CHAPTER 2

EXPERIMENTAL

2.1 MATERIALS

Phenyltrichlorosilane, 2,6-dimethyl aniline, 1,4-dithiane-2,5-diol, 3,3′,4,4′-benzophenone tetracarboxylic dianhydride, phthalic acid, polyphosphoric acid and pyromellitic dianhydride were purchased from Aldrich (USA). 2,6-diaminopyridine, anhydrous potassium carbonate, stannous chloride, hydrazine monohydrate, ethanol, methanol, toluene, benzyl trimethyl ammonium hydroxide/methanol, 5% Pd/C and MWCNTs (+95%, 10-20nm) were purchased from Sisco Research Laboratory Pvt Ltd, India. Fuming nitric acid was purchased from Fischer Chemicals Ltd, India. Hydrochloric acid, acetic acid, phosphorous oxytrichloride, tetrahydrofuran, hexane, ethyl acetate, formic acid, N-methyl-2-pyrrolidone and triethylamine were purchased from Spectrochem Pvt Ltd, India. 1,2-Phenylene diamine, N,N-dimethylformamide, dimethylsulphoxide and N,N-dimethylacetamide (Aldrich, USA) were used as received.

2.2 PURIFICATION OF SOLVENTS

2.2.1 N-Methyl Pyrrolidone

N-Methyl pyrrolidone was dried by removing water as benzene azeotrope and fractionally distilled at 10 Torr through a 100 cm column packed with glass helices. The fraction boiling at 202°C/760 mm was collected (lit.b.p.202°C/760 mm) (Perrin and Armarego 1988).
2.2.2  N, N Dimethyl Formamide

N, N-Dimethyl formamide was purified by azeotropic distillation with benzene. 500 ml of DMF with 50 ml of benzene azeotrope which distilled between 70-75°C was collected. The residual DMF was shaken with powdered barium oxide, filtered, distilled under nitrogen atmosphere at reduced pressure and the fraction boiling point at 76°C/39mm Hg was collected (b.p 76°C/39mm Hg) (Furniss et al 1994).

2.2.3  Dimethyl Sulphoxide

Dimethyl sulphoxide was dried over anhydrous calcium sulphate overnight and then distilled under reduced pressure. The fraction distilled at 75-76°C/12 mm Hg, was collected (lit.b.p.75-76°C/12 mm Hg) (Furniss et al 1994).

2.2.4  Ethyl Alcohol

Rectified spirit was refluxed with freshly ignited and cooled calcium oxide for 6 hrs, set aside overnight and then distilled. The fraction boiling at 80°C was collected. The distillate was refluxed with few turnings of Mg for 6 hrs and distilled (lit.b.p.79-80°C) (Furniss et al 1994).

2.2.5  Methyl Alcohol

Dry methanol was obtained by refluxing the commercial methanol (Sd-fine) (1000 ml) over anhydrous calcium oxide and distilled. The methanol thus obtained was treated with magnesium metal and re-distilled. The fraction boiling at 65°C was collected (lit.b.p.65°C) (Furniss et al 1994).
2.2.6 Acetone

Acetone was refluxed with successive quantities of potassium permanganate until the violet color persists. It was then dried with anhydrous potassium carbonate and distilled. The fraction boiling at 57 °C was collected (lit. b.pt. 57°C) (Furniss et al 1994).

2.2.7 Chloroform

Chloroform was shaken several times with half of its volume of 10% aqueous sodium bicarbonate and then with water. The chloroform layer was separated, dried over calcium chloride and distilled. The fraction boiling at 62 °C was collected (lit. b.p. 62°C) (Furniss et al 1994).

2.2.8 Tetrahydrofuran

Tetrahydrofuran was shaken with sodium hydroxide pellets and distilled. The distillate was dried over anhydrous calcium sulphate. The mixture was refluxed for 6 hrs on a water bath and distilled. The fraction boiling at 65°C was collected and stored over metallic sodium wire (lit.b.p. 65-66°C) (Furniss et al 1994).

2.3 PURIFICATION OF REAGENTS

2.3.1 Pyromellitic Dianhydride

Pyromellitic dianhydride was recrystallized from ethyl methyl ketone, dried and sublimed in vacuum (m.p.286°C, lit.m.p.286°C) (Perrin and Armarego 1988).
2.3.2 4,4’,3,3’-Benzophenonetetracarboxylic Acid Dianhydride

4,4’,3,3’-Benzophenonetetracarboxylic acid dianhydride was recrystallized from acetic anhydride and dried at 150°C under reduced pressure prior to use.

2.3.3 2,6-Dimethylaniline

2,6-Dimethylaniline was converted to its hydrochloric acid salt by treating with HCl, which after recrystallization was decomposed with alkali to give the free base. It was then dried over magnesium sulphate for 24 hrs and fractionally distilled at 210-211°C/736 mm Hg (Perrin and Armarego 1988).

2.3.4 Acetic Anhydride

Acetic anhydride was refluxed with coarse magnesium fillings at 80-90°C for 5 days followed by fractional distillation at 138°C/75 mm Hg (Perrin and Armarego 1988).

2.3.5 Triethyl Amine

Triethyl amine (1 Lit) was treated with potassium hydroxide pellets and refluxed for 1 hour. The fraction boiling at 89.3°C was collected. (Perrin and Armarego 1988).

