Electronic Supplementary Material (ESI) for RSC Advances.

Fabrication of highly photoluminescent quantum dot-polymer composite micropatterned surface using thiol-ene chemistry

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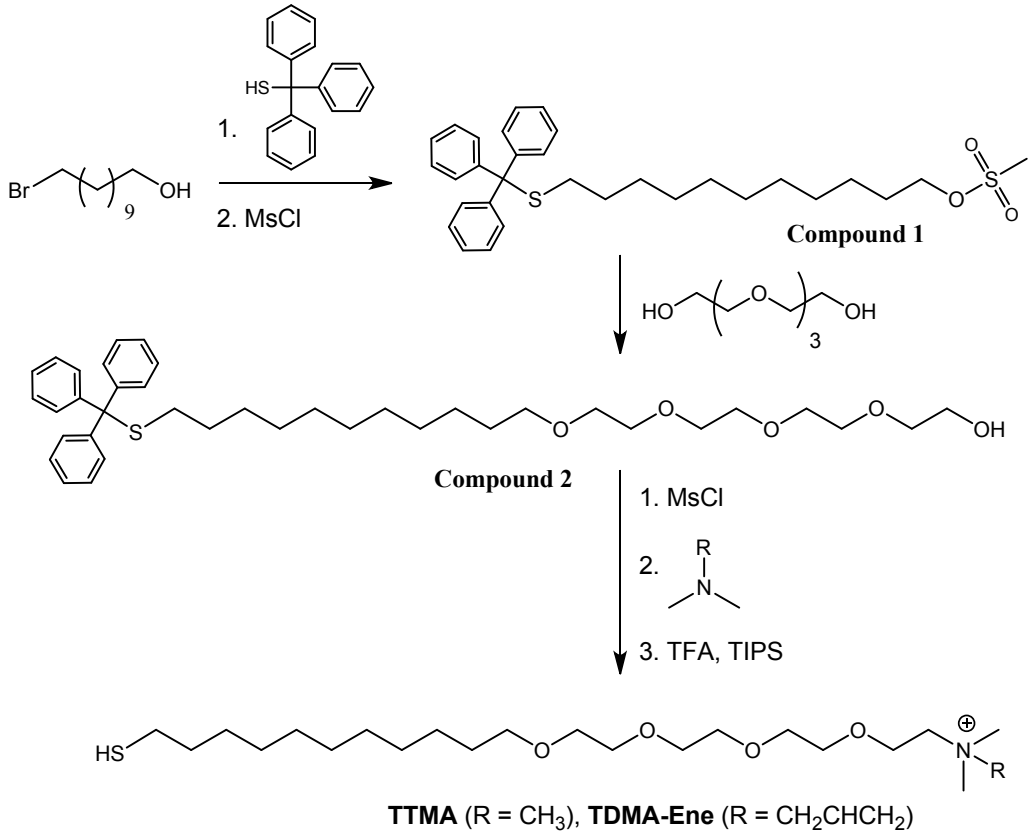

Scheme S1. Scheme for the synthesis of functional ligands (TOH, TTMA, TDMA-Ene)

Synthesis of functionalized ligands

Compound 1: 10 mL NaOH solution (4 M) was added to triphenylmethanethiol (8.29 g, 30 mmol) solution in a mixture of toluene (25 mL) and ethanol (25 mL). After homogenous mixing, 11-Bromo-1-undecanol (5 g, 20 mmol) in a mixture of toluene (10 mL) and ethanol (10 mL) was added to the solution. After stirring the mixture at room temperature overnight, the solution was washed several times with saturated $NaHCO_3$ solution. After removing the solvent in the organic layer, the crude product obtained was purified by column chromatography using an eluent (hexane:ethyl acetate (EA) = 4:1). The product was dissolved in 200 mL dichloromethane (DCM) with TEA (5.58 mL, 40 mmol). After stirring at 0 °C for 0.5 h, CH_3SO_2Cl (MsCl, 2.3 mL, 30 mmol) was slowly added dropwise to the solution followed by stirring at room temperature overnight. After completing the reaction, the mixture was diluted with DCM and washed with $NaHCO_3$ and water. The solvent in the organic layer was removed, and compound **1** was obtained with 68% yield after performing column chromatography using hexane:EA (4:1) as the eluent. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.41–7.16 (m, 15H, H_{Ar}), 4.37 (t, 2H, -C$\underline{H}_2$-OMs), 2.97 (s, 3H, -O-SO_2C$\underline{H}_3$), 2.13 (t, 2H, trt-SC$\underline{H}_2$-), 1.74–1.70 (m, 2H, $MsOCH_2$-C$\underline{H}_2$-), 1.46–1.12(m, 16H, -C$\underline{H}_2$-).

