Synthesis, Optical, Electrochemical Properties and Anticancer Activity of (S)-BINOL Cored, Triazole Bridged, Dendrimers Decorated with Rhodamine B Surface Group

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Experimental Section

General procedure for Cu (I)-catalyzed ‘Click’ reaction (Procedure A)

A mixture of the azide and the alkyne in the presence of CuSO$_4$.5H$_2$O (5 mol\%) and sodium ascorbate (10 mol\%) in a mixture of THF–H$_2$O (1:1) was stirred for 12 h at room temperature and after the completion of the reaction, solvent was evaporated. The residue thus obtained after evaporation of the solvent was dissolved in CHCl$_3$ (150 mL) and washed with NH$_4$Cl solution (50 mL) and brine solution (50 mL) and dried over Na$_2$SO$_4$ and then concentrated to give a residue, which was purified by column chromatography (SiO$_2$), using the eluent specified under each compound.

General procedure for the conversion of chloride/bromide to azide (Procedure B)

To the dendritic chloride/bromide (1.0 mmol, 1.0 equiv.) dissolved in a mixture of acetone/water (4 : 1, 60 mL) was added NaN$_3$ (1.5 mmol, 1.5 equiv.) and the reaction mixture was heated to 60 °C for 6 h. The reaction mixture was then cooled to room temperature. The solvent was evaporated and the reaction mixture was diluted with water (100 mL), and extracted with EtOAc (2 ×100 mL). The combined organic layer was washed with saturated NaCl (100 mL), dried over Na$_2$SO$_4$ and then solvent was evaporated to give the corresponding azido compound.

Zeroth generation dendrimer 1

Following the general procedure A 1.0 equiv. of the bispropargyloxy (S) -BINOL 12 (0.8g, 0.20 mmol) was reacted with 2.1 equiv. of the dendritic azide 6 (0.30g, 0.62 mmol,) to give the
zeroth generation dendrimer 1 as brown solid, after purification from silica gel column with 
CHCl₃-MeOH as eluent (19.5:0.5). Yield : 87%. M.P : 112–114 °C. ¹H NMR : (300 MHz, 
CDCl₃): δH 1.14 (t, 24H, J = 7.2Hz); 3.32 (q, 16H, J = 6.3Hz); 3.59 (t, 4H, J = 7.5Hz), 4.16 (t, 
4H, J = 7.2Hz), 5.21 (s, 4H); 6.19 (d, 3H, J = 8.7Hz); 6.29-6.6. 34 (m, 5H); 6.38 (s, 4H); 6.49 (d, 
1H, J=  6.9Hz); 7.06-7.09 (m, 2H); 7.11-7.15 (m, 3H); 7.18-7.21 (m, 2H); 7.38-7.41 (m, 2H); 
7.46-7.49 (m, 6H); 7.73 (d, 2H, J = 7.8Hz); 7.81 (d, 2H, J = 8.4Hz); 7.9 (s, 2H). ¹³C NMR : (75 
MHz, CDCl₃): δC 12.5, 44.3, 46.2, 47.8, 61.8, 65.1, 97.8, 104.7, 108.2, 114.0, 122.9, 123.9, 
128.2, 128.4, 130.5, 132.8, 139.2, 148.9, 153.3, 153.4, 159.7, 168.3. Elemental Analysis. calcd 
for C₈₆H₈₆N₁₂O₆: C, 74.65 ; H, 6.26; N, 12.15%. Found: C, 73.38; H, 6.06; N, 11.91%.

First generation dendrimer 2

Following the general procedure A 1.0 equiv. of the bispropargyloxy (S)-BINOL 12 
(0.100g, 0.27 mmol) was reacted with 2.1 equiv. of the dendritic azide 9 (0.73g, 0.58 mmol) to 
give the first generation dendrimer 2 as dark red solid, after purification from silica gel column 
with CHCl₃-MeOH as eluent (19:1). Yield: 86%. M.P: 122–123 °C. ¹H NMR : (300 MHz, 
CDCl₃): δH 1.12 (s, 48H); 3.30 (s, 32H); 3.87 (t, 8H, J = 7.5Hz), 4.27 (t, 8H, J = 7.2Hz), 5.10 (s, 
8H); 5.26 (s, 4H); 5.38 (s, 4H); 6.18 (s, 9H); 6.23 (d, 9H, J=7.8Hz); 6.38 (s, 9H); 6.50 (s, 2H); 
6.62 (d, 3H, J = 8.1Hz); 6.79-6.91 (s, 2H); 7.06 (d, 6H, J = 3Hz); 7.20 (d, 2H, J = 5.4Hz); 7.43 
(s, 2H); 7.53 (s, 9H); 7.61-7.71 (m, 3H); 7.86 (s, 3H); 8.02 (s, 5H). ¹³C NMR : (75 MHz, 
CDCl₃): δC 12.5, 44.3, 46.2, 48.8, 59.0, 60.2, 61.8, 65.1, 97.9, 98.2, 104.7, 108.3, 114.0, 122.9, 
123.4, 123.9, 125.2, 126.3, 128.2, 128.4, 129.4, 130.5, 132.8, 133.08, 139.2, 148.9, 153.3, 153.4, 
159.7, 168.3. Elemental Analysis. calcd for C₁₇₂H₁₇₆N₃₀O₁₄: C, 71.55 ; H, 6.14; N, 14.55%. 
Found: C, 70.44; H, 6.01; N, 14.38%.
Second generation dendrimer 3