2.3.6 Potassium Carbonate

Potassium carbonate was stored in a desiccator and used after crushing into a powder and drying in an air oven at 120°C overnight (Perrin and Armarego 1994).
2.3.7 Toluene

Toluene was treated with P₂O₅ and distilled. The fraction boiling at 110°C was collected (lit. b.p. 110°C) and dried with calcium sulphate (Perrin and Armarego 1994).

2.4 SYNTHESIS OF MONOMERS

2.4.1 Bis (4-amino-3,5-dimethylphenyl)-2-chloro-3-quinolylmethane (BACQM) (Diamine-1)

Synthesis of 2-chloro-3-formylquinoline (CFQ)

CFQ was prepared according to the Vilsemeyer-Haack formylation method (Srivastava et al 2005). 9.6 ml of DMF was taken in a 250 ml round-bottomed flask and cooled to 0°C. To this cooled DMF, phosphorous oxy trichloride (53.7 g, 32.2 ml, 0.35 mol) was added drop wise with stirring. Acetanilide (6.7 g, 0.05 mol) was added to this mixture and refluxed for 18 h. The reaction mixture was cooled to room temperature, poured into ice-cold water (300 ml) and stirred for 1 h at 0–10 °C. The pale yellow coloured precipitate of CFQ obtained was filtered, washed with water (100 ml), dried and recrystallized from ethyl acetate. Yield 75.7%; M.pt: 148-149°C.
FT-IR (KBr, cm$^{-1}$): 3097 (C–H aromatic stretching), 1667 (C=O stretching), 1580 (C=N stretching), 1346 (C–N aromatic stretching), 751 (C–Cl stretching). $^1$H- NMR (CDCl$_3$, ppm): 8.5 (s, 1H,a), 7.4 (s,1H,b), 7.2 (m, 1H,c), 6.9(m, 1H,d), 8.1 (m, 1H,e), 10.5 (s, 1H,f). $^{13}$C- NMR (CDCl$_3$, ppm): C$_1$-150.9; C$_2$-123.0; C$_3$-133.9; C$_4$-133.6; C$_5$-129.4; C$_6$-129.3; C$_7$-137.1; C$_8$-165.1.

**Synthesis of bis(4-amino-3,5-dimethylphenyl)-2-chloro-3-quinolyl methane (BACQM)**

24.2 g of 2,6-dimethylaniline (0.2 mol) was taken in a 250 ml three-necked round-bottomed flask equipped with a reflux condenser, nitrogen inlet and an addition funnel. Con. HCl (23 ml) was added into the reaction vessel over 90 min and stirred under N$_2$ atmosphere. The white coloured solid obtained was separated by filtration and dissolved in 12 ml of DMF. To this mixture, a solution of CFQ (19.1 g, 0.1 mol) in DMF (4 ml) was added dropwise and the reaction mixture was refluxed for 6-7 hours. The mixture was cooled and neutralized (pH 7) by using dilute NaOH solution. The obtained crude product was filtered, washed with methanol twice and dried in a vacuum oven for 12 h at 70$^\circ$C. The obtained solid was purified by recrystallization from ethanol. Yield 33%; M.pt: 191-192$^\circ$C. (Amutha et al 2007).
FT-IR (KBr, cm\(^{-1}\)): 3082 (C-H aromatic stretching), 3453 and 3231 (N-H asymmetric and symmetric stretching), 1624 (N-H bending), 2952 and 2922 (C-H stretching of CH\(_3\) group), 1355 (C-N aromatic stretching), 1492 (C=C stretching), 749 (C-Cl stretching). \(^{1}\)H-NMR (CDCl\(_3\), ppm): 7.0 (s, 1H,a), 5.8 (s, 1H,b), 2.3 (s, 12H,c), 4.7 (s, 4H,d), 8.1 (s, 1H,e), 7.5 (m, 1H,f), 7.3 (m, 1H,g), 7.2 (m, 1H,h), 7.8 (m, 1H,i). \(^{13}\)C- NMR (CDCl\(_3\), ppm): C\(_1\)-18.7; C\(_2\)-127.72; C\(_3\)-133.11; C\(_4\)-135.27; C\(_5\)-140.2; C\(_6\)-59.0; C\(_7\)-132.4; C\(_8\)-164.9; C\(_9\)-159.3; C\(_{10}\)-128.2; C\(_{11}\)-127.73; C\(_{12}\)-150.2; C\(_{13}\)-140.1.
2.4.2 1,2-phenylene-2,2'-bis(5-aminobenzimidazole) (o-P5ABI)
(Diamine-2)

Synthesis of 1,2-phenylene-2,2'-bisbenzimidazole (o-PBI)

This monomer was synthesized using a previously reported procedure (Berrada et al 2002). However, phthalic acid was used in this work, instead of phthalic anhydride used by Berrada et al.