Compound 2: Tetraethylene glycol (TEG, 30.7 ml, 178 mmol) in 100 mL THF was mixed with 60 mL 4 M NaOH solution. The solution was heated to 100 °C with stirring for 1 h. Compound **1** (9.3 g, 17.8 mmol) was added to the solution under stirring followed by stirring the mixture further at 100 °C. After 24 h, the mixture was diluted with a mixture of EA and hexane (1:1) and washed with $NaHCO_3$ and water. The solvent in the organic layer was removed followed by purifying with column chromatography using hexane:EA (1:4) as the eluent. Finally, compound **2** was obtained with 45% yield. ^{1}H NMR (400 MHz, $CDCl_3$): δ =

7.41–7.16 (m, 15H, H_{Ar}), 3.71–3.54 (m, 16H, -OC$\underline{H}_2$C$\underline{H}_2$O-), 3.45 (t, 2H, -OC$\underline{H}_2$CH$_2$CH$_2$), 2.14 (t, 2H, -SC$\underline{H}_2$-), 1.57–1.53 (m, 2H, -OCH$_2$C$\underline{H}_2$CH$_2$), 1.46–1.12 (m, 16H, -C$\underline{H}_2$-).

23-mercapto-N,N,N-trimethyl-3,6,9,12-tetraoxatricosan-1-aminium (TTMA) and N-allyl-23-mercapto-N,N-dimethyl-3,6,9,12-tetraoxatricosan-1-aminium (TDMA-Ene): Compound **2** (3 g, 4.82 mmol) was dissolved in 30 mL DCM and cooled to 0 °C in an ice bath. A solution of TEA (1.34 mL, 9.64 mmol) and CH_3SO_2Cl (0.558 mL, 7.22 mmol) in DCM (20 mL) was added to the mixture under stirring at 0 °C. After stirring overnight at room temperature, the reaction mixture was washed with $NaHCO_3$ and water. The crude compound was reacted further with N(CH$_3$)$_2$-R/ethanol (6 mL) in the presence of TEA (1.39 ml, 10 mmol) at 80 °C for 24 h. After removing the solvent, the product was washed several times with hexane followed by purifying further by column chromatography (DCM:methanol = 4:1). The product obtained was dissolved in 20 mL DCM and TFA (2.75 g, 24.1 mmol) followed by adding TIPS (1.15 g, 7.26 mmol) to the mixture. The reaction mixture was stirred for 24 h at room temperature. After removing the solvent, the product was washed several times with hexane to produce TTMA or TDMA-Ene ligands. TTMA ^{1}H NMR (400 MHz, $CDCl_3$): δ = 3.99 (s, 2H, -N-C$\underline{H}_2$-CH$_2$-O-), 3.85 (t, 2H, -N-CH$_2$-C$\underline{H}_2$-O-), 3.71–3.54 (m, 12H, -OC$\underline{H}_2$C$\underline{H}_2$O-), 3.45 (t, 2H, -OC$\underline{H}_2$CH$_2$CH$_2$-), 3.35 (s, 9H, -N(C$\underline{H}_3$)$_3$), 2.47 (t, 2H, HS-C$\underline{H}_2$-), 1.62–1.23 (m, 18H, -C$\underline{H}_2$-). TDMA-Ene ^{1}H NMR (400 MHz, $CDCl_3$): δ = 5.96–5.90 (m, 1H, CH$_2$=C$\underline{H}$-CH$_2$-), 5.73–5.65 (m, 2H, C$\underline{H}_2$=CH-CH$_2$-), 3.95 (d, 2H, CH$_2$=CH-C$\underline{H}_2$-N-), 3.89 (s, 2H, -N-C$\underline{H}_2$-CH$_2$-O-), 3.68–3.54 (m, 12H, -OC$\underline{H}_2$C$\underline{H}_2$O-), 3.49 (t, 2H, -N-CH$_2$-C$\underline{H}_2$-O-), 3.45 (t, 2H, -OC$\underline{H}_2$CH$_2$CH$_2$-), 3.08 (s, 6H, -CH$_2$-N(C$\underline{H}_3$)$_2$CH$_2$-), 2.47 (t, 2H, HS-C$\underline{H}_2$-), 1.62–1.17 (m, 18H, -C$\underline{H}_2$-).

