Electronic Supplementary Material (ESI) for Journal of Materials Chemistry


# Supporting Information for:
# Surface Modification of Plasticized Poly(Vinyl Chloride)

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**Additional Figures**

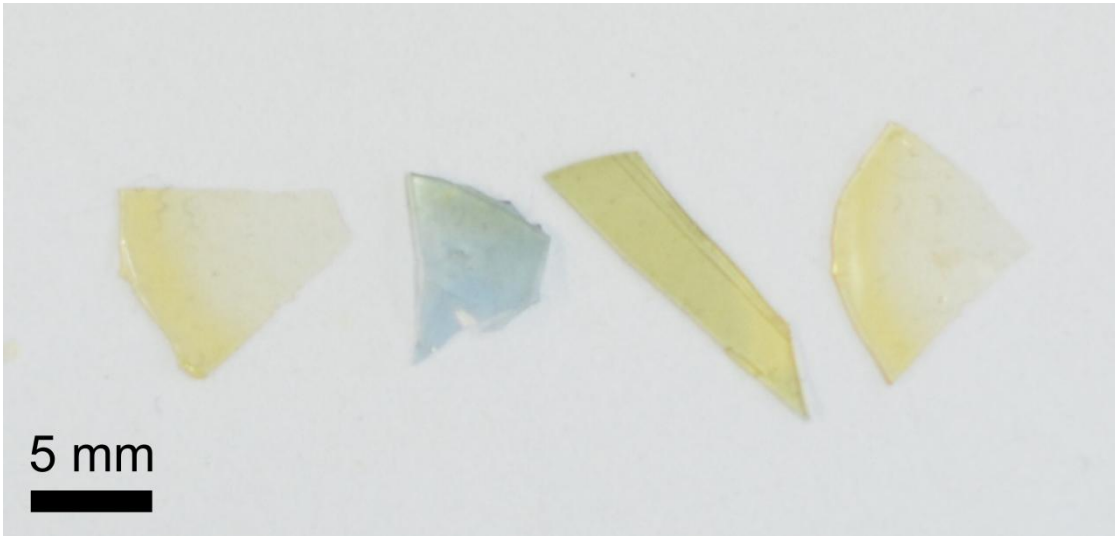


**Figure 1S**. Photo of membranes modified with Nile blue from left to right: membrane before modification, membrane modified in water/THF, membrane modified in water , membrane treated with water solution of the dye, without catalyst (blank experiment).