To a 250 ml three-necked round bottomed flask fitted with a condenser and nitrogen inlet, was added a mixture of 1,2-phenylene diamine (10.8 g, 0.1 mol), phthalic acid (8.3 g, 0.05 mol) and poly(phosphoric acid) (PPA, 90 g). The mixture was stirred until a thick paste was formed. 5 g of PPA was then added to form a smooth slurry. The reaction mixture was heated slowly to 220-230°C, maintained at this temperature for 6 h, cooled and poured into ice-cold water with stirring. The resulting mixture was filtered and the filtrate was neutralized (pH 7.5) using dilute NaOH to form a precipitate which was then filtered and washed with water. The obtained product was recrystallized from absolute ethanol, filtered and dried to form white crystals. Yield 71%; M.pt; 114-116°C.
FT-IR (KBr, cm$^{-1}$): 3091 (C-H aromatic stretching) 1638 (C-N aromatic stretching), 3352 cm$^{-1}$ (N-H stretching).

$^1$H-NMR (DMSO-d$_6$, ppm): 8.1 (d, 2H, a), 7.7 (m, 2H, b), 7.6 (d, 4H, c), 7.2 (m, 4H, d), 11.1 (s, 2H, e).

$^{13}$C-NMR (DMSO-d$_6$, ppm): C$_2$-151.6; C$_4$&C$_7$-112.2; C$_5$&C$_6$-115.6; C$_8$-131.8; C$_9$-130.3; C$_{10}$-122.7; C$_{11}$-129.8; C$_{12}$-138.9.

**Synthesis of 1,2-phenylene-2,2'-bis(5-nitrobenzimidazole) (o-P5NBI)**

8 g (0.026 mol) of o-PBI and concentrated H$_2$SO$_4$ (11 ml) were taken in a 250 ml round bottomed flask. The mixture was stirred and cooled to below 5°C. A mixture of fuming HNO$_3$ (2.7 ml) and concentrated H$_2$SO$_4$ (2.3 ml) was added drop wise over a period of 10 min. Then, the mixture was again stirred for 1 h at room temperature and poured into an ice bath. The precipitate obtained was filtered, neutralized with a solution of sodium carbonate (which had a pH of 9) and finally washed with distilled water. The
obtained solid was then recrystallized in ethanol to form yellow crystals. Yield 68%; M.pt; > 300°C. (Berrada et al 2002).

FT-IR (KBr, cm$^{-1}$): 3109 (C-H aromatic stretching) 1627 (C-N aromatic stretching), 1531 (NO stretching), 1351 (NO stretching) and 3353 cm$^{-1}$ (N-H stretching). $^1$H-NMR (DMSO-d$_6$, ppm) 8.5 (d, 2H, a), 8.2 (m, 2H, b), 7.9 (d, 2H, c), 7.8 (d, 2H, d), 9.6 (s, 2H, e), 8.1 (s, 2H, f). $^{13}$C-NMR (DMSO-d$_6$, ppm) C$_2$- 154.6; C$_4$-112.4; C$_5$-140.3; C$_6$-119.8; C$_7$-115.4; C$_8$-144.2; C$_9$-131.7; C$_{10}$- 127.2; C$_{11}$-132.3; C$_{12}$-136.7.

![Chemical structure](image)

**Synthesis of 1,2-phenylene-2,2'-bis(5-aminobenzimidazole) (o-P5ABI)**

6 g of o-P5NBI (0.015 mol) was dissolved in 100 ml of glacial acetic acid in a beaker and stannous chloride (7 g, 0.0037 mol) was dissolved in concentrated hydrochloric acid (8 ml) in another beaker. Both the solutions were heated. The acetic acid solution was added drop wise to the stannous
chloride solution over 30 min and the mixture was cooled to 5°C. An orange coloured precipitate was obtained in the solution. It was filtered and dried for 3 h at 50°C under vacuum. The dried product was then refluxed with ethanol containing activated charcoal, filtered and recrystallized from ethanol to form pale yellow crystals. Yield 88%; M.pt; > 300°C (Berrada et al 2002).

FT-IR (KBr, cm⁻¹): 3093 (C-H aromatic stretching), 1639 (C-N aromatic stretching) and 3301 cm⁻¹ (N-H stretching). ¹H-NMR (DMSO-d₆, ppm): 8.5 (d, 2H, a), 8.1 (m, 2H, b), 7.8 (d, 2H, c), 7.7 (d, 2H, d), 13.5 (s, 2H, e), 8.0 (s, 2H, f), 4.9 (s, 4H, NH₂). ¹³C-NMR (DMSO-d₆, ppm): C₂-156.0; C₄-113.1; C₅-139.1; C₆-118.3; C₇-115.3; C₈-143.1; C₉-131.1; C₁₀-129.7; C₁₁-131.8; C₁₂-136.3.
2.4.3 2,4-Bis(4-aminophenylamido)-6-chloroquinazoline (BAPCQ)  
(Diamine-3)

Synthesis of 2,4-bis(4-nitrophénylamido)-6-chloroquinazoline (BNPCQ)

A mixture of 2,4-diamino-6-chloroquinazoline (0.012 mol, 2.3 g) in NMP (30 ml) was taken in a 250 ml round-bottomed flask and stirred at 0°C for 1 hr under nitrogen atmosphere. Then, 10 ml of CH₂Cl₂ and 4-nitrobenzoylchloride (0.024 mol, 4.4 g) were added. The reaction mixture was again stirred at 0 °C for 1 hr, at room temperature for 24 hrs and then poured into water. The obtained product was filtered, washed with hot water and methanol successively. It was dried under vacuum at 50 °C. Yield = 92%; M.pt; 297-298 °C. (Fatemeh Taremi et al 2010 and Danuta Drozdowsca et al 2009)

