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Dendrons as Active Clicking Tool for Generating Non-Leaching Antibacterial Materials

Hadi Bakhshi, Seema Agarwal*

Macromolecular Chemistry II and Bayreuth Center for Colloids and Interfaces, University of Bayreuth, Universitätsstraße 30, 95440, Bayreuth, Germany

*Corresponding author: E-mail: agarwal@uni-bayreuth.de, Telephone: +49-921-553397, Fax: +49-921-553393Experimental

1. Experimentals

1.1. Materials

Hexamethylene diisocyanate (HDI)-uretdione (Desmodur® N 3400) was kindly provided by Covestro (Germany). All reagents were analytical grades and used without further purification except mentioned otherwise. Tetrahydrofuran (THF), *n*-hexane, diethyl ether (Et_2O) and ethanol (EtOH) were technical grade and vacuum-distillated before use. THF was dried over calcium hydride (CaH_2) and sodium before use.

1.2. Synthesis of dendrons

Dendrons were synthesized using HDI-uretdione as the starting molecule [1, 2]. HDI-uretdione was a colorless viscose liquid with NCO content of 21.8% and monomeric HDI of ≤0.3%. ^{1}H-NMR (300 MHz, $CDCl_3$, δ ppm): 1.31 (tt, 8H, OCNCH$_2$CH$_2$*CH$_2$CH$_2$*), 1.56 (tt, 8H, OCNCH$_2$*CH$_2$*CH$_2$CH$_2$*CH$_2$*), 3.14 (t, 4H, *CH$_2$*NCON), 3.22 (t, 4H, OCN*CH$_2$*). ^{13}C-NMR (75 MHz, $CDCl_3$, δ ppm): 25.9 (*CH$_2$*CH$_2$CH$_2$NCON), 26.0 (OCNCH$_2$CH$_2$*CH$_2$*), 28.4 (OCNCH$_2$*CH$_2$*), 31.1 (*CH$_2$*CH$_2$NCON), 40.2 (*CH$_2$*NCON), 42.8 (OCN*CH$_2$*), 121.9 (*NCO*), 157.7 (*NCON*). FTIR (1/λ cm^{-1}): 2936 and 2860 (C–H, ν), 2261 (N=C=O, ν), 1762 (NC=ON, ν), 1485 and 1343 (CH_2, δ).

1.2.1. Synthesis of G0.5

A solution of 9.30 g of HDI-uretdione (27.6 mmol, 1 Eq.) with or without 32 mg of dibutyltin dilaurate (DBTDL) in 25 mL of dried THF was poured in a three-necked round bottomed flask. The flask had a cooling condenser, a dropping funnel, an inert gas inlet and a thermometer for monitoring the reaction temperature. The internal temperature of the flask was kept constant in the range of 25-67 °C using an external oil bath. A solution of 6.30 g of 3-dimethylaminopropanol (3DMAPrOH, 61.1 mmol, 2.2 Eq.) in 25 mL of dried THF was added drop-wise to the HDI-uretdione solution using the dropping funnel within 15 min. At different time intervals, samples from the reactor were taken and their FTIR spectra were immediately recorded. The completion of reaction was followed by monitoring the peak at 2270 cm^{-1} which corresponded to isocyanate groups. The complete disappearance of this peak showed the completion of the reaction. Finally, the reaction contents were brought to the room temperature. THF was removed and the remaining solid was washed with *n*-hexane and dried overnight at 30^{o}C under vacuum. The obtained product was a white waxy solid (12.84 g). ^{1}H-NMR (300 MHz, $CDCl_3$, δ ppm): 1.30 (tt, 8H, OCONHCH$_2$CH$_2$*CH$_2$CH$_2$*), 1.46 (t, 4H, OCONHCH$_2$*CH$_2$*), 1.57 (tt, 4H, *CH$_2$*CH$_2$NCON), 1.74 (tt, 4H, *CH$_2$*CH$_2$OCONH), 2.19 (s, 12H, (*CH$_3$*)$_2$N), 2.29 (t, 4H, N*CH$_2$*), 3.13 (t, 4H, *CH$_2$*NCON), 3.15 (t, 4H, OCONH*CH$_2$*), 4.04 (t, 4H, *CH$_2$*OCONH) 4.95 (s, 2H, OCON*H*). ^{13}C-NMR (75 MHz, $CDCl_3$, δ ppm): 26.0 (*CH$_2$*CH$_2$CH$_2$NCON), 26.3 (*CH$_2$*CH$_2$OCONH), 27.4 (OCONHCH$_2$CH$_2$*CH$_2$CH$_2$*), 29.8 (*CH$_2$*CH$_2$NCON), 40.3 (*CH$_2$*NCON), 40.7 (OCONH*CH$_2$*), 45.4 ((*CH$_3$*)$_2$N), 56.3 (N*CH$_2$*), 63.0 (*CH$_2$*OCONH), 156.7 (*OCONH*), 157.8 (*NCON*). FTIR (1/λ cm^{-1}): 3308 (OCON–H, ν), 2934 and 2859 (C–H, ν), 2816 and 2767 (NC–H, ν), 1763 (NC=ON, ν), 1713 and 1681 (OC=ONH, ν), 1531 (OCO–NH, ν, OCON–H, δ), 1462 (CH_2, δ), 1250 (N–CH_3, ν).

1.2.2. Synthesis of G1

A solution of 2.00 g of G0.5 (3.7 mmol, 1 Eq.) in 10 mL of THF was poured in a three-necked round bottomed flask The flask had a cooling condenser, a dropping funnel, an inert gas inlet and a thermometer for monitoring the reaction temperature. The internal temperature of the flask was kept constant at 25 or 67 °C using an oil bath. A solution of 0.52 g of 6-aminohexanol (4.4 mmol, 1.2 Eq.) in 10 mL of THF was added to the G0.5 solution in one portion. After different time intervals, samples from the reactor were taken and their FTIR spectra were immediately recorded. The reaction was run until the peak at 1768 cm^{-1} corresponding to the uretdione groups was completely disappeared. Finally, the reaction mixture was brought down to room temperature. THF was removed and the remaining viscous liquid was washed with Et_2O and dried at 50°C for 24 h in vacuum. The obtained product was a yellow viscous liquid (2.40 g). ^{1}H-NMR (300 MHz, $CDCl_3$, δ ppm): 3.10 (t, 2H, CH_2NHCON), 3.64 (t, 2H, NHCONCH_2, t, 2H, CH_2OH). ^{13}C-NMR (75 MHz, $CDCl_3$, δ ppm): 29.8 (CH_2CH_2NHCON), 32.6 (CH_2CH_2OH), 32.7 (NHCONCH$_2CH_2$), 40.5 (CH_2NHCON), 42.8 (NHCONCH_2), 63.0 (CH_2OH). FTIR (1/λ cm^{-1}): 3306 (O–H, ν, OCON–H, ν), 2932 and 2857 (C–H, ν), 2817 and 2765 (NC–H, ν), 1712 and 1679 (OC=ONH, ν), 1628 (NHC=ONC=ONH, ν), 1531 (CO–NH, ν, CON–H, δ), 1462 (CH_2, δ), 1254 (N–CH_3, ν), 1042 (C–OH, ν).

1.2.3. Direct synthesis of G1

A solution of 30.00 g of HDI-uretdione (89.2 mmol, 1 Eq.) and 80 mg of DBTDL in 40 mL of dried THF was poured in a three-necked round bottomed flask. A solution of 19.05 g of 3DMAPrOH (182.8 mmol, 2.05 Eq.) in 30 mL of dried THF was added drop-wise to the HDI-uretdione solution using the dropping funnel in 15 min and the reaction was carried out under Ar at 25 °C for 40 min. Within this time, the FTIR peak at 2270 cm^{-1} (isocyanate groups) totally disappeared. Then, a solution of 11.31 g of 6-aminohexanol (93.6 mmol, 1.05 Eq.) in 30 mL THF was poured in the reactor in one portion. The reaction mixture was stirred at 25 °C under Ar atmosphere for 10 min until the peak at 1760 cm^{-1} corresponding to uretdione rings completely disappeared. Finally, THF was removed via a rotary evaporator and the product was washed with Et_2O and dried in a vacuum oven at 50 °C overnight. The obtained product was a yellow viscous liquid (58.00 g).