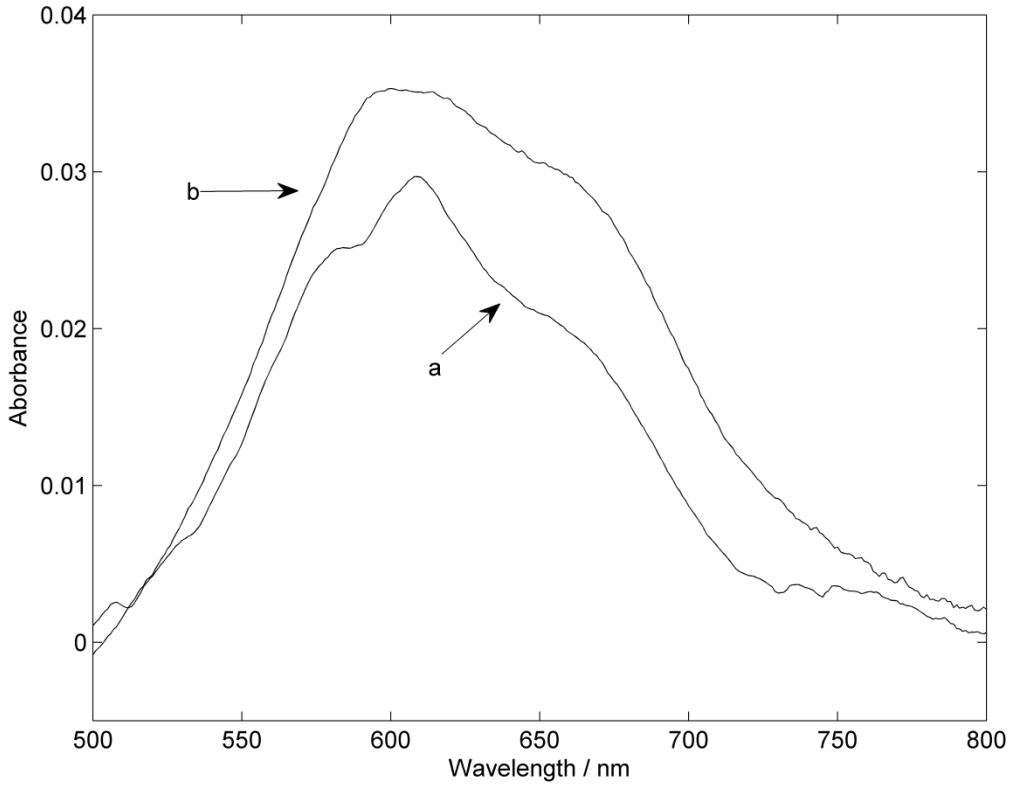


**Figure 2S**. VIS spectra of Nile blue modified membranes: a) membrane modified in water, b) membrane modified in water/THF. In both cases spectrum of the blank membrane was subtracted for better clarity.