Following the general procedure A 1.0 equiv. of the bispropargyloxy (S)-BINOL 12 (0.17g, 0.46 mmol, 1.0 equiv.) was reacted with 2.1 equiv. of the dendritic azide 11 (1.26g, 0.98 mmol) to give the second generation dendrimer 3 as dark red solid, after purification from silica gel column with CHCl₃-MeOH as eluent (19:1). Yield: 78%. M.P: 131–132 °C. ¹H NMR : (300 MHz, CDCl₃): δH 1.14 (s, 96H); 3.31 (s, 64H); 3.81 (t, 16H, J = 7.5Hz); 4.60 (t, 16H, J = 7.2Hz), 5.01 (s, 4H); 5.26 (s, 24H); 5.37 (s, 12H); 6.25 (s, 16H); 6.35-6.38 (m, 19H); 6.71 (m, 10H); 6.91 (s, 12H); 7.08 – 7.14 (m, 8H); 7.44 (s, 12H); 7.51-7.54 (m, 22H); 7.57-7.87(m, 16H); 7.97 (m, 10H). ¹³C NMR : (75 MHz, CDCl₃): δC 12.6, 44.3, 47.4, 53.8, 62.5, 64.1, 65.1, 97.9, 98.2, 104.8, 108.2, 109.0, 120.7, 122.4, 122.9, 123.9, 125.3, 126.3, 128.0, 128.2, 128.4, 128.5, 129.5, 130.4, 132.8, 133.0, 133.8, 144.2, 148.9, 153.2, 153.3, 153.7, 153.9, 168.6. Elemental Analysis. calcd for C₃₄₅H₃₅₇N₆₅O₃₀: C, 70.30; H, 6.11 ; N, 15.45%. Found: C, 69.89; H, 6.01; N, 15.01%.

Second generation chloro dendron 10

Using general procedure A the dendritic chloride 10 was obtained as pink solid from the 3,5-bispropargyloxy benzyl chloride 7 (0.250 g, 1.07 mmol) and the rhodamine azide 6 (1.14 g, 2.24 mmol) after purification from silica gel column with CHCl₃:MeOH as eluent (19:1). Yield: 86%. ¹H NMR : (300 MHz, CDCl₃): δH 1.15 (t, 48H, J = 6.6Hz); 3.30-3.32 (q, 32H, J = 6.6Hz); 3.59 (t, 8H, J = 7.5Hz), 4.16 (t, 8H, J = 7.2Hz); 4.68 (s, 2H); 5.03 (s, 12H); 5.40 (s, 4H); 6.25 (s, 11H); 6.37 (d, 12H, 8.2Hz); 6.45-6.49 (m, 10H); 7.08 (m, 4H); 7.44 (s, 8H); 7.58 (s, 6H); 7.87 (s, 4H). ¹³C NMR: (75 MHz, CDCl₃): δC 12.5, 41.9, 42.0, 44.3, 64.8, 69.3, 98.3, 105.8,
108.5, 122.8, 123.7, 127.9, 128.5, 130.8, 132.4, 149.2, 153.3, 153.5, 167.8, 168.0. Elemental Analysis. calcd for C₅₉H₁₆₉ClN₃O₁₄: C, 69.20; H, 6.17; N, 15.23%. Found: C, 68.91; H, 5.89; N, 14.92%.

**Second generation azido dendron 11**

Using the general procedure B, the dendritic azide 11 was obtained as pink solid from the dendritic chloride 10 (1.02 g, 0.40 mmol) and sodium azide (0.06 g, 1.20 mmol) after purification from silica gel column with CHCl₃ as eluent. Yield: 92%. ¹H NMR (300 MHz, CDCl₃): δH 1.14 (t, 48H, J = 6.0 Hz); 3.30-3.31 (q, 32H, J = 6.3Hz); 3.57 (s, 2H); 3.59 (t, 8H, J = 7.5Hz), 4.16 (t, 8H, J = 7.2Hz), 5.03 (s, 12H); 5.13 (s, 4H); 6.23 (d, 10H, J = 8.4Hz); 6.36 (d, 12H, 7.8Hz); 6.46 (s, 3H); 6.53 (s, 8H); 7.07 (s, 4H); 7.44 (s, 8H); 7.57(s, 6H); 7.87 (s, 4H). ¹³C NMR: (75 MHz, CDCl₃): δC 12.6, 40.1, 44.3, 47.8, 61.8, 65.2, 97.8, 104.7, 108.3, 114.0, 122.9, 123.9, 128.2, 128.4, 130.4, 132.8, 139.2, 148.9, 153.3, 153.4, 159.8, 168.4.
$^1$H NMR Spectrum (300MHz, CDCl$_3$) of dendrimer 1
$^{13}$C NMR spectrum (75MHz, CDCl$_3$) of dendrimer 1
$^1$H NMR Spectrum (300MHz, CDCl$_3$) of dendrimer 2
$^{13}$C NMR spectrum (75MHz, CDCl$_3$) of dendrimer 2
$^1$H NMR Spectrum (300MHz, CDCl$_3$) of dendrimer 3
$^{13}$C NMR spectrum (75MHz, CDCl$_3$) of dendrimer 3
$^1$H NMR Spectrum (300MHz, CDCl$_3$) of rhodamine b bromo dendron 5$^{19}$
$^{13}$C NMR spectrum (75MHz, CDCl$_3$) of rhodamine b bromo dendron 5$^{19}$
$^1$H NMR Spectrum (300MHz, CDCl$_3$) of rhodamine b chloro dendron 8$^{19}$
$^{13}$C NMR spectrum (75MHz, CDCl$_3$) rhodamine b chloro dendron 8$^{19}$