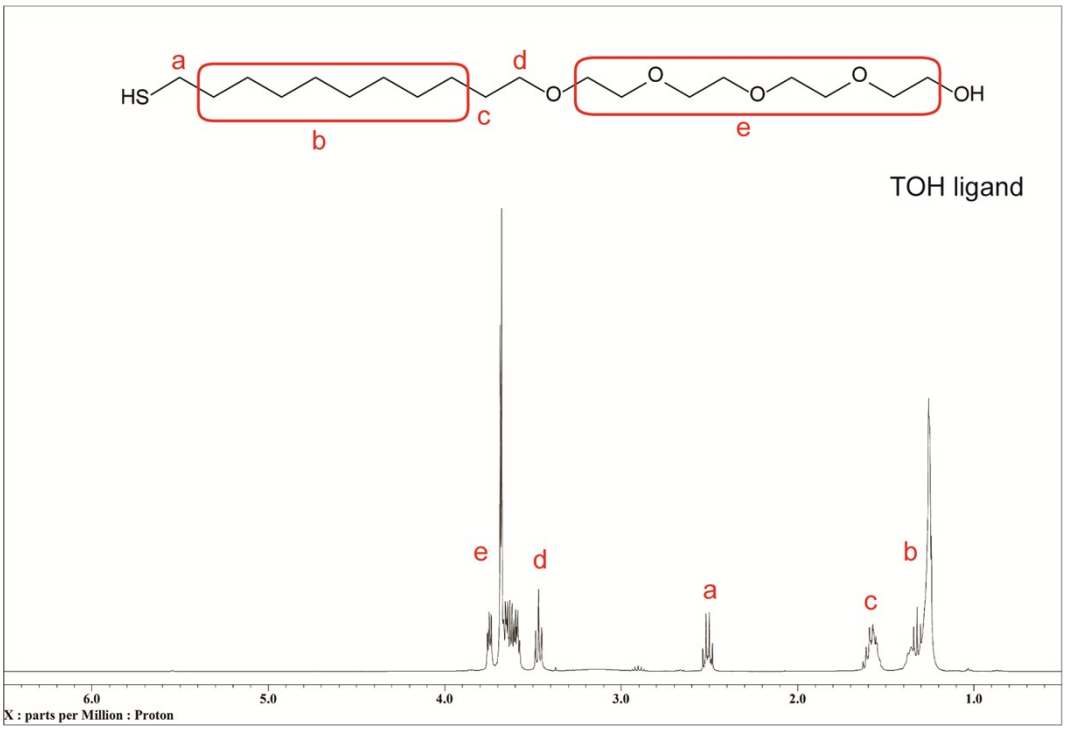

Figure S1. ^{1}H-NMR spectrum of a TOH ligand in $CDCl_3$.