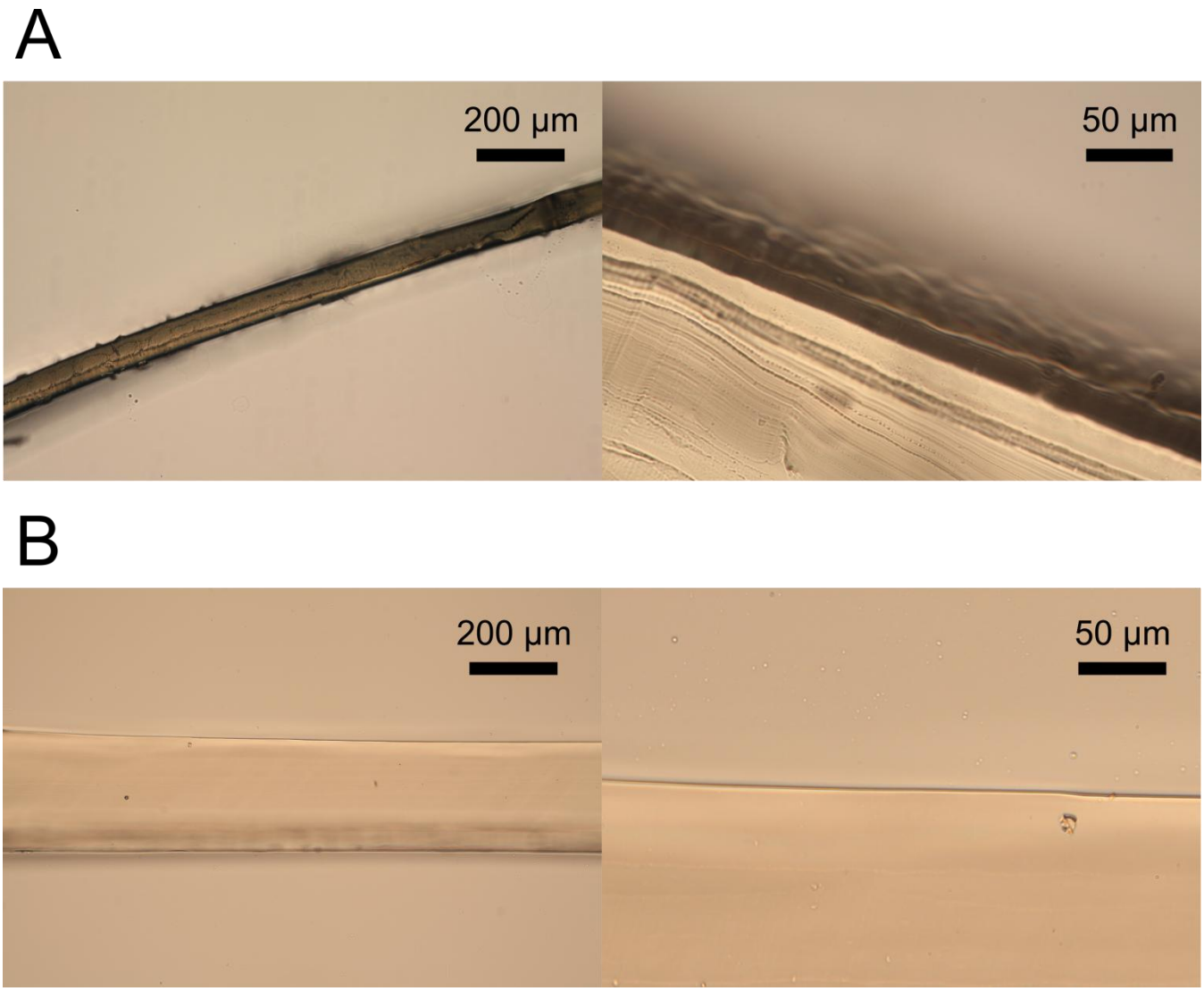


**Figure 3S**. Microscope images of a cross-section through a Nile blue modified membrane from water/THF reaction (A) and unmodified membrane (B).

