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Solution processible new blue light emitting polymers based on 9-sila fluorenes and p-diphenylacenes.

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Abstract:

Two series of solution processible blue light emitting polymers from 9-substituted-9-silafluorenes and p-phenyl anthracene and p-phenyl tetracene were synthesized successfully. The alternate polymers derived from 9-substituted-9-silafluorenes and p-phenyl tetracene were found to have improved thermal spectral stability compared to other polymers discussed, shown by their elevated glass transition temperature, due to close crystal packing. The structural and optoelectronic characterization of the copolymers were done with NMR, FTIR, GPC, UV-Visible, Photoluminescence and Cyclic Voltammetric studies. In THF solution all these polymers showed pure blue emission with PL Λ_{max} ranging from 430 to 457nm and with high quantum yields (up to 0.91). The electrochemical studies of the fabricated polymeric light emitting diodes show that the polymeric layer acts as good emitting materials for optoelectronic devices.

Keywords: *Silafluorene, p-phenyl acene, photoluminescence, cyclic voltammetry, GPC, glass transition temperature.*

Introduction:

Conjugated polymers show unusual optical and electrical properties which make them efficient in the development of materials for fabrication of commercially viable light emitting display devices (Gal et.al, 2007; Grem et.al, 1992; Kim et.al, 2006; Li et.al, 2004; Ranger, 1997). Molecular designing of optoelectronic materials has gained a very important place in research now-adays (Kim et.al,2001). The organic light emitting devices (OLEDs) using polymeric materials have most promising prospects (Zhang et.al, 2006; Kreyenschmidt et.al, 1998; Lemmer et.al, 1996; Cimrova et.al, 1996; Gong et.al, 2003; Zhao et.al, 2004; Zhou et.al, 2005). Organic polymer LEDs have many advantages for the development of a large display, because of good processability, low operation voltage, fast response time and colour tunability over the full range of control of HOMO- LUMO band gap of emissive layer (Chen et.al, 2006). The electroluminescence properties of red and blue light emitting organic polymers have to be improved by structural modifications of polymers that it achieves greater efficiency, colour purity and long-term stability (Chan et.al, 2005).

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Since last two decades polyfluorenes have emerged as a prominent class of polymers for commercial applications due to their high luminescence quantum efficiency, thermal stability and good solution processability (Jones, 1947; Raut et.al, 2013; Raut et.al, 2010). Though polyfluorenes showed potent applications, many a times they developed unwanted long wavelength, green emission due to the photo or electrooxidized cleavage of the C-9 substituted alkyl pendant groups resulting in the formation of carbonyl groups at C-9 position (Gopalakrishnan, 2020). The quenching effect is called as keto effect, results in poor colour purity, inhibiting prospective utilization (Kim et.al, 2001). There are papers reporting polymer of tert(9,9-diarylfluorene)s in which they claim to have improved EL characteristics, morphological and thermal stability, due to Csp3-Csp2 bonds between the pendant and aryl groups and the C-9 carbon of fluorene (Kim et.al, 2001).

This present study was to explore structurally modified fluorene monomeric unit present in the copolymers, where the vulnerable C-9 in fluorene is replaced by hetero atom silicon. The various publications on polysilafluorenes mentioned the improved optoelectronic properties and the involvement of the d-orbital of silicon atom with special mention of them as blue or violet light emitting materials, with high thermal stability and as host materials (Zhou et.al, 2005).

The intrinsically large optical bandgaps of the polyfluorenes based LEDs require higher driving voltages (Gal et.al, 2007), which leads to rapid failure of devices due to chemical or physical degradation of polymers (Chen, 2005). Diphenylanthracenes in LEDs emissive layer have higher EL quantum yields, long life time and blue colour has been reported in papers.

In this paper we describe the synthesis, characterization of blue light emitting alternating polymers from alkyl substituted silafluorenes and 7,12-dihydroxy-bis(phenyl)tetraphene.

Experimental part

Materials:

All reagents were purchased from Aldrich Chemical Company. Only analytical grade chemicals were used throughout the synthesis. Spectroscopic grade $CHCl_3$ and Tetrahydrofuran (THF) were purchased from Aldrich and were used for absorption and emission experiments.

Instrumentation:

The elemental analyses were carried out on a micro-analytical technique on the instrument EuroVector EA-3000. The UV-visible spectra were recorded by using Shimadzu UV-2100 spectrophotometer. Fluorescence spectra were recorded on Shimadzu spectrofluorophotometer RF-5310(PC). FTIR spectra were recorded on a Perkin Elmer Spectrum one FTIR spectrometer with 400-4000cm^{-1} range and resolution of 4cm^{-1}. The ^{1}H and ^{13}C NMR spectra were recorded on Bruker AMX-300 spectrometer in $CDCl_3$ and chemical shifts were reported in δ ppm using tetra methyl silane (TMS) as reference. GC-MS studies were done on Shimadzu GC-MS/QP-2010. Thermolysis of the polymers were performed on PerkinElmer/Pyrin of the Diamond thermoanalyser so as to obtain TG-DTA assembly curves. Cyclic voltammetry studies of the polymers were carried out with three electrode cells consisting of Glassy carbon as working electrode, Platinum as an auxiliary and Ag/AgCl/$LiCl_{(sat)}$(EtOH)/ $TMACl_{(sat)}$(DMSO) in pure DMSO (99% pure, S. D. Fine Chemicals, Mumbai) solvent as reference electrode. The voltammetric system used for the electrochemical studies was Electrochemical Work Station,