FT-IR (KBr, cm⁻¹): 3091 (C-H aromatic stretching), 1634 (C-N aromatic stretching), 1574 (NO stretching), 1359 (NO stretching), 720 (C-Cl aromatic stretching) and 3381 cm⁻¹ (N-H stretching). ¹H-NMR (DMSO-d₆, ppm): 7.6 (d, 1H, a), 7.9 (d, 1H, b), 8.1 (s, 1H, c), 7.7 (m, 8H, d&e), 8.2 (s, 2H, f). ¹³C-NMR (DMSO-d₆, ppm) C₁- 124.3; C₂- 124.0; C₃- 151.1; C₄- 123.9; C₅- 125.1; C₆- 133.0; C₇- 150.2; C₈- 144.3; C₉-153.7; C₁₀- 113.8; C₁₁- 113.1; C₁₂- 111.1; C₁₃- 142.0.
Synthesis of 2,4-bis(4-aminophenylamido)-6-chloroquinazoline (BAPCQ)

To a 250 ml three-necked round bottomed flask equipped with a reflux condenser, nitrogen inlet and an addition funnel, was added a mixture of 2,4-bis(4-nitrophenylamido)-6-chloroquinazoline (BNPCQ) (0.004 mol, 1.9 g), absolute ethanol and 5 wt% Pd/C (0.006 g). A solution of hydrazine monohydrate (10 ml) was then added drop wise over a period of one hour. The mixture was refluxed for 24 hrs and filtered while hot to remove Pd/C. The filtrate was concentrated in a vacuum evaporator, the resulting solid was precipitated in ice-cold water and purified by recrystallization from ethanol. Yield 89%; M.pt; 294-295°C.
FT-IR (KBr, cm\(^{-1}\)): 3083 (C-H aromatic stretching), 1639 (C-N aromatic stretching), 1618 (N-H bending vibration), 714 (C-Cl stretching) and 3344 cm\(^{-1}\) (N-H stretching). \(^1\)H-NMR (DMSO-d\(_6\), ppm): 7.7 (d, 1H, a), 7.9 (d, 1H, b), 8.1 (s, 1H, c), 7.0 (d, 4H, d), 5.9 (d, 4H, e), 8.3 (s, 2H, f), 5.4 (s, 4H, g). \(^13\)C-NMR (DMSO-d\(_6\), ppm) C\(_1\) - 129.3; C\(_2\) - 129.0; C\(_3\) - 146.2; C\(_4\) - 126.8; C\(_5\) - 129.6; C\(_6\) - 133.8; C\(_7\) - 141.9; C\(_8\) - 138.2; C\(_9\) - 158.5; C\(_{10}\) - 124.3; C\(_{11}\) - 123.9; C\(_{12}\) - 121.9; C\(_{13}\) - 137.0.
2.4.4 2,5-Bis (4-aminophenoxy)-1,4-dithiane (BAPD) (Diamine-4)

Synthesis of 2,5-bis (4-nitrophenoxy)-1,4-dithiane (BNPD)

To a 250 ml three-necked round bottomed flask equipped with a reflux condenser, nitrogen inlet and an addition funnel, was added 2,5-dihydroxy-1,4-dithiane (1.8 g, 0.012 mol), DMAc (20 ml) and triethylamine (5.8 ml, 0.025 mol). A solution of p-chloronitrobenzene (3.9 g, 0.025 mol) in DMAc (10 ml) was added dropwise over a period of one hour at room temperature. The reaction mixture was stirred for 8 hrs at 80°C, cooled and then poured into ice-cold water. The obtained product was filtered, washed with methanol and dried under vacuum at 70°C for 12 hrs. The crude product was recrystallized from ethanol. Yield 94%; M.pt; 155°C.

FT-IR (KBr, cm\(^{-1}\)): 3085 (C-H aromatic stretching), 1521, 1361 (asymmetric and symmetric stretching vibration of NO\(_2\) group), 1211, 1165 (asymmetric and symmetric stretching vibration of C-O-C group).
\(^1\)H-NMR (CDCl\(_3\), ppm): 8.0(d,4H,a), 7.0(d,4H,b), 3.3(s,2H,c). \(^{13}\)C-NMR (CDCl\(_3\), ppm): C\(_1\)-140-0, C\(_2\)-121.7, C\(_3\)-115.3, C\(_4\)-163.6, C\(_5\)-88.2, C\(_6\)-36.1.

**Synthesis of 2,5-bis(4-aminophenoxy)-1,4-dithiane (BAPD)**

To a 250 ml three-necked round bottomed flask equipped with a reflux condenser, nitrogen inlet and an addition funnel, was added 2,5-bis(4-nitrophenoxy)-1,4-dithiane (BNPD) (1.57 g, 0.004 mol), absolute ethanol and 5 wt% Pd/C (0.06 g). A solution of hydrazine monohydrate (10 ml) was added to the reaction mixture drop wise over a period of one hour. The mixture was refluxed for 24 hrs and filtered while hot to remove Pd/C. The filtrate was concentrated in a vacuum evaporator, the resulting solid was precipitated in ice-cold water and purified by recrystallization from ethanol. Yield 75%; M.pt; 189°C (Sivasankari et al 2012).
FT-IR (KBr, cm⁻¹): 3087 (C-H aromatic stretching), 3426, 3389 (asymmetric and symmetric stretching vibration of NH₂ group), 1619 (N-H bending vibration), 1212, 1169 (asymmetric and symmetric stretching vibration of C-O-C group). 