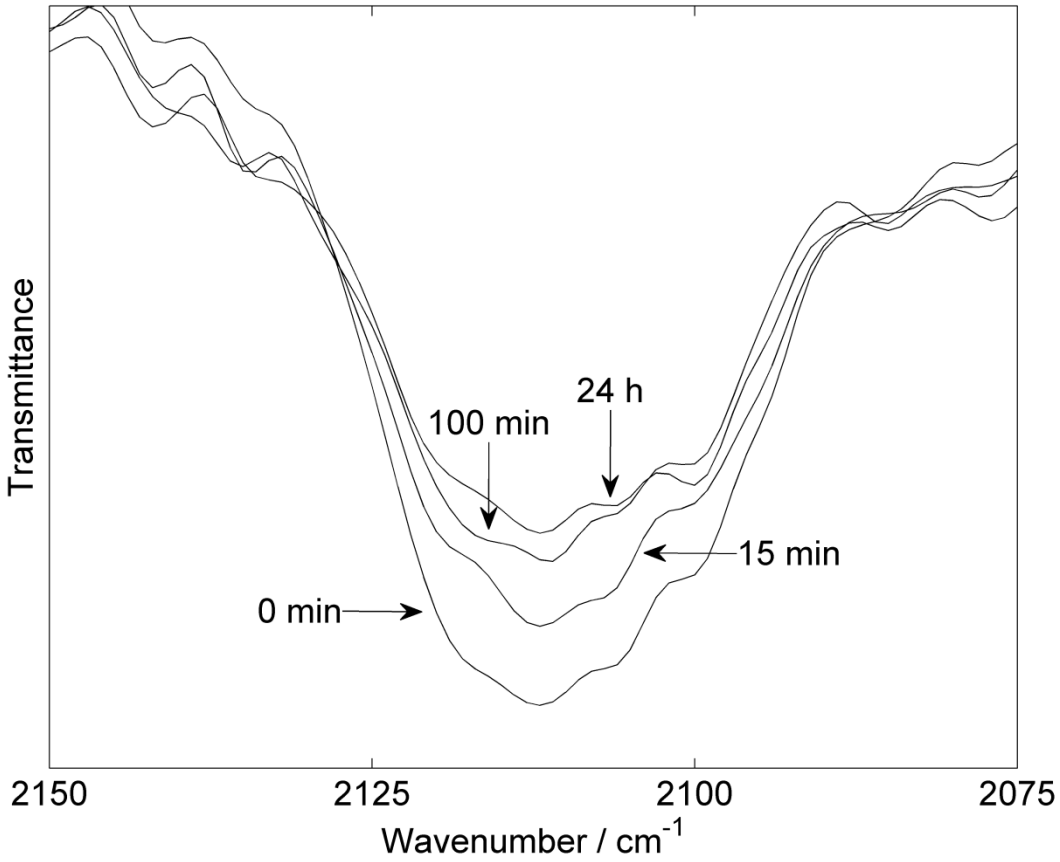


**Figure 4S**. Magnification of FTIR triazole signal at 2100 $cm^{-1}$ showing decrease of peak intensity with the reaction time.

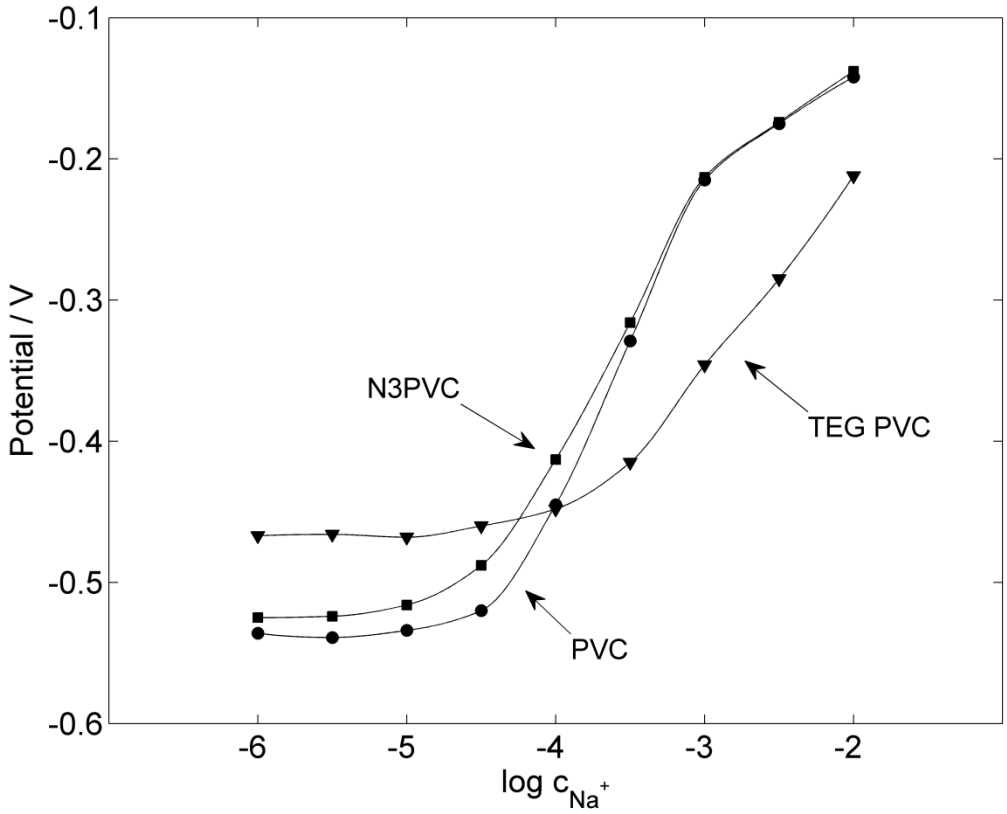


**Figure 5S**. Calibration curves for sodium in 1mM TRIS buffer 7.4 pH + 10mM $Mg(NO_3)_2$ background solution obtained for PVC (circles), $N_3$PVC (squares) and TEG-modified PVC electrode (triangles).