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model Autolab 30; the electrode assembly being a 663VA stand with GPES computer software for recording and processing analyses of voltammograms was supplied by Eco Chemie, The Netherlands. Before each measurement a stream of pure nitrogen de-aerated the solution. A known volume of supporting electrolyte 0.05molL^{-1} TEAP (Tetra butyl ammonium perchlorate) in DMSO was taken in sample cell. To this solution a concentrated solution of the polymer in DMSO was added to get the desired working concentration in the cell and the cyclic voltammogram was run. Gel Permeation Chromatography was done using Perkin-Elmer series 200GPC equipped with an isocratic pump, a solvent degasser, a column oven, a refractive index(RI) detector and chromatographic column PL gel 10μm Mixed B, 300 x 7.5mm (THF 40°C), flow rate of 1mL per minute and polystyrene used for calibration.

Experimental

Synthesis – I) Monomer preparation:

Silafluorene monomers: Steps involved in the synthesis of 4,4'-dibromo-3,3'-dimethoxyl biphenyl, Synthesis of 4,4'-dibromo-6,6'-diiodo-3,3'-dimethoxyl biphenyl and the general method of preparation of derivatives 2,7-dibromo-3,6-dimethoxy-9-sila fluorenes are from the already reported procedure (Chen et.al, 2006; Chan et.al, 2005).

Synthesis of derivatives 2,7-dibromo-3,6-dimethoxy-9-sila fluorenes

To the mixture of 4,4'-dibromo-6,6'-diiodo-3,3'-dimethoxyl biphenyl (8.5mmol) and dry THF (80mL) was added a 1.6mol/L n-butyl lithium/hexane solution (17.1mmol) at -100°C. The resulting mixture was put on stirring at this temperature for 30minutes and then derivative of dichlorosilane (9mmol) was added into the mixture. After the addition, the mixture was kept for cooling and stirred overnight. Then the reaction mixture was hydrolyzed with water and extracted with ether. The combined organic layers were dried over Na_2SO_4 and the solvent was evaporated. The crude product was chromatographed on a silica gel column with PET/ ethyl acetate (7:1) as eluent. The further purification involved recrystallization with ethanol to get the compound as crystals (Chen et.al, 2006; Chan et.al, 2005).

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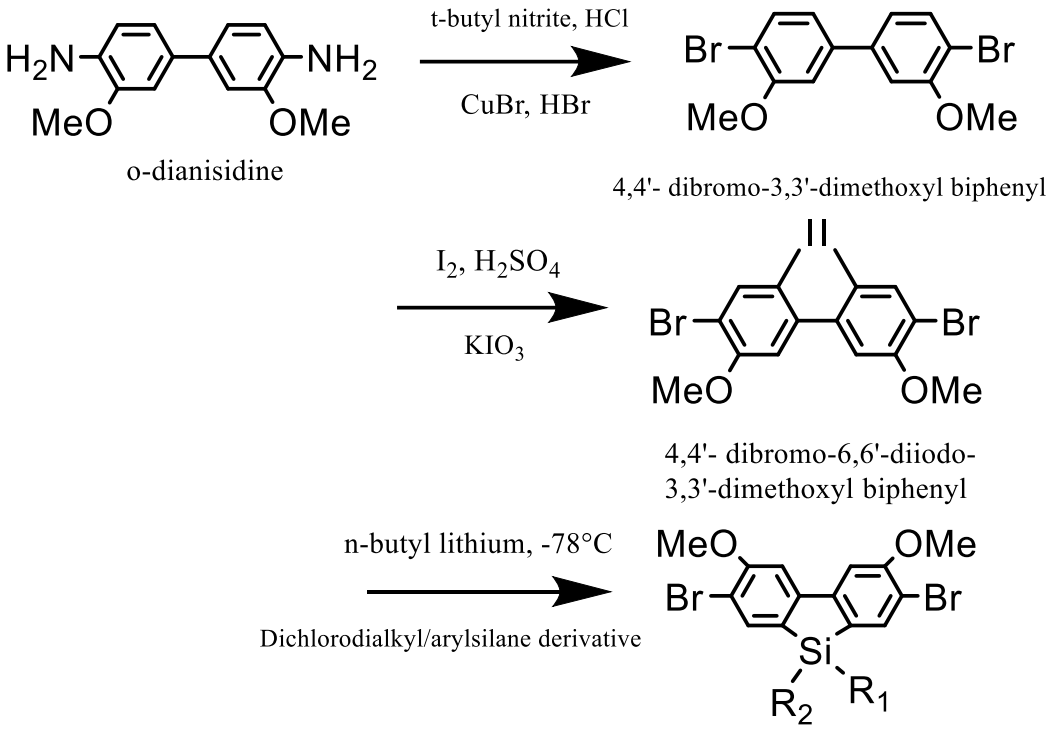


Scheme.1 Synthesis of derivatives 2,7-dibromo-3,6-dimethoxy-9-sila fluorenes

Physicochemical data of 4,4'-dibromo-3,3'-dimethoxyl biphenyl
[Yield =98%, Colourless solid, MP = 168°C; ^{1}H NMR: ($CDCl_3$, δ in ppm)6.96-7.38(m,6H, Ar-H), 3.73(s, 6H,-OCH_3); Mass spectrum: m/z 372(M^+).