¹H-NMR (CDCl₃, ppm): 4.0(s, 4H, a), 6.3(d, 4H, b), 6.5(d, 4H, c), 3.3(s, 2H, d). 

¹³C-NMR (CDCl₃, ppm): C₁-140.0, C₂-116.9, C₃-115.2, C₄-147.5, C₅-88.2, C₆-36.1.

2.4.5 Amino functionalized polyhedral oligomeric silsesquioxane (POSS) - octa(aminophenyl)silsesquioxane (OAPS)

Synthesis of octaphenylsilsesquioxane (OPS)

OPS was synthesized using a previously reported procedure (J C. Huang et al 2003 and J F. Brown et al 1964).

In a 250 ml round-bottomed flask, a solution of phenyltrichlorosilane (10.9 g, 0.05 mol) in 50 ml of benzene and 100 ml of water were taken and stirred for 5 h at room temperature. The solution separated into an aqueous layer and a benzene layer. The aqueous layer was removed and the benzene layer was washed twice with water and a solution (1.2 ml, 3 mmol) of 40% benzyltrimethylammonium hydroxide/methanol was added. The mixture was refluxed for 4 h and allowed to stand for 4 days. The obtained mixture was refluxed again for another 24 h, cooled, filtered and dried. A white solid was obtained. Yield 65%.
FT-IR (KBr, cm$^{-1}$): 3020 (C-H stretching of phenyl group), 1598 (C=C stretching of phenyl ring), 1174 (Si-O stretching); solid state $^{29}$Si NMR (ppm): -70.21.

**Synthesis of octa(nitrophenyl)silsesquioxane (ONPS)**

The ONPS was synthesized according to the reported method (Huang et al 2003 and R. Tanaki et al 2001). 10 gms of octa phenyl silsesquioxane (OPS) (9.7 mmol) was taken in a 250 ml round-bottomed flask. 50 ml fuming nitric acid was then added drop wise. The mixture was stirred for half an hour at 0°C and then continuously stirred for 20 h at room temperature. The reaction mixture was then poured into 50 g of ice. The pale yellow precipitate obtained was filtered and washed with water. The crude product was dried at 40°C. Yield 98%.
FT-IR (KBr, cm\(^{-1}\)): 3084 (C-H aromatic stretching), 1599 (N=O stretching), 1435 (N=O stretching), 1137 (Si–O–Si stretching). \(^1\)H-NMR (acetone-d\(_6\), ppm): 8.7-7.8 (aromatic protons). \(^{13}\)C-NMR (acetone-d\(_6\), ppm): 153.03, 148.0, 140.2, 137.6, 134.4, 133.3, 131.3 (small), 130.0, 128.7, 126.2, 124.2; solid state \(^{29}\)Si-NMR (ppm): -59.02 (PhSiO\(_3\)), -66.22 (PhSiO\(_3\)).

GPC(THF): Mn 1136, Mw 1191, PDI= 1.04.

**Synthesis of octa(aminophenyl)silsesquioxane (OAPS)**

The OAPS was prepared according to the reported procedure (Huang et al 2003 and R. Tanaki et al 2001).

To a 250 ml three-necked round bottomed flask fitted with a condenser, was added a mixture of octa (nitrophenyl) silsesquioxane (ONPS) (5.0 g, 3.58 mmol) and 5 wt% Pd/C (0.61 g, 0.287 mmol) under N\(_2\) atmosphere. A solution of triethylamine (40 ml, 0.287mol) in anhydrous THF (40 ml) was then added to the mixture and then heated to 60 °C. A solution of 98% formic acid (4.4 ml, 0.115mol) was added drop wise to the mixture. The reaction mixture was allowed to stand at room temperature for 5 h, when it was separated into two layers. The THF layer was separated. An excess of THF (30 ml) was added to the solution, stirred and the THF layer was
separated again. The total THF extract from the reacting mixture was filtered using Celite pad. 40 ml of ethyl acetate was added to the filtrate and washed three times using H₂O. The organic layer was dried with MgSO₄ and mixed with 1 l of hexane. The white precipitate formed was collected by filtration. This was further purified by re-dissolving in a mixture of THF(30%)/ethyl acetate (50%) and precipitating by stirring with 600 ml of hexane. The purified product was separated by filtration and dried under vacuum. Yield 96%.

FT-IR (KBr, cm⁻¹): 3097 (C-H aromatic stretching), 3418 (asymmetric stretching of N-H group), 1106 (Si–O–Si stretching). ¹H-NMR (acetone-d₆, ppm): 8.1 (aromatic protons), 8.3 (NH₂ protons). ¹³C- NMR (acetone-d₆, ppm): 154.0, 148.5, 136.2, 132.5, 129.3, 123.7, 119.8, 116.8, 115.4; ²⁹Si Solid NMR (ppm): -61.32 (PhSiO₃), -69.08 (shoulder, PhSiO₃). GPC (THF): Mn 600, Mw 775, PDI=1.29.