1.2.4. Synthesis of G2

A solution of 10.20 g of HDI-uretdione (30.3 mmol, 1 Eq.) and 32 mg of DBTDL in 40 mL of dried THF was poured in a three-necked round bottomed flask equipped with a condenser, a dropping funnel, an Ar inlet, a thermometer and mechanical stirrer. Another solution of 40.00 g of G1 (60.6 mmol, 2 Eq.) in 80 mL of dried THF was added drop-wise to the flask using dropping funnel in 15 min. The reaction mixture was stirred under Ar atmosphere at 25 °C for 60 min until the FTIR peak at 2270 cm^{-1} corresponding to isocyanate groups completely disappeared. Then, a solution of 3.55 g of 6-aminohexanol (30.3 mmol, 1 Eq.) in 30 mL THF was poured in the reactor in one portion. The reaction mixture was stirred at 25 °C under Ar atmosphere for 10 min until the peak at 1760 cm^{-1} corresponding to uretdione rings completely disappeared. At this stage, the viscosity of the reaction mixture increased significantly. Finally, THF was removed via a rotary evaporator and the product was washed with Et_2O and dried in a vacuum oven at 50 °C overnight. The obtained product was a

yellow rubbery solid (50.58). ^{1}H-NMR (300 MHz, $CDCl_3$, δ ppm): 3.09 (t, 2H, *CH_2*NHCON), 3.66 (t, 2H, NHCON*CH_2*, t, 2H, *CH_2*OH). ^{13}C-NMR (75 MHz, $CDCl_3$, δ ppm): 29.8 (*CH_2*CH_2NHCON), 32.6 (*CH_2*CH_2OH), 32.7 (NHCONCH_2*CH_2*), 40.4 (*CH_2*NHCON), 42.8 (NHCON*CH_2*), 63.0 (*CH_2*OH). FTIR (1/λ cm^{-1}): 3323 (O–H, ν, OCON–H, ν), 2931 and 2858 (C–H, ν), 2820 and 2784 (NC–H, ν), 1683 (OC=ONH, ν), 1635 (NHC=ONC=ONH, ν), 1521 (CO–NH, ν, CON–H, δ), 1463 (CH_2, δ), 1253 (N–CH_3, ν) 1046 (C–OH, ν).

1.2.5. Quaternization of dendrons

QAS-functionalized dendrons were prepared via alkylation reaction of tertiary amine groups with alkylbromides. As a general procedure, a solution of 2 g of dendrons and alkylbromide (2 Eq. regarding to 1 Eq. tertiary amines) in 5 mL THF was stirred at room temperature for 4 days. The product was precipitated out from THF during the reaction. Finally, the product was separated from reaction medium, washed three times with Et_2O and dried in a vacuum oven at 50 °C overnight.

G0-C7Br: The obtained product was a white powder (2.66 g). According to H-NMR spectrum, the purity was of 100%. ^{1}H-NMR (300 MHz, DMSO-d_6, δ ppm): 1.95 (tt, 2H, N^+CH_2*CH_2*), 3.00 (s, 6H, (*CH_3*)$_2N^+$), 3.37 (t, 4H, *CH_2N^+* and N^+*CH_2*), 3.58 (tt, 2H, *CH_2*OH), 4.64 (s, 2H, C_6H_8*CH_2N^+*), 4.80 (m, 1H, *OH*). 7.52 and 7.59 (s, 10H, *C_6H_8*CH_2N^+). ^{13}C-NMR (75 MHz, $CDCl_3$, δ ppm): 25.9 (N^+CH_2*CH_2*), 49.6 ((*CH_3*)$_2N^+$), 58.1 (N^+*CH_2*), 61.9 (*CH_2*OH), 63.3 (*CH_2N^+*). 67.5 (C_6H_8*CH_2N^+*), 128.7, 129.3, 130.7 and 133.5 (*C_6H_8*CH_2N^+). FTIR (1/λ cm^{-1}): 3302 (O–H, ν), 3006 (=C–H, ν), 2913 and 2885 (C–H, ν), 1479 (CH_2, δ), 1252 (N–CH_3, ν), 1076 (C–OH, ν).

G0-C10Br: The obtained product was a white powder (6.28 g). According to H-NMR spectrum, the purity was of 100%. ^{1}H-NMR (300 MHz, DMSO-d_6, δ ppm): 0.84 (t, 3H, *CH_3*CH_2), 1.25 (tt, 14H, CH_3(*CH_2*)$_7$), 1.64 (tt, 2H, *CH_2*CH_2N^+), 1.80 (tt, 2H, N^+CH_2*CH_2*), 3.01 (s, 6H, (*CH_3*)$_2N^+$), 3.30 (t, 4H, *CH_2N^+* and N^+*CH_2*), 3.47 (tt, 2H, *CH_2*OH), 4.80 (t, 1H, *OH*). ^{13}C-NMR (75 MHz, $CDCl_3$, δ ppm): 14.4 (*CH_3*CH_2), 22.1 (CH_3*CH_2*), 25.8 (*CH_2*CH_2N^+), 26.2 (N^+CH_2*CH_2*), 50.6 ((*CH_3*)$_2N^+$), 58.1 (N^+*CH_2*), 61.5 (*CH_2*OH), 63.3 (*CH_2N^+*). FTIR (1/λ cm^{-1}): 3306 (O–H, ν), 2920 and 2852 (C–H, ν), 1466 (CH_2, δ), 1225 (N–CH_3, ν), 1061 (C–OH, ν).

G0.5-C10Br: The obtained product was a white highly viscose solid (1.26 g). According to H-NMR spectrum, the yield for quaternization of tertiary amine groups was of 100%. ^{1}H-NMR (300 MHz, DMSO-d_6, δ ppm): 0.85 (t, 6H, *CH_3*$(CH_2)_5N^+$), 2.94 (t, 8H, *CH_2N^+* and N^+*CH_2*), 3.03 (s, 12H, (*CH_3*)$_2N^+$. ^{13}C-NMR (75 MHz, $CDCl_3$, δ ppm): 14.4 (*CH_3*$(CH_2)_5N^+$), 50.6 ((*CH_3*)$_2N^+$), 60.5 (N^+*CH_2*), 63.4 (*CH_2N^+*). FTIR (1/λ cm^{-1}): 3309 (OCON–H, ν), 2928 and 2856 (C–H, ν), 2766 (N^+C–H, ν), 1766 (NC=ON, ν), 1690 (OC=ONH, ν), 1531 (OCO–NH, ν, OCON–H, δ), 1462 (CH_2, δ), 1252 (N–CH_3, ν).

G0.5-C7Br: The obtained product was a white highly viscose solid (3.88 g). According to H-NMR spectrum, the yield for quaternization of tertiary amine groups was of 96.0%. ^{1}H-NMR (300 MHz, DMSO-d_6, δ ppm): 2.11 (tt, 4H, N^+CH_2*CH_2*), 2.99 (m, 16H, (*CH_3*)$_2N^+$ and N^+*CH_2*), 4.59 (s, 4H, *CH_2N^+*), 7.53 and 7.55 (s, 10H, *C_6H_8*CH_2N^+). ^{13}C-NMR (75 MHz, $CDCl_3$, δ ppm): 22.9 (*CH_2*CH_2N^+) 49.7 ((*CH_3*)$_2N^+$), 61.0 (CH_2*CH_2*N^+), 66.5 (C_6H_8*CH_2N^+*), 128.5, 129.3 and 133.3 (*C_6H_8*CH_2N^+). FTIR (1/λ cm^{-1}): 3342 (OCON–H, ν), 3008 (=C–H, ν), 2933 and 2859 (C–H, ν), 1761 (NC=ON, ν), 1697 (C=C, ν, OC=ONH, ν), 1530 (OCO–NH, ν, OCON–H, δ), 1463 (CH_2, δ), 1248 (N–CH_3, ν).