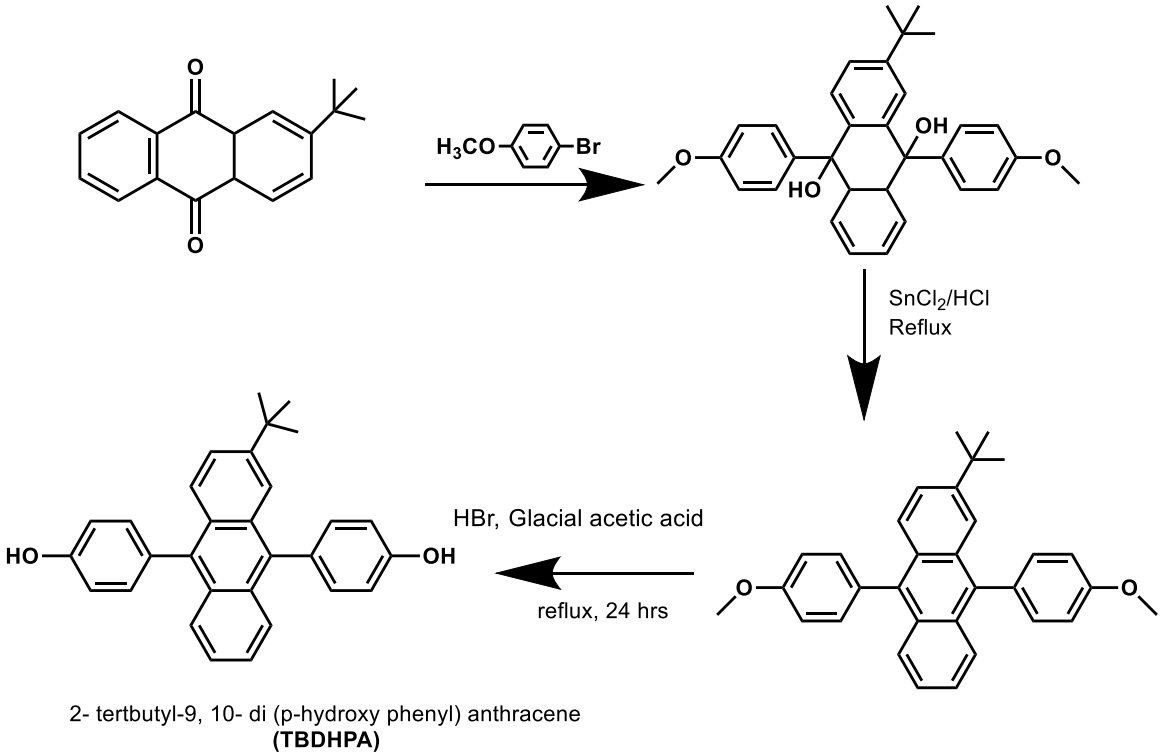
Physicochemical data of 4,4'-dibromo-6,6'-diiodo -3,3'-dimethoxyl biphenyl
[Yield =97%, Cream coloured solid, MP = 183°C; ^{1}H NMR: ($CDCl_3$, δ in ppm)6.65-7.76(s,2H, Ar-H), 3.73(s, 6H,-OCH_3); Mass spectrum: m/z 624(M^+).

Physicochemical data of 2,7-dibromo-3,6-dimethoxy-9-silafluorene monomers
DMSiF : Yield= 97%; M.P. =182°C; IR (cm^{-1}): 2962.57(C-H stretch), 1546-1569(C=C stretch),1258.80(C-O asymmetric stretch), 1015.23(C-O symmetric stretch) 1049.2 (C-Br symmetric stretch); ^{1}H NMR: ($CDCl_3$, δ in ppm)6.98(s,2H,Ar-H), 7.66(s,2H,Ar-H), 3.73(s,6H,-OCH_3),0.66(s,6H,-CH_3); ^{13}C NMR: ($CDCl_3$, δ in ppm)110-143.9(aromatic carbon),158.9(=C-O),110.7(=C-Br), 55.2(-OCH_3), -1.5(-CH_3); Mass spectrum: m/z426 (M^+).
MPSiF: Yield= 90%; M.P. =163°C; IR (cm^{-1}): 2962.38(C-H stretch), 1548-1567.71(C=C stretch), 1259.03(C-O asymmetric stretch), 1017.62(C-O symmetric stretch) 1049.2 (C-Br symmetric stretch); ^{1}H NMR: ($CDCl_3$, δ in ppm):6.98-7.66(s,7H,Ar-H),3.93(s,6H,-OCH_3),0.66(s,3H, -CH_3); ^{13}C NMR: ($CDCl_3$, δ in ppm)110-143.9(aromatic carbon), 158.9(=C-O),110.7(=C-Br),55.2(-OCH_3), 0.7 (-CH_3); Mass spectrum: m/z 490 (M^+).
DPSiF: Yield= 96%; M.P. =178°C; IR (cm^{-1}): 2934.35(C-H stretch), 1548-1567.71(C=C stretch), 1241.13(C-O asymmetric stretch), 1033.92 (C-O symmetric stretch), 1049.2 (C-Br

