Hz), 6.84 (4H, d, $J = 2.8$ Hz), 5.38 (1H, s), 4.57 (2H, bs), 2.20 (12H, s). ^{13}C NMR ($CDCl_3$, 100 MHz): 152.7, 150.9, 146.3, 134.4, 130.1, 129.3, 123.4, 123.1, 55.3, 15.9.

Preparation of bis-(4-hydroxy-3,5-dimethylphenyl)(4-aminophenyl)methane, **1**: bis-(4-hydroxy-3,5-dimethylphenyl)(4-nitrophenyl)methane (0.820 g, 2.02 mmol) was dissolved in methanol (5 ml) in a 50-ml round bottom flask equipped with a condenser and Pd/C (20% Pd content; 0.04 g) was added slowly with constant stirring. Then hydrazine hydrate (1 ml) dissolved in methanol (1 ml) was added dropwise to the stirred solution of the bis-phenol and brisk evolution of N_2 was observed almost immediately. This reaction mixture was put under mild reflux for 4 h and then cooled. The contents in the flask are diluted with MeOH (10 ml) and filtered through celite. The product, bis-(3,5-dimethyl-4-hydroxyphenyl)(4-aminophenyl)methane is obtained after removal of the solvent in vacuo as pink solid (85%) which is purified by column chromatography over silica gel (hexanes:diethyl ether 7:3). *m*/*e* 347. ^1H NMR

($CDCl_3$, 400 MHz): δ (ppm) 6.92 (2H, d, $J = 8.4$ Hz), 6.74 (4H, s), 6.52 (2H, d, $J = 8.4$ Hz), 5.23 (1H, s), 4.05 (2H, bs), 3.48 (2H, s), 2.20 (12H, s). ^{13}C NMR ($CDCl_3$, 100 MHz): 150.6, 144.2, 136.5, 135.4, 130.1, 129.6, 129.3, 123.2, 118.0, 115.5, 115.2, 114.9, 54.6, 40.8, 16.3.

Preparation of bis-(4-hydroxy-3,5-dimethylphenyl)(4-*N*,*N*′-dimethylaminophenyl)methane, **2**: 2,6-dimethylphenol (0.5 g, 4.1 mmol) and 4-*N*,*N*-dimethylaminobenzaldehyde (0.298 g, 2 mmol) were dissolved in glacial acetic acid (7 ml) and the solution was cooled in ice (0 °C). To this a mixture of H_2SO_4–AcOH (1:4, 10 ml) was added dropwise over a period of 30 min. After the addition of acid the reaction mixture was kept under ice-cold condition for 3 days. Then cold water (10 ml) was added to the reaction mixture and the solids were filtered, washed thoroughly with water to remove all the acids and dried in air. The bis-phenol **2** was obtained as pale yellow solid (84%) after recrystallisation from dichloromethane. *m*/*e* 375; IR (KBr, cm^{-1}) 3462 (b), 2914 (s), 1603 (s), 1481 (s). ^1H NMR ($CDCl_3$, 400 MHz): 6.98 (2H, d, $J = 8.4$ Hz), 6.74 (4H, s), 6.73 (2H, d, $J = 8.4$ Hz), 5.22 (1H, s), 4.63 (2H, bs), 2.93 (6H, s), 2.19 (12H, s). ^{13}C NMR ($CDCl_3$, 100 MHz): 150.4, 149.0, 136.8, 133.3, 129.9, 129.5, 122.7, 112.7, 55.3, 40.8, 16.0.