G1-C4Br: The obtained product was a yellow highly viscose solid (2.83 g). According to H-NMR spectrum, the yield for quaternization of tertiary amine groups was of 90.5%. ^{1}H-NMR (300 MHz, DMSO-d_6, δ ppm): 0.92 (t, 6H, $CH_3(CH_2)_3N^+$), 2.95 (t, 8H, CH_2N^+ and N^+CH_2), 3.04 (s, 12H, $(CH_3)_2N^+$. ^{13}C-NMR (75 MHz, $CDCl_3$, δ ppm): 14.0 ($CH_3(CH_2)_3N^+$), 19.6 ($CH_3CH_2(CH_2)_2N^+$), 24.1 ($CH_3CH_2CH_2CH_2N^+$), 50.6 (($CH_3)_2N^+$), 60.5 (N^+CH_2), 63.2 (CH_2N^+). FTIR (1/λ cm^{-1}): 3204 (O–H, ν, OCON–H, ν), 2932 and 2860 (C–H, ν), 1686 (C=C, ν), 1635 (NHC=ONC=ONH, ν), 1521 (OCO–NH, ν, OCON–H, δ), 1466 (CH_2, δ), 1249 (N–CH_3, ν), 1054 (C–OH, ν).

G1-C6Br: The obtained product was a yellow highly viscose solid (3.00 g). According to H-NMR spectrum, the yield for quaternization of tertiary amine groups was of 99.3%. ^{1}H-NMR (300 MHz, DMSO-d_6, δ ppm): 0.87 (t, 6H, $CH_3(CH_2)_5N^+$), 2.94 (t, 8H, CH_2N^+ and N^+CH_2), 3.04 (s, 12H, $(CH_3)_2N^+$. ^{13}C-NMR (75 MHz, $CDCl_3$, δ ppm): 14.3 ($CH_3(CH_2)_5N^+$), 50.6 (($CH_3)_2N^+$), 60.5 (N^+CH_2), 63.4 (CH_2N^+). FTIR (1/λ cm^{-1}): 3281 (OCON–H, ν), 2930 and 2850 (C–H, ν), 1685 (C=C, ν), 1635 (NHC=ONC=ONH, ν), 1521 (OCO–NH, ν, OCON–H, δ), 1465 (CH_2, δ), 1248 (N–CH_3, ν), (C–OH, ν).

G1-C7Br: The obtained product was a yellow solid (3.04 g). According to H-NMR spectrum, the yield for quaternization of tertiary amine groups was of 97.9%. ^{1}H-NMR (300 MHz, DMSO-d_6, δ ppm): 2.13 (tt, 4H, $N^+CH_2CH_2$), 3.01 (m, 16H, $(CH_3)_2N^+$ and N^+CH_2), 4.63 (s, 4H, CH_2N^+), 7.56 and 7.59 (s, 10H, $C_6H_8CH_2N^+$). ^{13}C-NMR (75 MHz, $CDCl_3$, δ ppm): 22.9 ($CH_2CH_2N^+$) 49.6 (($CH_3)_2N^+$), 61.1 ($CH_2CH_2N^+$), 66.4 ($C_6H_8CH_2N^+$), 128.5, 129.2 and 133.3 ($C_6H_8CH_2N^+$). FTIR (1/λ cm^{-1}): 3310 (O–H, ν, OCON–H, ν), 2924 and 2855 (C–H, ν), 1687 (NC=ON, ν), 1636 (NHC=ONC=ONH, ν), 1521 (OCO–NH, ν, OCON–H, δ), 1464 (CH_2, δ), 1249 (N–CH_3, ν), 1052 (C–OH, ν).

G1-C8Br: The obtained product was a yellow highly viscose solid (3.17 g). According to H-NMR spectrum, the yield for quaternization of tertiary amine groups was of 75.8%. ^{1}H-NMR (300 MHz, DMSO-d_6, δ ppm): 0.86 (t, 6H, $CH_3(CH_2)_5N^+$), 2.94 (t, 8H, CH_2N^+ and N^+CH_2), 3.03 (s, 12H, $(CH_3)_2N^+$. ^{13}C-NMR (75 MHz, $CDCl_3$, δ ppm): 14.4 ($CH_3(CH_2)_5N^+$), 50.6 (($CH_3)_2N^+$), 60.5 (N^+CH_2), 63.4 (CH_2N^+). FTIR (1/λ cm^{-1}): 3281 (O–H, ν, OCON–H, ν), 2927 and 2857 (C–H, ν), 1686 (NC=ON, ν), 1635 (NHC=ONC=ONH, ν), 1521 (OCO–NH, ν, OCON–H, δ), 1465 (CH_2, δ), 1249 (N–CH_3, ν), 1052 (C–OH, ν).

G1-C10Br: The obtained product was a yellow highly viscose solid (3.34 g). According to H-NMR spectrum, the yield for quaternization of tertiary amine groups was of 100%. ^{1}H-NMR (300 MHz, DMSO-d_6, δ ppm): 0.85 (t, 6H, $CH_3(CH_2)_5N^+$), 2.94 (t, 8H, CH_2N^+ and N^+CH_2), 3.02 (s, 12H, $(CH_3)_2N^+$. ^{13}C-NMR (75 MHz, $CDCl_3$, δ ppm): 14.4 ($CH_3(CH_2)_5N^+$), 50.6 (($CH_3)_2N^+$), 60.5 (N^+CH_2), 63.3 (CH_2N^+). FTIR (1/λ cm^{-1}): 3292 (O–H, ν, OCON–H, ν), 2925 and 2855 (C–H, ν), 1687 (NC=ON, ν), 1635 (NHC=ONC=ONH, ν), 1521 (OCO–NH, ν, OCON–H, δ), 1464 (CH_2, δ), 1252 (N–CH_3, ν), 1052 (C–OH, ν).

G1-C12Br: The obtained product was a yellow highly viscose solid (3.03 g). According to H-NMR spectrum, the yield for quaternization of tertiary amine groups was of 97.7%. ^{1}H-NMR (300 MHz, DMSO-d_6, δ ppm): 0.85 (t, 6H, $CH_3(CH_2)_5N^+$), 2.94 (t, 8H, CH_2N^+ and N^+CH_2), 3.03 (s, 12H, $(CH_3)_2N^+$. ^{13}C-NMR (75 MHz, $CDCl_3$, δ ppm): 14.4 ($CH_3(CH_2)_5N^+$), 50.6 (($CH_3)_2N^+$), 60.5 (N^+CH_2), 63.3 (CH_2N^+). FTIR (1/λ cm^{-1}): 3310 (O–H, ν, OCON–H, ν), 2924 and 2855 (C–H, ν), 1687 (NC=ON, ν), 1636 (NHC=ONC=ONH, ν), 1521 (OCO–NH, ν, OCON–H, δ), 1464 (CH_2, δ), 1249 (N–CH_3, ν), 1049 (C–OH, ν).

G2-C7Br: The obtained product was a yellow solid (2.77 g). According to H-NMR spectrum, the yield for quaternization of tertiary amine groups was of 100%. ^{1}H-NMR (300 MHz, DMSO-d_6, δ ppm): 2.12 (tt, 4H, N+CH2CH2), 3.00 (m, 16H, (CH3)2N+ and N+CH2), 4.61 (s, 4H, CH2N+), 7.56 and 7.76 (s, 10H, C6H8CH2N+). ^{13}C-NMR (75 MHz, $CDCl_3$, δ ppm): 23.0 ($CH_2CH_2N^+$) 49.7 ((CH_3)$_2N^+$), 61.1 ($CH_2CH_2N^+$), 66.5 ($C_6H_8CH_2N^+$), 128.5, 129.3 and 133.4 ($C_6H_8CH_2N^+$). FTIR (1/λ cm^{-1}): 3283 (O–H, ν, OCON–H, ν), 3000 (=C–H, ν), 2931 and 2858 (C–H, ν), 1682 (C=C, ν, OC=ONH, ν), 1633 (NHC=ONC=ONH, ν), 1519 (OCO–NH, ν, OCON–H, δ), 1464 (CH_2, δ), 1246 (N–CH_3, ν), 1051 (C–OH, ν).