symmetric stretch); ^{1}H NMR: ($CDCl_3$, δ in ppm):6.78-7.66(s,14H,Ar-H),3.93(s,6H,-OCH_3); ^{13}C NMR: ($CDCl_3$, δ in ppm) 110-158.9(aromatic carbon), 158.9(=C-O), 110.7(=C-Br),55.2(-OCH_3); Mass spectrum: m/z 554 (M^+).

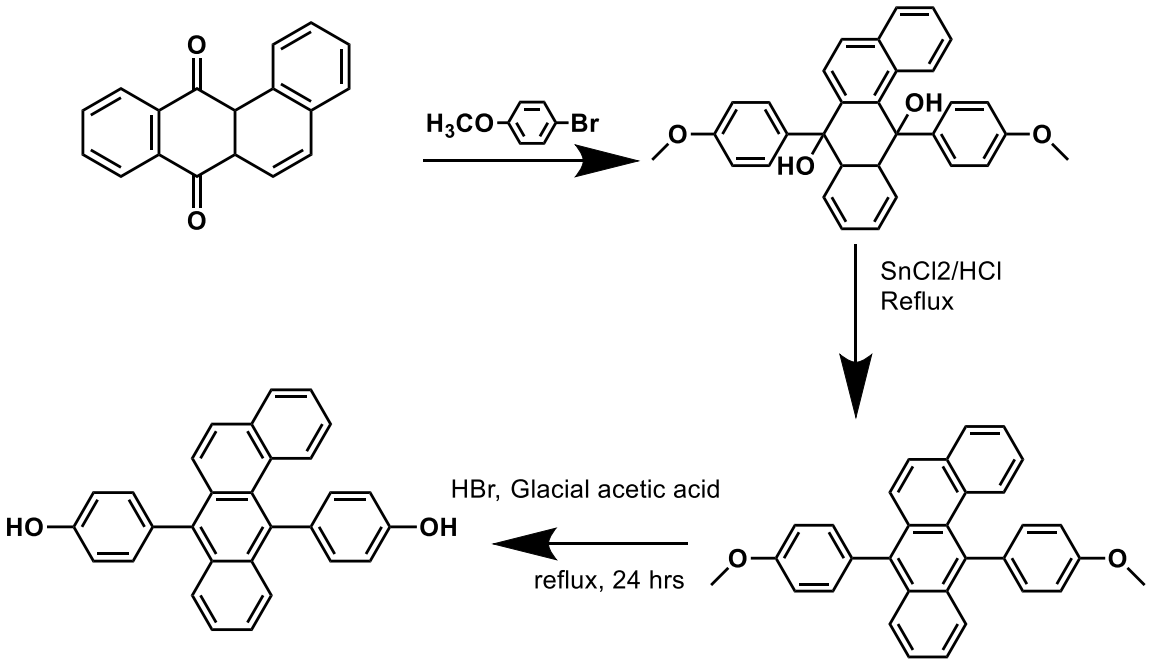
II) Synthesis of 2-tert butyl 9,10-di (p-methoxy phenyl) anthracene derivative

This synthesis is carried out using an already reported procedure (Jones, 1947; Raut, 2013; Raut,2010)



2- tertbutyl-9, 10- di (p-hydroxy phenyl) anthracene
(TBDHPA)

Scheme.2 Synthesis of 2-tert butyl 9,10-di (p-methoxy phenyl) anthracene derivative