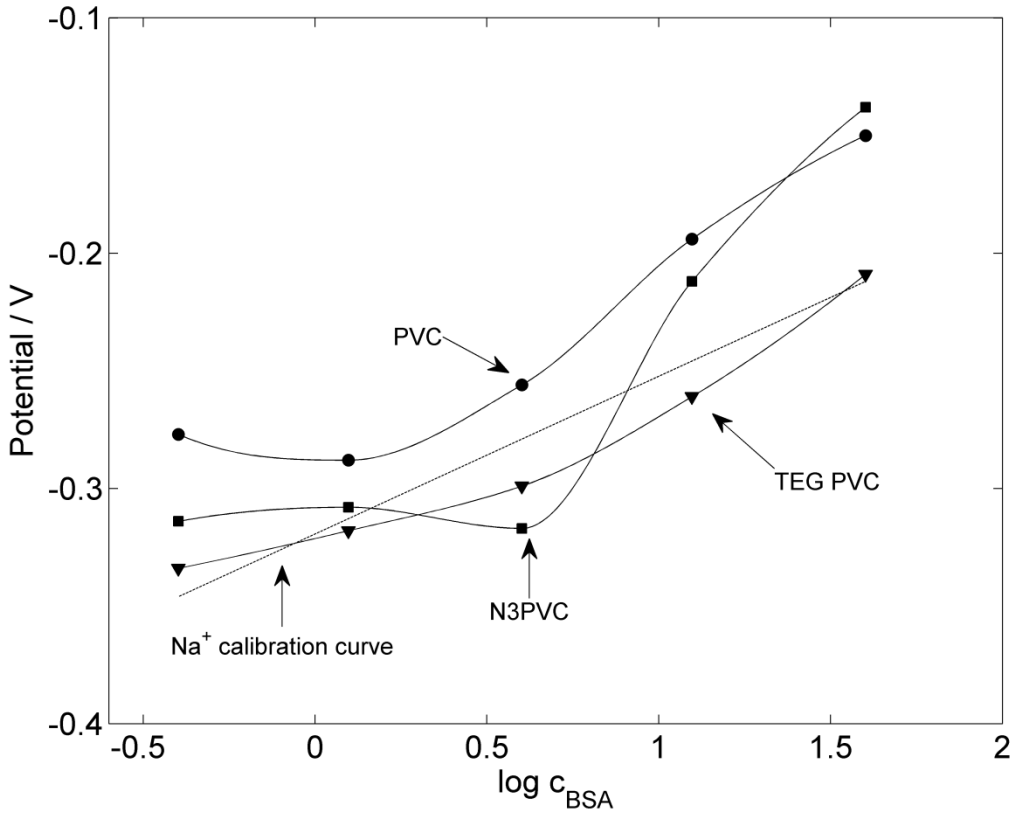


**Figure 6S**. PVC (circles), $N_3$PVC (squares) and TEG-modified PVC electrode (triangles) response to increasing concentration of albumin (mg/ml)

Experimental

Synthesis

$N_3$PVC: The substitution reaction of PVC with $NaN_3$ was carried out using 1 g (16 mmol based on monomeric unit) of PVC and 1.04 g (16 mmol) of $NaN_3$ in 42 mL of DMF-water mixture (5:1 volume ratio) and heated at 60 °C under nitrogen for 92 h. When the desired degree of modification was achieved, the reaction mixture was cooled to room temperature, the product was filtered, washed with distilled water and methanol, and subsequently dried under reduced pressure. Azide content was determined using elemental analysis.