G2-C10Br: The obtained product was a yellow powder (2.57 g). According to H-NMR spectrum, the yield for quaternization of tertiary amine groups was of 78.7%. ^{1}H-NMR (300 MHz, DMSO-d_6, δ ppm): 0.85 (t, 6H, $CH_3(CH_2)_3N^+$), 2.95 (t, 8H, CH_2N^+ and N^+CH_2), 3.03 (s, 12H, (CH_3)$_2N^+$. ^{13}C-NMR (75 MHz, $CDCl_3$, δ ppm): 14.4 ($CH_3(CH_2)_3N^+$), 50.6 ((CH_3)$_2N^+$), 60.5 (N^+CH_2), 63.4 (CH_2N^+). FTIR (1/λ cm^{-1}): 3200 (O–H, ν, OCON–H, ν), 2927 and 2856 (C–H, ν), 1684 (OC=ONH, ν), 1637 (NHC=ONC=ONH, ν), 1520 (OCO–NH, ν, OCON–H, δ), 1464 (CH_2, δ), 1249 (N–CH_3, ν), 1052 (C–OH, ν).

1.3. Grafting of G2-C10Br on cotton mat

Dendrons were grafted onto non-woven cotton mats using oxalaldehyde as coupling agent and magnesium chloride ($MgCl_2$) as catalyst [3, 4]. Before grafting, cotton mat (diameter 57 mm, thickness 3 mm) was washed with acetone, EtOH and DW and then immersed in boiling Na_2CO_3 solution (10%) for 1 h, rinsed with DW and dried in a vacuum oven at 40 °C overnight. A solution of 0.3 g of G2-C10Br, 0.3 g of oxalaldehyde (40%) and 0.5 g of $MgCl_2.6H_2O$ in 1.25 g of DMF was poured on the mat and padded via a spatula to give pick up of 340% (owning to weight of the mat). Immediately after padding, the mat was pre-dried at 80-85 °C for 10 min and cured at 140 °C for 5 min. After curing, the mat was rinsed with DMF and DW several times and dried in a vacuum oven at 40 °C overnight. The weight of the cotton mat before and after grafting was measured as 0.61 and 0.64 g, respectively, that showed a weight gain of 4.9%. Meanwhile, grafting of the mat with G2-C10-Br changed its color from white to light brown. ATR-FTIR (1/λ cm^{-1}): 3335 (O–H, ν), 2903 (C–H, ν), 1689 (OC=ONH, ν), 1523 (OCO–NH, ν, OCON–H, δ), 1454, 1428 and 1362 (CH_2, δ), 1054 (C–O–C, ν) and 1030 (C–OH, ν).

1.4. Preparation of PU foam containing G2-C10Br

5.00 g of polyethylene glycol diol (PEG, average M_w 1000 g/mol), 5.00 g of polytetramethylene glycol diol (PTMG, average M_w 1000 g/mol), 1.00 g of glycerol, 0.30 g of G2-C10Br, 0.10 g of DW and 0.04g of DBTDL were mixed at 70 °C for 15 min and then cooled down to 40 °C for 10 min. Then, 5.10 g of HDI ([NCO]/[OH]=1.1) was added to this mixture vigorously stirred until the foaming reaction occurred. Finally, the viscous PUF was cured at 90 °C for 24 hours [5, 6]. Another sample with same formation but without G2-C10Br was also prepared for comparison. FTIR (1/λ cm^{-1}): 3330 (OCON–H, ν), 2931 and 2860 (C–H, ν), 1702 (OC=ONH, ν), 1531 (OCO–NH, ν, OCON–H, δ), 1462 and 1366 (CH2, δ), 1101 (C–O–C, ν).

1.5. Coating of dendrons on glass surface

Hydroxyl groups were generated on glass slides (18×18 mm^2) by dipping them in H_2SO_4/H_2O_2, 3:1 v/v at 80 °C for 1 hour after sonication in EtOH (for 10 min) [7]. Solutions of dendrons in DMF (100µL, 4 g/L) were casted on the treated slides. The coated surfaces were left at room temperature for 24h and then vacuum-dried at 50 °C to ensure removal of DMF.

1.6. Instruments

^{1}H-NMR and ^{13}C-NMR spectra were recorded on a Bruker spectrometer (model Avance 300, Germany) operating at 300 and 75 MHz, respectively, at room temperature using $CDCl_3$ or DMSO-d_6 as solvents. Digilab spectrometer (model Excalibur FTS-3000 series, USA) equipped with an ATR unit was used for recording FTIR spectra at a resolution of 0.5 cm^{-1} and signal averaged over 16 scans.

Thermogravimetric analysis (TGA) was performed on a Netzsch instrument (model TG 209 F1 Libra, Germany) at a heating rate of 10 °C/min under N_2 atmosphere. Differential scanning calorimetry (DSC) was done on a Mettler Toledo device (model DSC 821^e, Switzerland) at a heating rate of 10 °C/min under N_2 atmosphere. Glass transition temperature (T_g) was reported as middle point of baseline change and onset of the endothermic melting peak was considered as melting point (T_m).

Optical microscopy was performed by a Leica Mikrosysteme instrument (model Leica DMRX, Germany) equipped with a digital camera (Leica DC200, Germany). The scale bars were added to the images via Image J software (version 1.50i, USA). Zeiss instrument (model LEO 1530, Germany) was used for field emission scanning electron microscopy (FE-SEM). Standard holders were used for mounting the samples using conductive adhesion graphite-pad (Plano) and sputtered with platinum (2 nm) using a sputter coater (Cressington, model 208HR).

A drop shape analyzer (Krüss, model DSA25E, Germany) was used for the measurement of contact angle of water on the dendron coated glass surfaces using 3.0 µL drop volume. The images were analyzed through Advance drop shape software (version 1.3.1.0) using Sessile drop orientation and circle fitting mode. An average of five measurements is reported.

1.7. Antibacterial assays

The antibacterial activity of dendrons was studied via determining the minimum inhibition concentration (MIC), minimum bactericidal concentration (MBC) and inhibition zone. Due to water insolubility of the prepared dendrons, their solution in DMF were prepared. *Escherichia coli* (*E. coli*, DSM No. 1077, K12 strain 343/113, DSMZ) as Gram negative and *Bacillus subtilis* (*B. subtilis*, DSM No. 2109, ATCC 11774, ICI 2/4 strain, DSMZ) as Gram-positive bacteria were pre-cultured in nutrient broth in a shaking-oven at 37 °C overnight before assays. The nutrients were respectively CASO-Bouillon (30 g/L) and Meat Extract-Pepton (5 and 3 g/L). The OD of the bacteria suspensions (200 µL) were measured at 600 nm using a photometer (PerkinElmer, model Lambda XLS, Germany) to be able to dilute them to desired concentrations. Counting bacteria via serial dilution method on nutrient agar plate showed that an absorbance of 0.125 is equal to a concentration of 2×10^8 CFU/mL and 10^8 CFU/mL, respectively for *E. coli* and *B. subtilis*.

For determining the MIC, serial dilutions of the dendrons' solutions (1-1024 µg/mL) in nutrient broth containing 10^6 CFU/mL of bacteria were prepared in a 24-well plate (total volume was 1 mL for each well). For each series, a well containing bacteria and no dendrons was used as blank. Serial dilutions of DMF without dendrons was also studied as control. After incubation at 37 °C overnight, the wells were inspected for turbidity and the lowest concentration of dendrons that provide a clear solution was noted as MIC [8-11]. Each test was repeated three times. To determine the MBC, 100 mL of the first turbid well and three last clear wells was separately spread on nutrient agar plates and incubated at 37 °C overnight. The plates were then inspected for possible colony formation and the lowest concentration of dendrons that prevented bacterial growth was taken as MBC [8-11]. Each test was done in triplicate.

Agar diffusion (Kirby-Bauer) assay was used to determine the possible inhibition zone of samples. Toward that end, paper discs containing 40 µg of each dendrons was prepared by pouring 10 µL of dendrons' solutions (4 g/L) on blank discs (Oxoid, model CT0998B, UK, 6 mm diameter) and drying in a vacuum oven at 40 °C for 24h. Pure DMF solvent was also poured on a disc as blank. Samples were placed on nutrient agar plate seeded with 10^5 CFU of bacteria. Inhibition zone where no bacterial growth takes place was seen visually after incubation at 37 °C overnight. [8, 12-14].

The antibacterial activity of G2-C10Br grafted cotton mat and PU foam containing G2-C10Br was investigated via shaking flask method [8-10]. For this purpose, 40 mg of samples were put into a flask having 4 mL of bacteria suspension with a concentration of 10^6 CFU/mL in PBS. The flask was incubated in a rotary shaker at 200 rpm at 25 °C. 100 µL of the suspension was taken out at different intervals of time and their bacteria content was determined through serial dilution counting on nutrient agar plate. A negative (only bacteria) and a positive control (polyguanidine as a known antibacterial polymer) was run simultaneously.