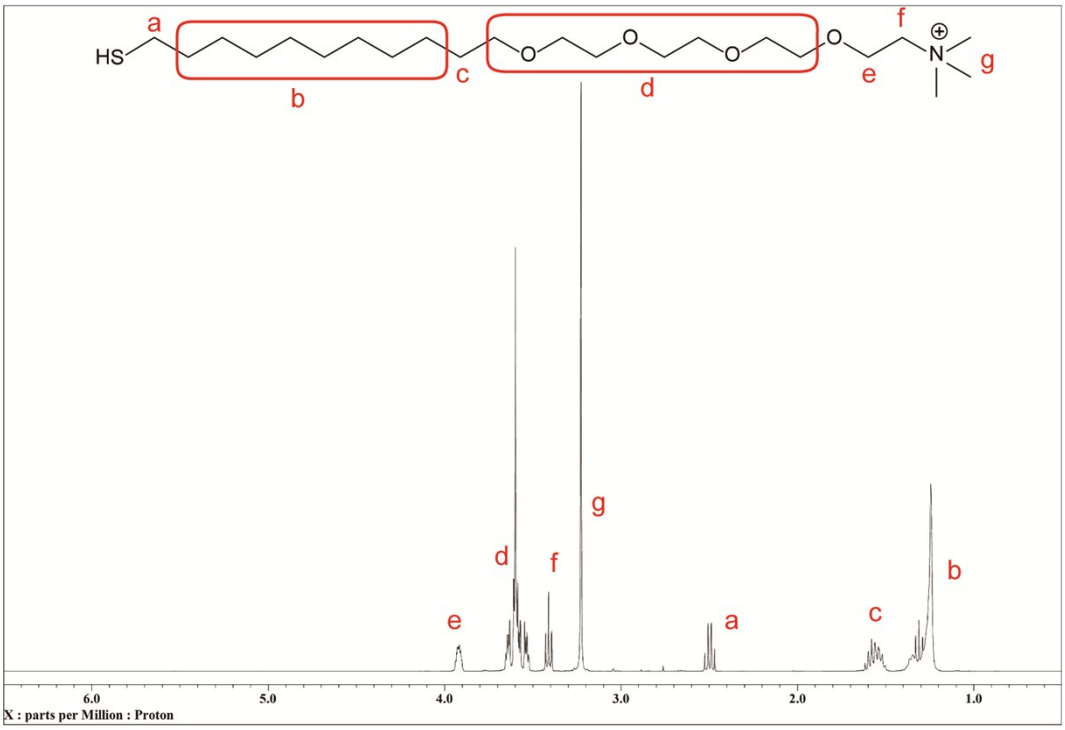

Figure S2. ^{1}H-NMR spectrum of a TTMA ligand in $CDCl_3$.

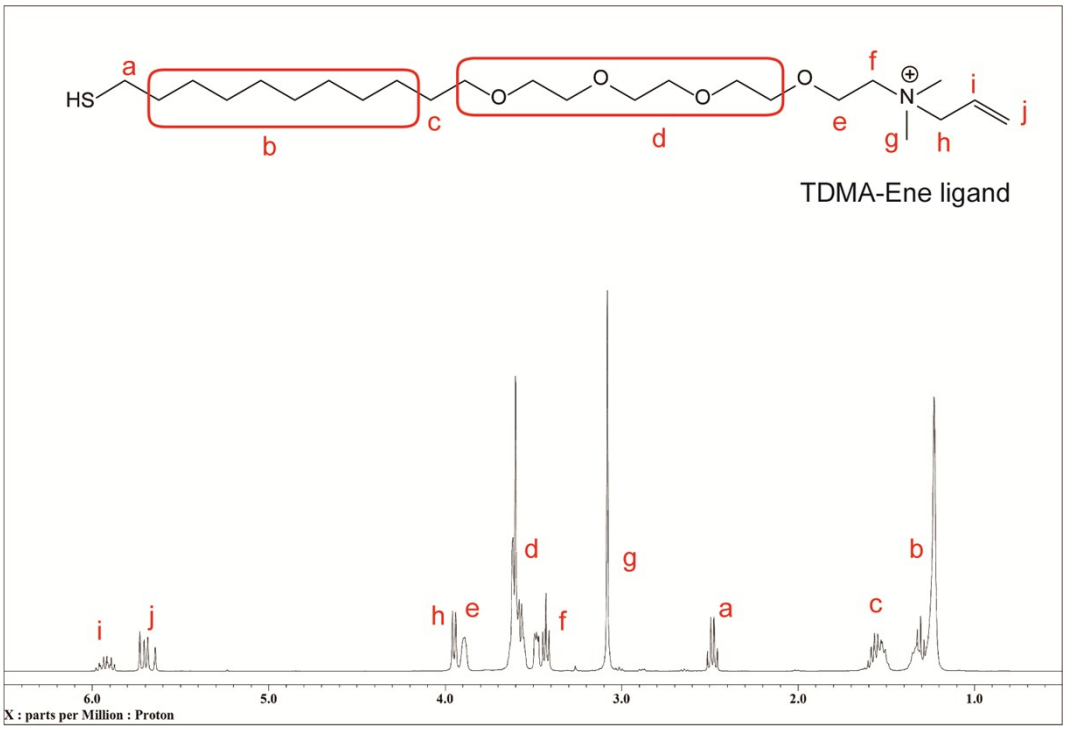

Figure S3. ^{1}H-NMR spectrum of a TDMA-Ene ligand in $CDCl_3$.