3,6,9,12-tetraoxapentadec-14-yn-1-ol [2a]: To a solution of 10.1 g (51.9 mmol) tetraetylene glycol in dry THF at 0°C under nitrogen atmosphere 0.85 g (21 mmol) of 60% NaH in oil was carefully added and after 15 min 2.37 ml (21 mmol) of 80% toluene solution of propargyl bromide was slowly added. Mixture was stirred at 0°C for another 3 h, and then allowed to warm to RT and left overnight. Then solvent was evaporated and residue extracted with ethyl acetate and after removal of the solvent product was purified using flash chromatography on silica gel using ethyl acetate as an eluent. Yield 3.4g (15 mmol, 71%).$^1$H NMR (400 MHz $CDCl_3$): δ 4.21 (d, J=2.4 Hz, 2H), 3.76-3.67 (m, 14H), 3.61 (t, J=4.2 Hz, 2H), 2.67 (s, 1H), 2.44 (t, J=2.4 Hz, 1H)

PEG600 propargyl ether [2b]: Above procedure was employed. Yield 28%. $^1$H NMR (400 MHz $CDCl_3$): δ 4.21 (d, J=2.4 Hz, 2H), 3.75-3.60 (m, 38H), 3.61 (t, J=4.2 Hz), 2.58 (s, 1H), 2.44 (t, J=2.4 Hz)

1-iodo-3,6,9,12-tetraoxapentadec-14-yne [3a]: A solution of 500 mg (2.15 mmol) of tetraethylene glycol and 1.3 g triethylamine (12.9 mmol) in methylene chloride under nitrogen atmosphere was cooled to 0°C and 490 mg (4.3 mmol) of mesyl chloride in 2 ml of $CH_2Cl_2$ was added dropwise. The reaction was maintained at 0°C for 3 h and then it was allowed to warm to room temperature and stirred overnight. Then reaction mixture was washed with water, dried with $MgSO_4$ and solvent was evaporated. 350 mg (52 %) of product was obtained in the form of yellow oil. It was then used in next step without further

purification.[1]H NMR (400 MHz $CDCl_3$): δ 4.38 (m, 2H), 4.19 (d, J=2.4 Hz), 3.77 (m, 2H), 3.69-3.64 (m, 12H), 3.08 (s, 3H), 2.45 (t, J=2.4 Hz, 1H)

To a 250 mg (0.8 mmol) of 2 in a 20 ml of acetone 1.5 g (10 mmol) of NaI was added and the mixture was refluxed overnight. Then solvent was evaporated and the residue was taken up in 50 ml 1:1 $CH_2Cl_2$ : H2O mixture. Organic layer was dried and evaporated giving pure product in 91% yield (250 mg, 0.78 mmol).[1]H NMR (400 MHz $CDCl_3$): δ 4.22 (d, J=2.4 Hz, 2H), 3.78 (t, J=6.7 Hz, 2H), 3.72-3.68 (m, 12H), 3.28 (t, J=6.7 Hz, 2H), 2.45 (t, J=2.4 Hz, 1H)

PEG600 propargyl ether iodide derivative [3b]: above procedure was used. Yield 55%. [1]H NMR (400 MHz $CDCl_3$): δ 4.22 (d, J=2.4 Hz, 2H), 3.78 (t, J=6.7 Hz, 2H), 3.75-3.62 (m, 36H), 3.31 (t, J=6.7 Hz, 2H), 2.45 (t, J=2.4 Hz, 1H)

N-(naphthalen-1-yl)-3,6,9,12-tetraoxapentadec-14-yn-1-amine [6]:300 mg (0.87 mmol) of 3, 129 mg (0.9 mmol) of 1-naphtylamine was dissolved in 10 ml of DMF. Then 1.24 g (9 mmol) of $K_2CO_3$ was added and mixture was stirred at 80°C overnight. After solvent evaporation product was purified by flash chromatography with 1:1 hexane:ethyl acetate as an eluent, yielding 50 mg (0.14 mmol, 16%). [1]H NMR (400 MHz $CDCl_3$): δ 7.91 (d, J=9.4 Hz, 1H), 7.81 (d, J=9.4 Hz, 1H), 7.49-7.43 (m, 2H), 7.37 (t, J=7.6 Hz, 1H), 7.27 (d, J=8.2Hz, 1H), 6.63 (d, J=7.9 Hz, 1H), 4.19 (d, J=2.4 Hz, 2H), 3.88 (t, J=5 Hz, 2H), 3.75-3.66 (m, 12H), 3.48 (t, J=5 Hz, 2H), 2.45 (t, J=2.4 Hz, 1H)