For studying the antibacterial activity of dendrons coated glass surfaces, 100 µL of bacteria suspensions with a concentration of 10^7 CFU/mL were poured onto slides in a fume hood. After 2 min, the resultant slides were placed in a Petri dish, covered with a layer of nutrient agar and incubated at 37°C for 24h. The bacterial colonies growth on the slides were monitored visually, using a Helmut Hund inverted optical microscope (model Wilovert AFL 30, Germany) equipped with a digital camera (Casio, model Exilim EX-N1, Germany) and finally through SEM.[15].

2. Results and Discussion

2.1. Monitoring the reaction progress of HDI-uretdione and 3DMAPrOH

The reaction of HDI-uretdione and 3DMAPrOH was monitored by FTIR spectroscopy. A representative sample (with DBTDL and at 25 °C) is shown in Figure S1. FTIR spectra showed that in the course of reaction, the peak at 2270 cm^{-1} corresponding to isocyanate groups gradually disappeared. Meanwhile, two new peaks at 1721 and 1531 cm^{-1} appeared, which correspond to the newly formed urethane groups. Furthermore, the peak at 1768 cm^{-1} corresponding to uretdione rings remained intact.

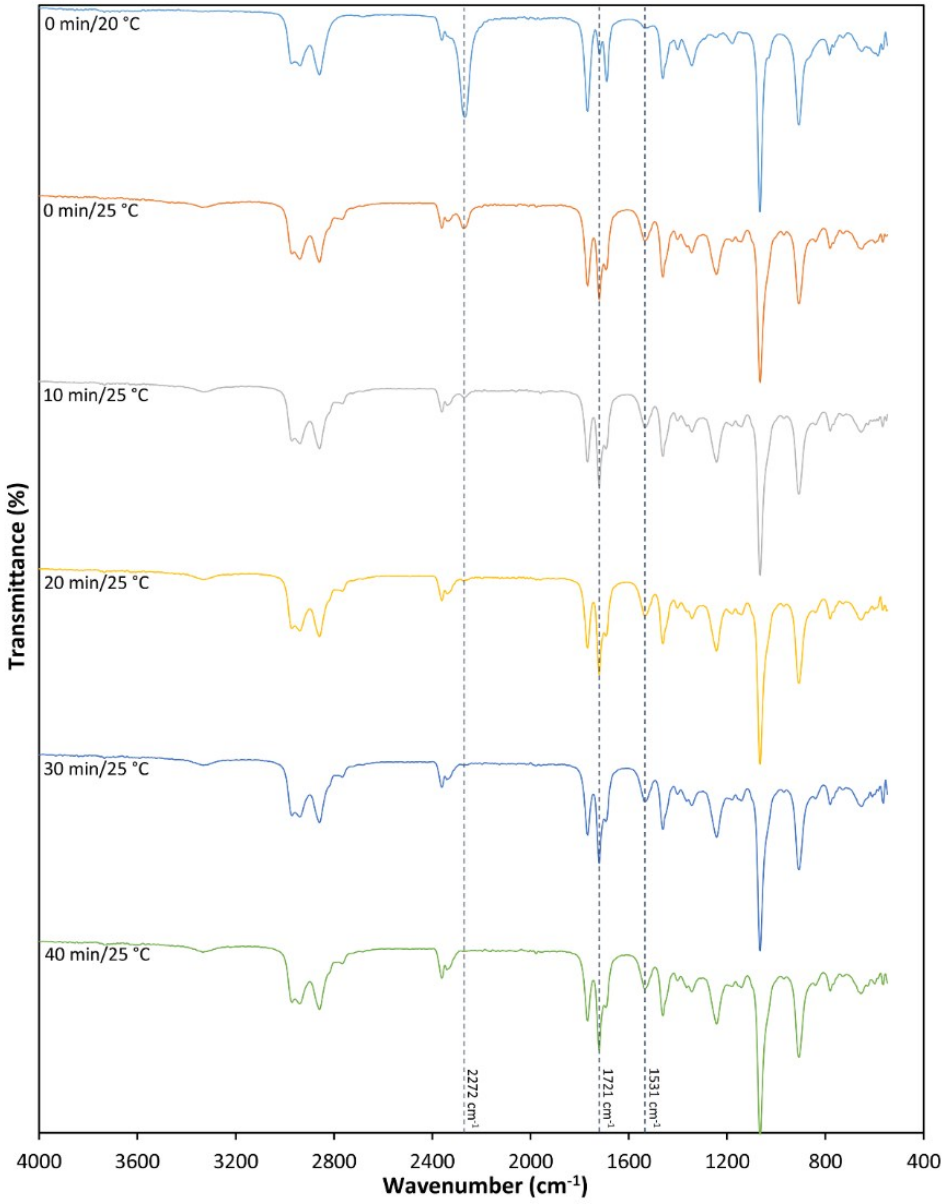

***Figure S1**. Representative FTIR spectra after different time intervals of a reaction mixture of HDI-uretdione and 3DMAPrOH. [NCO]/[OH]: 2.2/1, DBTDL: 0.3 wt% of HDI-uretdione, 25 °C.*

2.2. TGA results for QAS-functionalized dendrons

QAS-functionalized dendrons based on benzyl bromide (C7Br) showed higher decomposition onset values compared to corresponding non-functionalized dendrons made in this work, while their overall degradation shifted to lower temperatures (Figure S2).

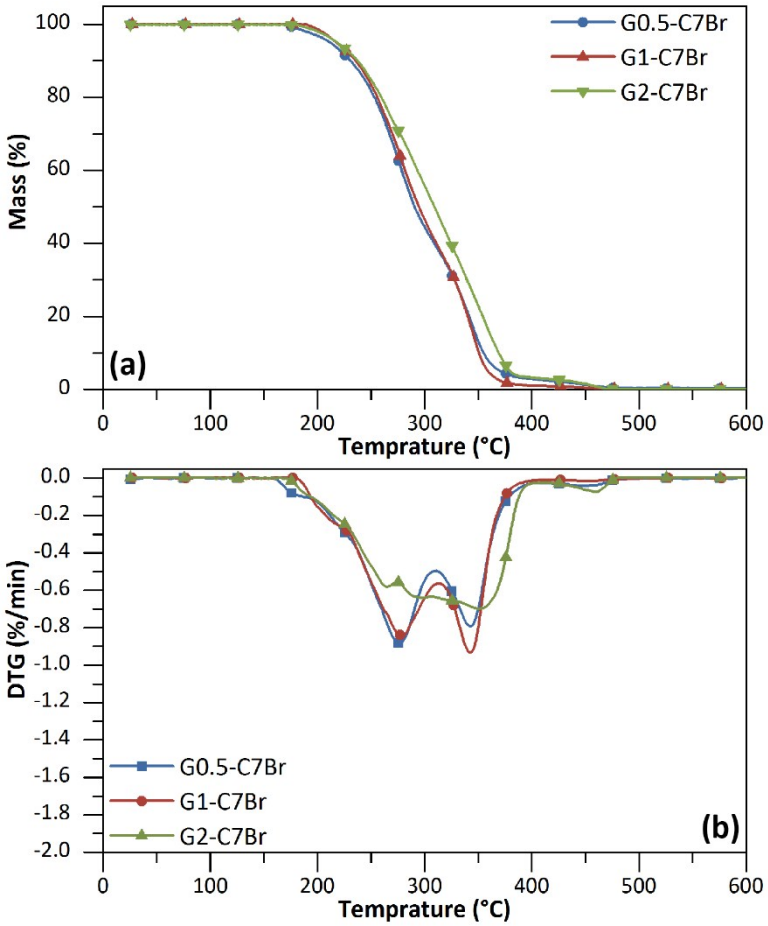

***Figure S2**. TGA (a) and DTG (b) curves of the QAS-functionalized dendrons based on C7Br at a heating rate of 10 °C/min under N_2 atmosphere.*

QAS-G1 dendrons with different alkyls length showed two-step degradation profile with almost similar decomposition onset values (Figure S3).