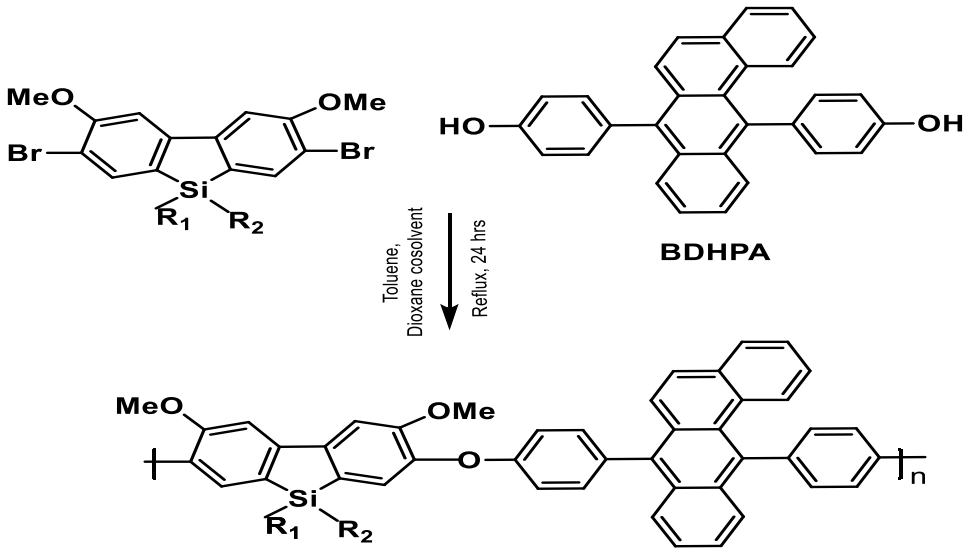
7, 12- di (p- hydroxyphenyl) tetraphene

Scheme.3 Synthesis of 7,12-di(p-hydroxyphenyl)tetraphene derivative

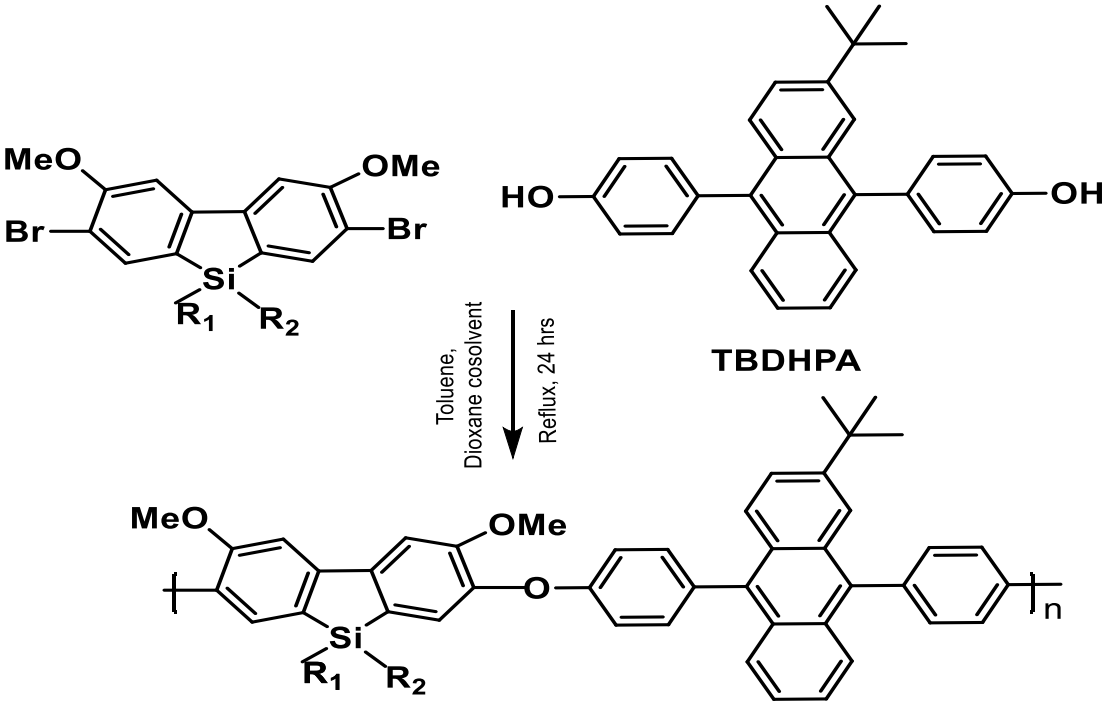
Physicochemical data of 2-tert butyl - 9, 10-di(p-hydroxyphenyl) anthracene (TBDHPA)
TBDHPA: Yield: 86%; Light green solid; M.P.196°C; IR (cm^{-1}): 3426(-OH stretch), 3059(C-H stretch), 1608-1399(C=C stretch), 809-880 (phenyl group); ^{1}H NMR ($CDCl_3$, δ ppm):6.939-7.670(m,13H,Ar-H), 3.971(s,2H,-OH), 1.269(s,9H, $-CH_3$); ^{13}C NMR: ($CDCl_3$, δ in ppm)116.4-157.4(aromatic carbon), 41.1(tert carbon), 31.4($-CH_3$); Mass spectrum: m/z 418 (M^+), Anal.Calcd for $C_{30}H_{26}O_2$: C 86.12, H 6.22, O 7.66; Found: C 86.33, H 6.08, O 7.59

II) Synthesis of 9,9-Di alkyl/aryl silafluorene derivative -diphenylacene polymers

The mixture of 9,9-dialkyl/aryl silafluorene monomer and 2-tert butyl - 9, 10-di(p-hydroxyphenyl) anthracene monomer were taken in a three necked round bottom flask and added potassium carbonate as a base. Co-solvent of toluene and dioxane (1:2) this mixture was added and refluxed for 12 hours. After the polymerization was completed, excess silafluorene monomer was added for end capping of hydroxyl groups. The reaction temperature was then reduced to room temperature and was added to water. The polymer was precipitated in methanol once the toluene solvent was evaporated and was extracted using dichloromethane. The polymer obtained was dried in oven (Raut et.al, 2013; Raut et.al, 2010). The crude product was dissolved in chloroform and re-precipitated from methanol. Repeated the above procedure to purify the polymer. Using the similar reaction scheme series of alkyl/aryl substituted silafluorenes - diphenylacene polymer was synthesized.