Typical procedure for **3**–**6**: In a typical procedure the bis-(4-hydroxy-3,5-dimethylphenyl)(4-aminophenyl)methane **1** (0.35 g, 1 mmol) was dissolved in dichloromethane (20 ml) and dry dimethylformamide (2 ml) to get a clear solution and this solution was cooled to 0 °C. Benzoyl chloride (0.106 g, 1 mmol) was dissolved in dichloromethane (5 ml) and pyridine (0.08 g, 1 mmol) was mixed with it. This acid chloride–pyridine solution was then added dropwise to the bis-phenol solution over 30 min; after which the reaction mixture was allowed to stir at 0 °C for another 1 h. Then, the solvents are removed and the residue washed with water (2 × 25 ml) to remove the hydrochloride salts. The compound **3** was obtained as a pale yellow solid after recrystallisation from ethanol–dichloromethane (76%). *m*/*e* 451; IR (KBr, cm^{-1}): 3422 (O–H stretch), 1682 (Amide N–H); ^1H NMR (DMSO-d_6, 400 MHz): δ (ppm) 9.76 (1H, s), 7.66 (2H, d, $J = 6.0$ Hz), 7.41 (2H, d, $J = 6.4$ Hz), 7.27 (1H, m), 7.18 (2H, t, $J = 6.0$ Hz), 6.80 (2H, d, $J = 6.4$ Hz), 6.39 (4H, s), 5.00 (1H, s), 3.45 (2H, bs), 1.9 (12H, s). ^{13}C NMR (DMSO-d_6, 100 MHz): δ (ppm) 166.8, 151.4, 140.6, 136.8, 135.5, 135.2, 131.7, 129.7, 128.5, 127.9, 123.9, 120.2, 54.6, 17.3.

4: *m*/*e* 451.91; IR (KBr, cm^{-1}): 3422 (O–H stretch, broad), 1682 (C=O stretch), 1646 (N–H bend); ^1H NMR (MeOD-d_4, 400 MHz): 9.12 (1H, s), 8.78 (2H, s, N–H), 8.43 (1H, d, $J = 7.6$ Hz), 7.67 (1H, t, $J = 6.4$ Hz), 7.58 (2H, d, $J = 8.0$ Hz), 7.12 (2H, d, $J = 8.0$ Hz), 6.76 (4H, s), 5.28 (1H, s), 2.19 (12H, s). ^{13}C NMR (MeOD-d_4; 100 MHz): 152.4, 151.9, 148.8, 138.1, 137.2, 137.0, 130.8, 130.3, 125.5, 125.3, 122.1, 56.3, 16.7.

5: *N*,*N*′-bis-{4-[bis-(4-hydroxy-3,5-dimethylphenyl)-methyl]-phenyl}-isophthalamide was obtained as a red solid (61%). *m*/*e* 825. IR (KBr, cm^{-1}): 3352 (O–H stretch, broad), 1648 (Amide I, C=O), 1593 (Amide II N–H); ^1H NMR (DMSO-d_6, 400 MHz): δ (ppm) 10.15 (2H, bs), 8.50 (1H, s), 8.06 (2H, d, $J = 8.0$ Hz), 7.90 (4H, bs), 7.62 (4H, d, $J = 8.0$ Hz), 7.55 (1H, t, $J = 7.6$ Hz), 6.98 (4H, d, $J = 8.0$ Hz), 6.57 (8H, s), 5.14 (2H, s), 2.07 (24H, s). ^{13}C NMR (DMSO-d_6, 400 MHz): δ (ppm) 169.9, 134.7, 128.8, 128.5, 123.6, 119.9, 59.5, 16.5.

Synthesis of **6**: *N*,*N*′-bis-{4-[bis-(4-hydroxy-3,5-dimethylphenyl)methyl]-phenyl}-terephthalamide was obtained as pale yellow solid (54%). *m*/*e* 825. IR (KBr, cm^{-1}): 3351 (O–H stretch, broad), 1656 (Amide I, C=O), 1531 (Amide II, N–H bend); ^1H NMR (DMSO-d_6, 400 MHz): 10.34 (2H, s), 8.06 (4H, s), 8.04 (4H, s), 7.67 (4H, d, $J = 6.8$ Hz), 7.52 (4H, d, $J = 6.8$ Hz), 6.62 (8H, s), 5.20 (2H, s), 2.08 (24H, s). ^{13}C NMR (DMSO-d_6, 100 MHz): 170.3, 164.6, 151.2, 140.7, 137.4, 136.6, 134.9, 129.0, 128.6, 127.6, 123.7, 120.3, 54.2, 16.5.

Compound **7** was prepared by oxidation of **2** with ammonium persulphate by similar procedure as described for analogous compound [13].

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