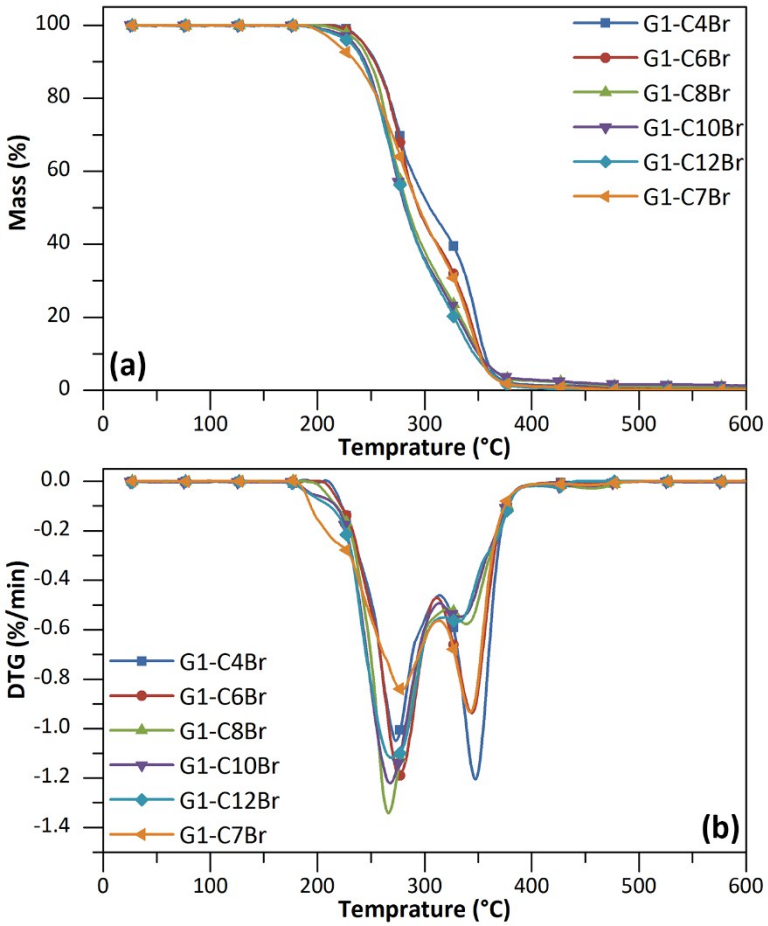

***Figure S3**. TGA (a) and DTG (b) curves of the QAS-G1 dendrons with different alkyls length at a heating rate of 10 °C/min under N_2 atmosphere.*

2.3. Antibacterial activity of QAS-functionalized dendrons

All QAS-functionalized dendrons based on C7Br were highly active against G-positive and G-negative bacteria (Figure S4). The higher generation dendrons (QAS-G2) were not soluble in aqueous media and therefore could not be evaluated for MIC and MBC values.

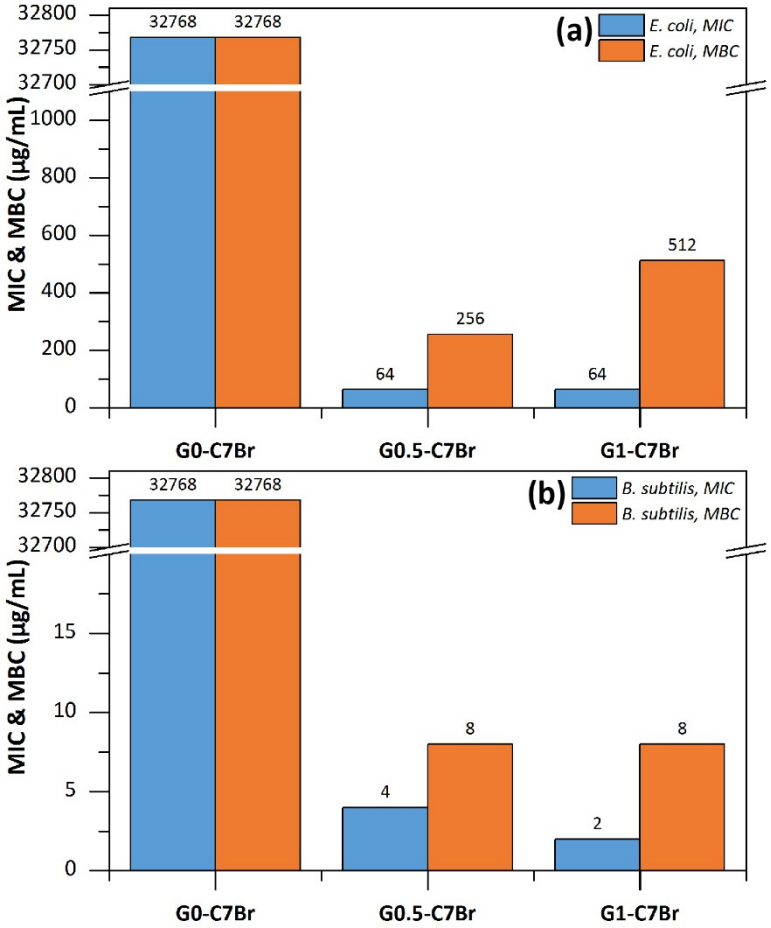

Figure S4*. MIC and MBC values of the QAS-functionalized dendrons based on C7Br determined by serial dilution of dendrons' solutions (1-1024 µg/mL) in nutrient broth containing 10^6 CFU/mL of E. coli (a) or B. subtilis (b).*

The possible leaching of the QAS-functionalized dendrons in aqueous media was studied through agar diffusion (Kirby-Bauer) method [8, 12-14] (Table S1). QAS-G2 dendrons did not show any inhibition zone against both *E. coli* and *S. subtilis* bacteria, but QAS-G0.5 and QAS-G1 dendrons showed significant inhibition zones especially against *S. subtilis* due to their lower molecular weight resulted in partial solubility in aqueous media. For QAS-G1 dendrons, the inhibition zone was initially enhanced with increasing the length of alkyl group and then decreased. The initial enhancement can be due to higher bactericidal activity arisen from longer alkyl group and the subsequent reduction can be related to lower solubility in aqueous media.

***Table S1**. Inhibition zone of the QAS-functionalized dendron against bacteria.[1]*

Sample	Inhibition Zone (mm)	
	E. coli	*S. subtilis*
G1-C7Br	0.0±0.0	2.5±0.0
G1-C10Br	1.0±0.0	1.0±0.0
G2-C7Br	0.0±0.0	0.0±0.0
G2-C10Br	0.0±0.0	0.5±0.0

[1]Values for discs containing 40 µg of each sample placed on nutrient agar plate seeded with 1×10^5 CFU of bacteria after incubation at 37 °C overnight.

2.4. Grafting of G2-C10Br on the cotton mat

Cotton is 99% cellulose after scouring and bleaching. The three hydroxyl groups, one primary and two secondary, in each repeating D-glucose units are chemically reactive and can undergo substitution reactions. G2-C10Br dendrons were grafted on non-woven cotton mat using glyoxal as coupling crosslinking agent and $MgCl_2$ as catalyst [3, 4]. The weight of the cotton mat before and after grafting was measured as 0.61 and 0.64 g, respectively, that showed a weight gain of 4.9%. Meanwhile, grafting of the mat with G2-C10-Br changed its color from white to light brown (Figure S5).