$R_1 = R_2 = -CH_3$, Poly(DMSiF-BDHPA)
$R_1 = -CH_3$, $R_2 = -C_6H_5$, Poly(MPSiF-BDHPA)
$R_1 = R_2 = -C_6H_5$, Poly(DPSiF-BDHPA)



$R_1 = R_2 = -CH_3$, Poly(DMSiF-TBDHPA)

$R_1 = -CH_3$, $R_2 = -C_6H_5$, Poly(MPSiF-TBDHPA)

$R_1 = R_2 = -C_6H_5$, Poly(DPSiF-TBDHPA)

Scheme 4 The general synthesis of alkyl/aryl substituted silafluorene - diphenylacene polymers.

Physicochemical data of the co-polymers:Poly(DMSiF-BDHPA): ^{1}H NMR ($CDCl_3$, δ ppm): 6.98-7.67 (m,Ar-H), 3.73 (s,-OCH_3), 1.40 (s,-CH_3), 0.66(s, -CH_3 on Si atom) ; ^{13}C NMR: ($CDCl_3$, δ in ppm)125.9-133.7(aromatic carbon), 40.1(tert carbon), 24.8(-CH_3), 56.2 (-OCH_3),1.5 (-CH_3 on Si atom);

Poly(MPSiF-BDHPA): ^{1}H NMR ($CDCl_3$, δ ppm): 6.98-7.67 (m,Ar-H), 3.73 (s,-OCH_3), 1.40 (s,-CH_3), 0.66(s, -CH_3 on Si atom); ^{13}C NMR: ($CDCl_3$, δ in ppm) 125.9-133.7 (aromatic carbon), 40.1 (tert carbon), 31.4 (-CH_3), 56.2 (-OCH_3),1.5(-CH_3on Si atom);

Poly(DPSiF-BDHPA): ^{1}H NMR ($CDCl_3$, δ ppm): 6.98-7.67 (m,Ar-H), 3.73 (s,-OCH_3), 1.30 (s,-CH_3); ^{13}C NMR: ($CDCl_3$, δ in ppm) 125.9-133.7 (aromatic carbon), 41.1 (tert carbon), 31.4 (-CH_3), 56.2 (-OCH_3)

Poly(DMSiF-TBDHPA): ^{1}H NMR ($CDCl_3$, δ ppm): 6.98-7.67 (m,Ar-H), 3.73 (s,-OCH_3), 1.40 (s,-CH_3), 0.66(s, -CH_3 on Si atom) ; ^{13}C NMR: ($CDCl_3$, δ in ppm)125.9-133.7(aromatic carbon), 40.1(tert carbon), 24.8(-CH_3), 56.2 (-OCH_3),1.5 (-CH_3 on Si atom);

Poly(MPSiF-TBDHPA): ^{1}H NMR ($CDCl_3$, δ ppm): 6.98-7.67 (m,Ar-H), 3.73 (s,-OCH_3), 1.40 (s,-CH_3), 0.66(s, -CH_3 on Si atom); ^{13}C NMR: ($CDCl_3$, δ in ppm) 125.9-133.7 (aromatic carbon), 40.1 (tert carbon), 31.4 (-CH_3), 56.2 (-OCH_3),1.5(-CH_3on Si atom);

Poly(DPSiF-TBDHPA): ^{1}H NMR ($CDCl_3$, δ ppm): 6.98-7.67 (m,Ar-H), 3.73 (s,-OCH_3), 1.30 (s,-CH_3); ^{13}C NMR: ($CDCl_3$, δ in ppm) 125.9-133.7 (aromatic carbon), 41.1 (tert carbon), 31.4 (-CH_3), 56.2 (-OCH_3)

Results and discussion:

Two series of polymers from 9-substituted-9-silafluorenes and p-phenyl anthracene and p-phenyl tetracene were synthesized successfully. Ether linkage in the polymers were verified with the incidence of FTIR peak in the range 1025-1042cm-1 (**Table 1**). The broad peak of -OH group and the peak corresponding to dibromofluorene monomers were found to be absent in the polymers. This showed that the polymers are formed through condensation of the monomers by removal of Hydrogen Bromide molecule.

Table 1: IR data of the polymers

Polymer	C-O-C bond stretching	C-H aliphatic stretching	C-H aliphatic bending	C=C bond stretching	C-H aromatic stretching
PolyDMSiF-TBDHPA	1032.11	2961.12	1456.77	1570.12	3025.37
PolyPMSiF-TBDHPA	1032.57	2959.22	1455.58	1570.99	3060.65
PolyDPSiF-TBDHPA	1031.58	2959.97	1457.45	1590.32	3066.25
PolyDMSiF-BDHPA	1038.9	2959.42	1457.35	1587.13	3026.03
PolyPMSiF-BDHPA	1037.78	2957.77	1456.69	1586.63	3060.62
PolyDPSiF-BDHPA	1038.43	2960.32	1456.33	1586.23	3008.87

The polymers synthesized were highly soluble in common organic solvents like chloroform, carbon tetrachloride, toluene, xylene and THF, in comparison to the diacene monomers. The GPC (Gel Permeation Chromatography) measurement gave values for the number average molecular weight of polymers Mn and the polydispersive index (PDI). These were suggesting linear polymers (**Table 2**).