2.4.6 Functionalization of MWCNTs

Synthesis of acid-functionalized MWCNTs (Ac-MWCNTs)

The acid-functionalized MWCNTs were prepared according to the reported procedure (Siu-Ming et al 2007 and Yizhi et al 2008).
The unmodified MWCNTs (1 gm) were taken in a round-bottomed flask. A mixture of sulphuric acid (98%) and nitric acid (68%) was added with a weight ratio of 3:1 to the MWCNTs. The reaction mixture was stirred for 24 hrs at 60°C, filtered and the precipitate obtained was washed with deionized water until a pH of 7 was obtained. The obtained product was dried under vacuum.

FT-IR (KBr, cm\(^{-1}\)): 1632 (C=O stretching vibration of COOH), 3443 (-OH stretching vibration of COOH).

**Synthesis of amino-functionalized MWCNTs (Am-MWCNTs)**

The amino-functionalized MWCNTs were prepared according to the reported procedure (Siu-Ming et al 2007 and Yizhi et al 2008). The acid-functionalized MWCNTs (500 mg) were taken in a round-bottomed flask. A solution of SOCl\(_2\) in DMF (20:1) was added with stirring at 70°C for 24 hrs. The chlorinated MWCNTs were filtered, washed with toluene thrice and dried under vacuum. The obtained product was heated with 50 ml of ethylene diamine for 2 days at 100°C. The reaction mixture was then cooled and washed with ethanol, to remove the excess of ethylene diamine. The obtained black precipitate was dried for 1 day under vacuum.
FT-IR (KBr, cm$^{-1}$): 3438 and 3431 (N–H asymmetric and symmetric stretching), 1637 (C=O stretching vibration), 2924 (C-H stretching vibration of CH$_2$ group).

**Table 2.1 Notation for precursors and monomers**

<table>
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<th>S.No.</th>
<th>Expansion</th>
<th>Monomer code</th>
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<td>1</td>
<td>2-chloro-3-formylquinoline</td>
<td>CFQ</td>
</tr>
<tr>
<td>2</td>
<td>Bis(4-amino-3,5-dimethylphenyl)-2-chloro-3-quinolyl methane</td>
<td>BACQM</td>
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<tr>
<td>3</td>
<td>1,2-phenylene-2,2′-bisbenzimidazole</td>
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<td>10</td>
<td>octaphenylsilsesquioxane</td>
<td>OPS</td>
</tr>
<tr>
<td>11</td>
<td>octa(nitrophenyl)silsesquioxane</td>
<td>ONPS</td>
</tr>
<tr>
<td>12</td>
<td>octa(aminophenyl)silsesquioxane</td>
<td>OAPS</td>
</tr>
<tr>
<td>13</td>
<td>acid-functionalized MWCNTs</td>
<td>Ac-MWCNTs</td>
</tr>
<tr>
<td>14</td>
<td>Amino-functionalized MWCNTs</td>
<td>Am- MWCNTs</td>
</tr>
</tbody>
</table>
2.5 PREPARATION OF POLYIMIDE AND POLYIMIDE / OCTA (AMINOPHENYL) SILSESQUIOXANE (OAPS) NANOCOMPOSITES

The polyimide and polyimide/amino-functionalized POSS nanocomposites were prepared by the reaction of a diamine monomer, BTDA and OAPS as shown in Figure 2.1. The diamine BACQM (10 mmol, 3.4 g) was dissolved in NMP (40 ml) and then BTDA (10.5 mmol, 3.38 g) was added to the solution under N$_2$ atmosphere. The mixture was stirred for 6 h at room temperature to form a highly viscous poly(amic acid) (PAA) solution. To the PAA solution, a predetermined (0.06, 0.12, 0.25 and 0.50 mmol) amount of OAPS and NMP (10 ml) were added. The mixture was stirred again for an additional 2 h at room temperature. The resulting viscous, transparent solution was cast on a glass substrate and was subjected to thermal imidization at 80°C for 12 h, 120°C for 4 h, 200°C for 2 h, and 270°C for 2 h. The film formed was then stripped from the glass substrate using deionized water and was further dried in vacuum oven at 100°C.

The other polyimide and polyimide/POSS nanocomposites were synthesized by adopting a similar procedure using the heterocyclic diamine o-5APBI, BTDA and OAPS.
Figure 2.1 Synthesis of polyimide/OAPS nanocomposites
The unmodified MWCNTs, Ac-MWCNTs and Am-MWCNTs were dispersed in dimethyl acetamide by sonication for 2 hrs.

In a 250 ml round-bottomed flask, a mixture of BACQM (2 mmol, 0.83 g) and PMDA (2.5 mmol, 0.545 g) were taken. 10 ml of dimethyl formamide was added to the mixture and stirred for 6 hrs at room temperature under N₂ atmosphere. A highly viscous poly(amic acid) was formed in solution. A dispersion of unmodified MWCNTs (0.5%) in DMAc (10 ml) was added to the prepared poly(amic acid) solution and stirred for another 2 hrs followed and then subjected to thermal imidization by microwave irradiation at 100°C for 20 min, 200°C for 20 min and 260°C for 30 min using 400 W of energy.