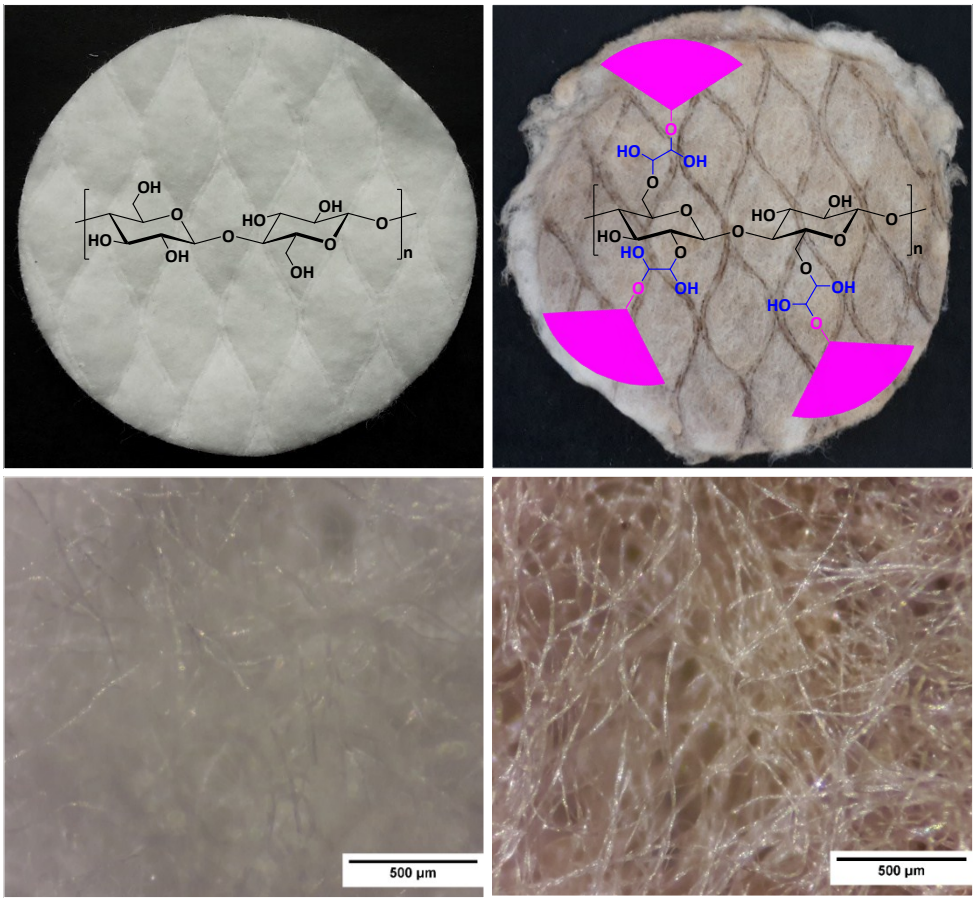

Figure S5. *Images of cotton mat before (left) and after (right) grafting with G2-C10Br.*

The grafting of G2-C10Br on the cotton mat was studied via ATR-FTIR spectroscopy. The FTIR spectrum of grafted mat was same as that of neat cotton mat, except of the appearance of a new peaks at 1689 and 14523 cm^{-1} that is related to urethane and biuret bonds (NC=ON, ν, CO–NH, ν, OCON–H, δ) in the structure of grafted dendrons. Thus, dendrons were successfully attached on cotton mat.

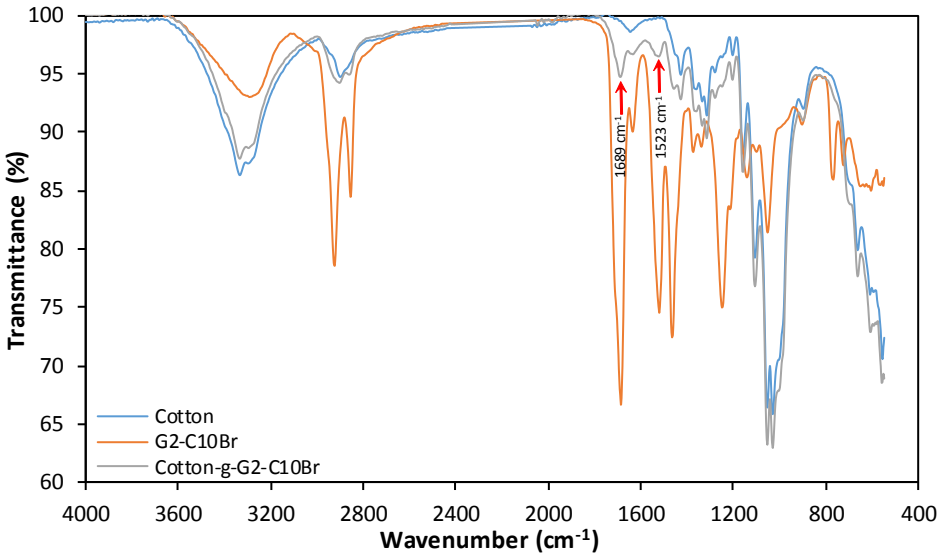

***Figure S6**. ATR-FTIR spectra for cotton mat, G2-C10Br and grafted cotton mat.*

Cotton-*g*-G2-C10Br did not show any inhibition zone against either *E. coli* or *S. subtilis* bacterial (Figure 7). It approved the chemical anchoring of dendrons on cotton fibers preventing their possible leaching into the environment.

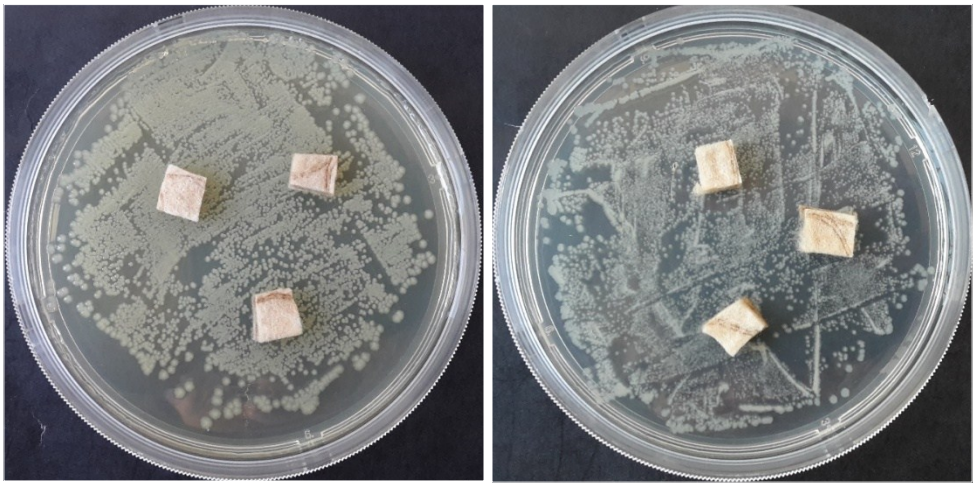

***Figure S7**. Images of agar diffusion assay for cotton-g-G2-C10Br on nutrient agar plate seeded with 10^5 CFU of E. coli (left) or B. subtilis (right) after incubation at 37 °C overnight.*

2.5. Preparation of PU foam containing G2-C10Br

Optical microscopy images (Figure S8) showed that incorporation of G2-C10Br in the formulation of PU foam decreased the cell size from 500-1500 to 200-400 µm and yielded to a more homogenous structure In fact, G2-C10Br acted as a surfactant to decrease the surface tension and emulsified the water molecules resulted in uniform foaming reactions, promoted nucleation of CO_2 bubbles, and stabilized the cell walls during polycondensation reaction [16].