Table 2: GPC data of the polymers:

Polymers	Mn	Mw	PDI	DP
PolyDMSiF-TBDHPA	8890	8970	1.01	13
PolyPMSiF-TBDHPA	11206	11362	1.01	15
PolyDPSiF-TBDHPA	10527	10750	1.02	13

PolyDMSiF-BDHPA	8800	8970	1.02	13
PolyPMSiF-BDHPA	8883	8970	1.01	12
PolyDPSiF-BDHPA	11268	11352	1.01	14

Thermograms of all the polymers showed them to be stable with glass transition temperature ranging from 75 to 93˚C. (Table 3)

Table 3: **Thermal Data of the Polymers:**

Polymer	**Number of decomposition steps[(a)]**	**DTA peak temperature(˚C)**	**Glass transition Temperature (Tg) (˚C)[(b)]**
Poly(DMSiF-TBDHPA)	2	380,520	75
Poly(PMSiF-TBDHPA)	3	150,393,550	85
Poly(DPSiF-TBDHPA)	3	150,390,550	91
Poly(DMSiF-BDHPA)	3	160,380.560	90
Poly(DPSiF-BDHPA)	3	130,390,550	93

(a) Number of the steps in which dissociation has taken place

(b) Glass transition temperature obtained from Differential Scanning Calorimetry (DSC)

Figure 1 shows the overlay of the UV-Visible analysis of the polymers and **Figure 2** shows that of fluorescence emission spectroscopy. The onset absorption was found to be in the range 410 to 435nm for both the series. The absorption peaks showing the fluorene, phenylene and anthracene rings were shown by all the polymers and matched with the references.