The same procedure was followed for the synthesis of Ac-MWCNTs and Am-MWCNTs/polyimide nanocomposites as shown in Figure 2.2 and 2.3 respectively.

All other polyimide and polyimide/MWCNTs nanocomposites were synthesized by adopting a similar procedure using the other two newly synthesized heterocyclic diamine monomers also (BAPCQ and BAPD) and PMDA.

In the synthesis of organic/polymer molecules, the microwave irradiation method is easier and more effective than conventional heating as with the former method it is possible to achieve high product yield, fast
processing/time saving and side reactions can be avoided (Kappe 2004 and Selvakumar et al 2010).

Figure 2.2 Synthesis of polyimide/AC-MWCNTs nanocomposites
Figure 2.3 Synthesis of polyimide/Am-MWCNTs nanocomposites
Table 2.2  Notation for polyimides, polyimide/f-POSS and polyimide/f-MWCNTs nanocomposites

<table>
<thead>
<tr>
<th>S.No.</th>
<th>Polymer code</th>
<th>Polymer</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>PI-I</td>
<td>BTDA+BACQM</td>
</tr>
<tr>
<td>2</td>
<td>PI/POSS-I&lt;sub&gt;a&lt;/sub&gt;</td>
<td>BTDA+BACQM+OAPS (0.06 mmol)</td>
</tr>
<tr>
<td>3</td>
<td>PI/POSS-I&lt;sub&gt;b&lt;/sub&gt;</td>
<td>BTDA+BACQM+OAPS (0.12 mmol)</td>
</tr>
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<td>PI/POSS-I&lt;sub&gt;c&lt;/sub&gt;</td>
<td>BTDA+BACQM+OAPS (0.25 mmol)</td>
</tr>
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<td>BTDA+BACQM+OAPS (0.50 mmol)</td>
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<tr>
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<td>PI-II</td>
<td>BTDA+&lt;sub&gt;o&lt;/sub&gt;-P5ABI</td>
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<td>PI/POSS-II&lt;sub&gt;a&lt;/sub&gt;</td>
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<td>9</td>
<td>PI/POSS-II&lt;sub&gt;c&lt;/sub&gt;</td>
<td>BTDA+&lt;sub&gt;o&lt;/sub&gt;-P5ABI +OAPS (0.25 mmol)</td>
</tr>
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<td>10</td>
<td>PI/POSS-II&lt;sub&gt;d&lt;/sub&gt;</td>
<td>BTDA+&lt;sub&gt;o&lt;/sub&gt;-P5ABI +OAPS (0.50 mmol)</td>
</tr>
<tr>
<td>11</td>
<td>PI-III</td>
<td>PMDA+BACQM</td>
</tr>
<tr>
<td>12</td>
<td>PI/MWCNTs-III&lt;sub&gt;a&lt;/sub&gt;</td>
<td>PMDA+BACQM+0.5% MWCNTs</td>
</tr>
<tr>
<td>13</td>
<td>PI/MWCNTs-III&lt;sub&gt;b&lt;/sub&gt;</td>
<td>PMDA+BACQM+0.5% Ac-MWCNTs</td>
</tr>
<tr>
<td>14</td>
<td>PI/MWCNTs-III&lt;sub&gt;c&lt;/sub&gt;</td>
<td>PMDA+BACQM+0.5% Am-MWCNTs</td>
</tr>
<tr>
<td>15</td>
<td>PI-IV</td>
<td>PMDA+BAPCQ</td>
</tr>
<tr>
<td>16</td>
<td>PI/MWCNTs-IV&lt;sub&gt;a&lt;/sub&gt;</td>
<td>PMDA+BAPCQ+0.5% MWCNTs</td>
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<td>17</td>
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<td>18</td>
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<td>PMDA+BAPCQ+0.5% Am-MWCNTs</td>
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<tr>
<td>19</td>
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<td>PMDA+BAPD</td>
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<td>PMDA+BAPD+0.5% MWCNTs</td>
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<tr>
<td>21</td>
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<td>PMDA+BAPD+0.5% Ac-MWCNTs</td>
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<tr>
<td>22</td>
<td>PI/MWCNTs-V&lt;sub&gt;c&lt;/sub&gt;</td>
<td>PMDA+BAPD+0.5% Am-MWCNTs</td>
</tr>
</tbody>
</table>
2.7 CHARACTERIZATION TECHNIQUES

2.7.1 FT-IR Spectroscopy

Nicolet Impact 400 Fourier Transform Infrared (FT-IR) spectrometer was used to examine the structure of the precursors, monomers, prepolymerms and polymers. The solid samples were recorded by making pellets with potassium bromide (E-Merck, India, IR Grade). All the spectra were recorded at a resolution of 4 cm\(^{-1}\) with a maximum of 100 scans. A background spectrum was run before recording the spectrum for each sample. The spectral calibration of the instrument was made using polystyrene film at regular intervals of time.