Fluorescein derivative [7a]: A mixture of 267 mg of fluorescein (0.8 mmol) and 380 mg of 3 (0.73 mmol) in 5 ml of DMSO and 221 mg of $K_2CO_3$ solid (1.6 mmol) was stirred in an oil bath at 65°C for 20 h. The red precipitate that formed upon addition of 10 m1 saturated NaCl was filtered, washed with deionized water and redissolved in ethyl acetate with 1 M HCl. The yellow orange, organic phase was separated, dried and evaporated to dryness under reduced pressure. The product was purified by flash chromatography using 10% MeOH in $CH_2Cl_2$ as an eluent, giving 130 mg (0.28 mmol, 46%) of 7. [1]H NMR (400 MHz $CDCl_3$): δ 8.28 (d, J=6.6 Hz, 1H), 7.72 (t, J=7.5, 1H); 7.66 (t, J=7.5, 1H), 7.28 (d, J=6.3 Hz, 1H), 6.90 (d, J=6.3 Hz, 2H), 6.79 (d, J=2.1 Hz, 2H), 6.71 (dd, J=9.2, 2.1 Hz, 2H), 4.15 (d, J=2.4 Hz, 2H), 4.09 (m, 2H), 3.68-3.57 (m, 8 H), 3.49-3.47 (m, 2H), 3.40-3.37 (m, 2H), 3.34-3.32 (m, 2H), 2.42 (t, J=2.4 Hz, 1H)

Fluorescein derivative [7b] above procedure was used. Yield 20%. [1]H NMR (400 MHz $CDCl_3$): δ 8.28 (d, J=6.6 Hz, 1H), 7.72 (t, J=7.5, 1H); 7.66 (t, J=7.5, 1H), 7.28 (d, J=6.3 Hz, 1H), 6.90 (d, J=6.3 Hz, 2H), 6.79 (d, J=2.1 Hz, 2H), 6.71 (dd, J=9.2, 2.1 Hz, 2H), 4.15 (d, J=2.4 Hz, 2H), 4.13 (m, 2H), 3.60-3.57 (m, 34 H), 3.49-3.47 (m, 2H), 3.40-3.37 (m, 2H), 3.34-3.32 (m, 2H), 2.42 (t, J=2.4 Hz, 1H)

3,3'-((3-hydroxy-4-((4-nitrophenyl)diazenyl)phenyl)azanediyl)bis(propane-1-sulfonic acid) [8] was synthesized according to the literature procedure.[1]

Nile blue derivative [9]: 60 mg (0.12 mmol) of 8, 50 mg of 6 (0.14 mmol) and 0.1 ml of 70% of perchloric acid were dissolved in 3 ml of DMF and heated to 160°C for 24 h. Then solvent was removed under reduced pressure and residue was purified by flash chromatography on C18 silica gel water as an eluent, giving 30 mg (0.04 mmol, 33%) of 9. [1]H NMR (400 MHz MeOD): δ 8.47 (d, J=7.9 Hz, 1H), 8.11 (d, J=8.2 Hz, 1H), 7.76 (t, J=7.3 Hz, 1H), 7.64 (t, J=9.2 Hz, 1H), 7.46 (d, J=9.2 Hz, 1H), 7.17 (d, J=8, 1H), 6.85 (s, 1H), 6.75 (s, 1H), 4.10 (d, J=2.4 Hz, 2H), 4.02-3.92 (m, 4H), 3.83-3.53 (m, 20H), 3.01 (t, J=7 Hz, 4H), 2.84 (t, J=2.4 Hz, 1H), 2.20 (m, 4H)

**References**

**1. N.-h. Ho, R. Weissleder and C.-H. Tung, *Tetrahedron*, 2006, 62.**