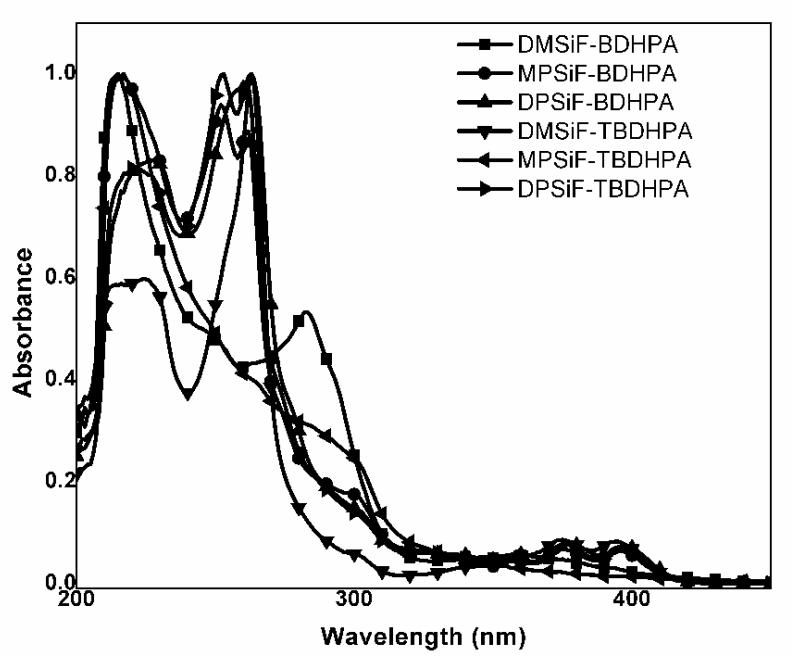


Figure 1 : The overlay of the UV-Visible analysis of the polymers

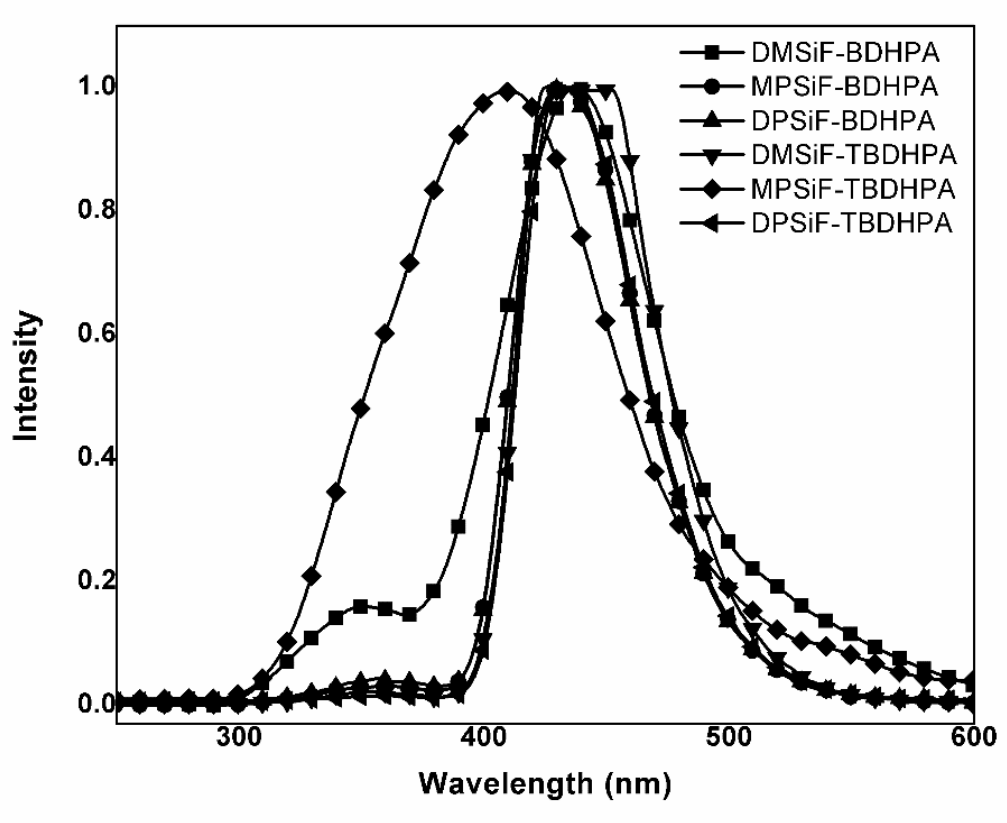


Figure 2 : The overlay of the Fluorescence analysis of the polymers

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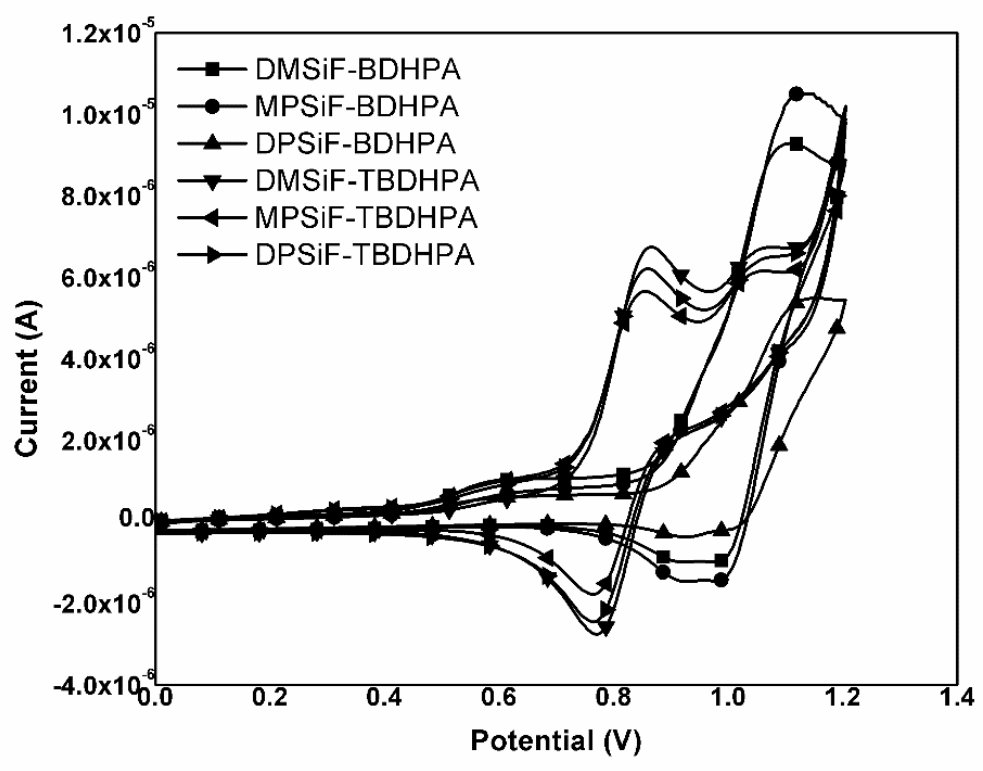

Figure 3: The overlay of the Cyclic Voltammetric analysis of the polymers

From the Cyclic voltammetry studies of polymers the ionization potential was found from the anodic scan and was in the range -5.58 to -5.54eV. These values were calculated from the onset oxidation of the polymers. Ea was calculated from onset reduction of polymers, -2.5 to -2.71eV. Band gap of the polymers were in range 2.85 to 2.92 and this is in high concordance with the values obtained from the photo chemical calculations.

Conclusion:

The two series of polymers obtained from 9-substituted-9-silafluorenes and p-phenyl anthracene and p-phenyl tetracene were synthesized and analyzed. They all were found thermally stable and soluble in almost all common organic solvents. They were characterized with pure blue emission. The electrochemical studies of the fabricated polymeric light emitting diodes show that the polymeric layer acts as good emitting materials for optoelectronic devices.

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