2.7.2 NMR Spectroscopy

Proton, Carbon-13 and \(^{29}\)Si NMR spectra were used to obtain the chemical structure of the monomers synthesized. Samples were dissolved in deuterated solvents (deuterated dimethyl sulphoxide [Aldrich, DMSO-d\(_6\), 99.9% containing 0.03% v/v TMS] or deuterated chloroform [Aldrich, CDCl\(_3\), 99.8% containing 0.03% v/v tetramethylsilane TMS] or deuterated acetone at a concentration of 2-10% solid. NMR spectra were recorded using a Bruker NMR 500 MHz spectrometer. The \(^1\)H-NMR spectra were recorded using broadband inverse probe where the inner coil is for the protons and the outer coil is for ‘X’ nuclei. Solvent suppression was applied in some cases where the solvent signal is very strong compared to the sample signals. \(^{13}\)C-NMR spectra were recorded in the dual (\(^{13}\)C/ \(^1\)H) probe where the inner coil is for \(^{13}\)C and the outer coil is for protons.
2.7.3 Differential Scanning Calorimetry (DSC)

Differential scanning calorimetry was performed on a TA instruments Q10 series instrument. The experiments were carried out in nitrogen atmosphere at a heating rate of 10°C/min from ambient to 400°C with a nitrogen flow of 50 ml/min. The instrument was calibrated for enthalpy and the temperature values using pure tin and indium.

2.7.4 Thermogravimetric Analysis (TGA)

TGA was performed to assess the relative thermal stability of the polymers. Thermograms were obtained using a TA instruments Q600 series thermogravimetric analyzer. The sample weight was approximately 10 mg. All the runs were carried out under nitrogen atmosphere with a gas flow rate of 10 ml/min. All the experiments were carried out at a heating rate of 20°C/min. α-Alumina was used as the reference material on platinum pans; α-Alumina exhibited a linear calorimetric trace with no thermal transition in the temperature range of 100-800°C. The thermal analyzer was calibrated using calcium sulphate as standard.

2.7.5 X-ray Diffraction

Wide angle X-ray diffraction measurements were performed at room temperature (about 25°C) on a X-pert PAN analytical X-ray diffractometer using Ni filtered Cu Kα radiation. The scanning rate was 20°C/min over a range of 2θ=5-40°.
2.7.6 Dynamic Mechanical Analysis

Dynamic mechanical analysis (DMA) is one of the most useful techniques for studying the damping behavior of the polymeric materials and is directly related to molecular structure.

A TA Q800 series dynamic mechanical analysis (DMA) instrument was used to measure the thermo mechanical properties of the nanocomposite films. For DMA, a sample film was subjected to a dynamic strain and the resultant stress was recorded. Storage modulus, loss modulus and tan δ values were determined using a temperature frequency sweep programme with a tension clamp on this sample films.

2.7.7 Dielectric Properties

The dielectric constant (5 cm x 0.5 cm x 0.15 to 0.20 mm) of the polyimide films were determined using LCR Hi Tester (HIOKI-3532, ASTM E-1530) impedance/Gain phase analyzer using a silver electrode at 30 ºC at a frequency of 1 MHz.

2.7.8 Melting Point of Monomers by Capillary Method

The melting point of the purified compounds were determined in a capillary tube in a melting point apparatus at a heating rate of not greater than 10ºC/min. Samples were ground before measuring and the formation of a meniscus was used to identify the beginning of the melting.
2.7.9 **Scanning Electron Microscopy**

SEM (FEI Quanta FEG 200 and Tescan vega II XMU high resolution scanning electron microscope) was used to study the morphology of the polyimide/f-POSS and polyimide/f-MWCNT nanocomposites with an accelerating voltage of 20 kV.

2.7.10 **Moisture Absorption Properties**

Moisture absorption of the polyimides and polyimide/f-POSS nanocomposite films (1 cm x 3 cm x 0.15 mm) was studied by immersing the specimens in water at room temperature for three days and determining the weight difference.

Water uptake = \( \frac{W_2 - W_1}{W_1} \times 100\% \)

- \( W_1 \) – Initial weight of the sample
- \( W_2 \) – Weight of the test sample after immersion in water

2.7.11 **Gel Permeation Chromatography**

Molecular weights and molecular weight distributions of the prepared POSS monomers were determined using a Polymer Laboratories PL-GPC-50 integrated gel permeation chromatography (GPC) system interfaced with a WellChom K-2301 refractive index detector. A 5 µm PL gel column with THF (0.01 mol/LiBr) as the eluent was used. Polystyrene was used as standards. The prepared sample solutions were filtered through 0.2 µm Teflon membranes before analysis.
2.7.12 Transmission Electron Microscopy

The TEM test was used to get the visual information of the nanocomposites. It gives information about the size and dispersion of nanofillers. TEM images were recorded using a FEI TECNAI T30, with an acceleration voltage of 250 kV. The samples were trimmed using a ultramicrotome machine and ultrathin sections were placed in 200 mesh copper grids for observations.

2.7.13 Antimicrobial Activity

The antimicrobial activity of the pure polyimide and the polyimide/f-POSS nanocomposites were studied by agar-well diffusion method. Escherichia coli culture was spread on the prepared nutrient broth agar medium in the sterile petri dish using L-rod and the prepared samples were placed on the plate. The plate was incubated at 37°C overnight.