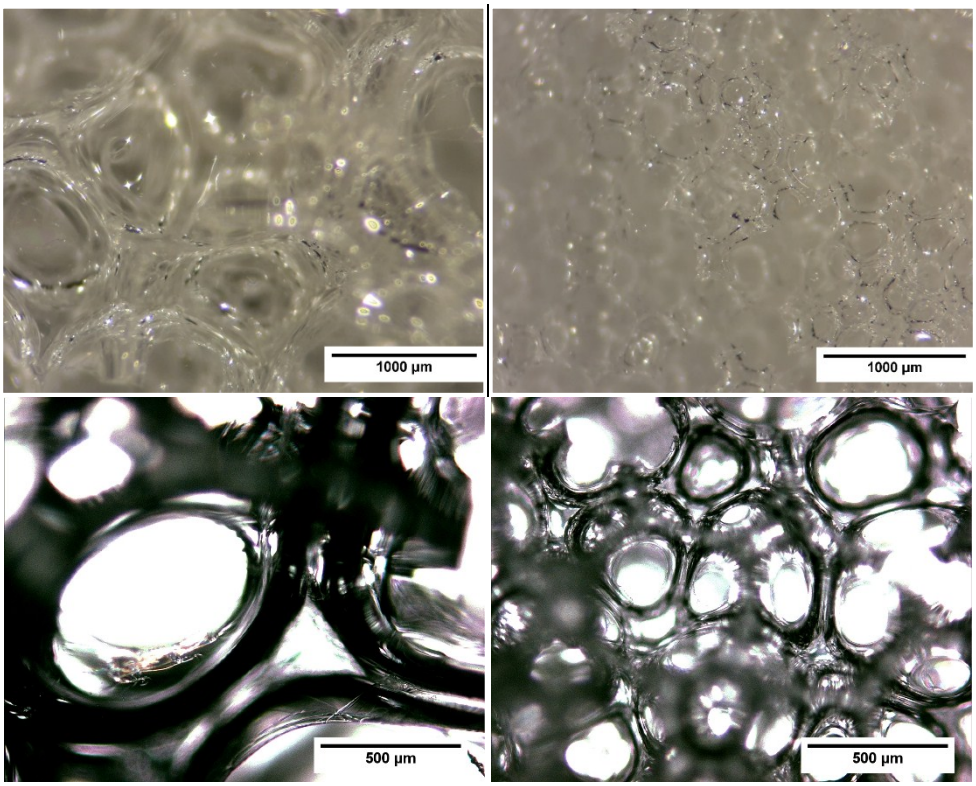

***Figure S8**. Optical microscopy images of PU foams without (left) or with (right) 2wt% of G2-C10Br.*

As expected, no inhibition zone was detected for PU foam containing G2-C10Br against both *E. coli* and *S. subtilis* bacterial (Figure S9). It approved the chemical attachment of dendrons the foam backbone preventing their possible leaching into the environment.

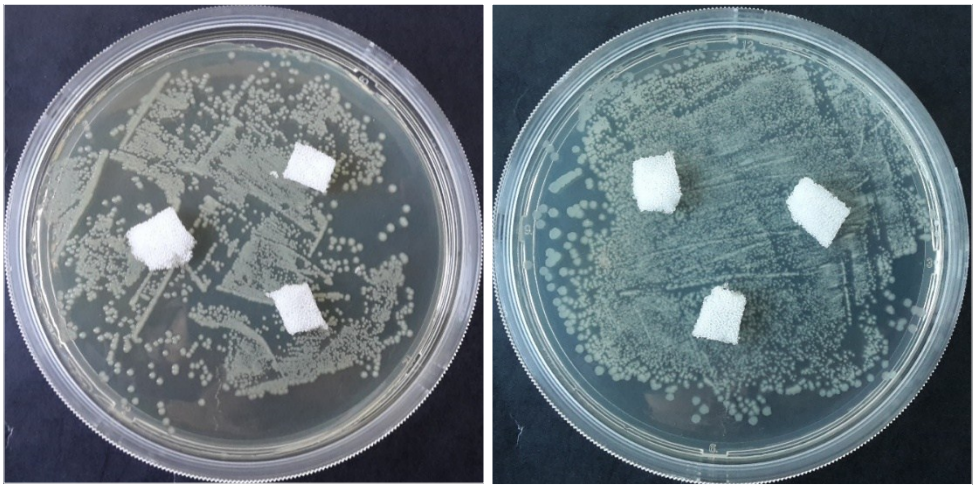

***Figure S9**. Image of Agar diffusion assay for PU foam-g-G2-C10Br on nutrient agar plate seeded with 10^5 CFU of E. coli (left) or B. subtilis (right) after incubation at 37 °C overnight.*

2.6. Coating of QAS-functionalized dendrons on glass surface

The QAS-functionalized dendrons made a smooth and transparent layer on glass slides (Figure S10).

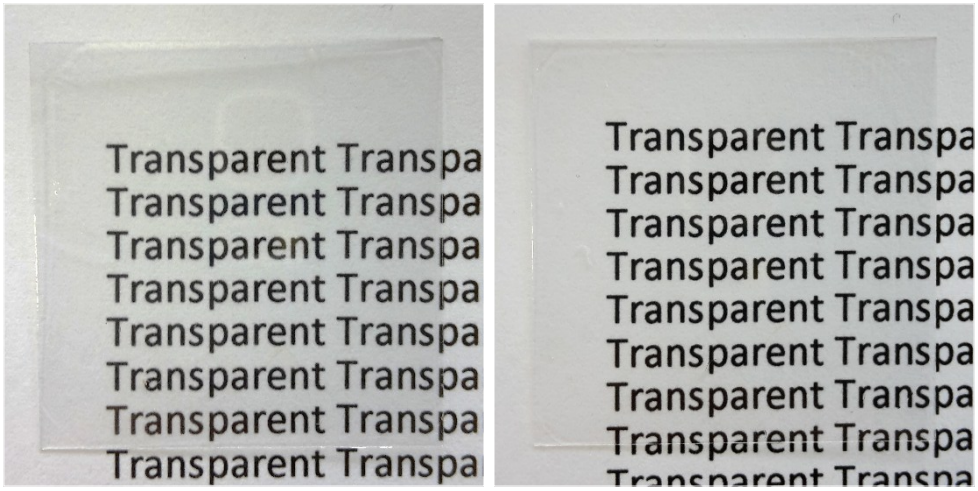

***Figure S10**. Transparency of glass slides coated with G1-C10Br (left) or G2C10Br (right) dendrons.*

The G2-C10Br coated glasses displayed effective bactericidal activity against *B. subtilis* and no white dot corresponds to colony growth was observed (Figure S11b), while bacteria grew on the surface of uncoated glass (Figure S11a). SEM images of these surfaces indicated the formation of bacteria biofilm on uncoated glass slide (Figure S11c), but no bacteria survived and grew on the surface of glasses coated with G2-C10Br (Figure S11d).

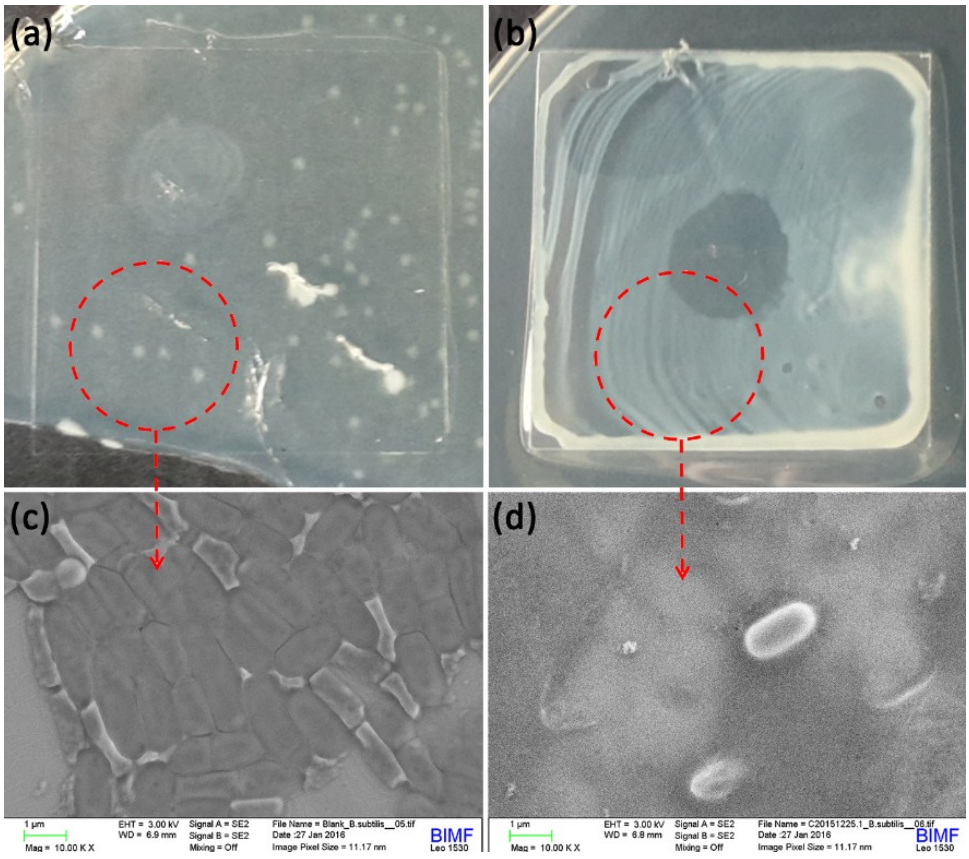

***Figure S11**. Pictures and SEM Images for uncoated (a, c) and coated (b, d) glass slides contacted with B. subtilis (10^6 CFU) after incubation at 37°C overnight. SEM images are at 10000 magnifications.*

3. References:

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