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Asghari Gul[a,b], Zareen Akhter[b*,] Rumana Qureshi[b], Arshad S. Bhatti[a]

Graphical Abstract

Electrostatic Potential Map, PI; Yellow colour around 'N' and 'O' atoms indicate electron rich area prone to the electrophillic attack
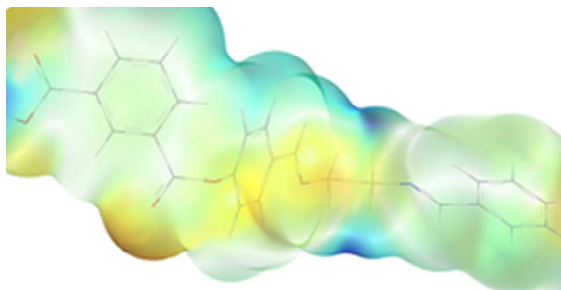
Conducting Poly(azomethine)ester: Synthesis, Characterization and Insight into electronic properties using DFT calculations.

Asghari Gul[a,b], Zareen Akhter[b*,] Rumana Qureshi[b], Arshad S. Bhatti[a]

Abstract

A poly(azomethine)ester was synthesized via solution phase polycondensation of isophthaloyl chloride and preformed 4-((2-(4-hydroxibenzylideneamino)ethylimino)methyl)phenol (SB). Various aliphatic and aromatic moieties were incorporated in the parent chain to process them and for examining their effect on the conducting properties. To provide an insight into the electronic properties, DFT calculations at 6-31G/B3LYP level was carried out. Emphasize was placed on exploring the frontier electron density, energy gaps and electrostatic potential maps to predict their conducting behaviour and electrophillic/nucleophillic reactivity. Our results based on experimental data and theoretical studied showed that in spite of some discrepancies, the electronic properties can be approximated theoretically to design material of desired properties for organic electronic devices. Material was characterized employing FTIR, ^{1}HNMR spectroscopic studies and elemental analysis.

Key words: Poly(azomethine)ester, DFT calculations, HOMO/LUMO coefficients, 3D electron density maps.

Introduction

Conducting polymers are the most recent generation of the material that has facilitated the understanding of the fundamental chemistry and physics of π bonded macromolecules. Desire to develop new conducting macromolecules with anticipated properties began to attract synthetic chemist in 1980s. Conducting material like poly(azomethine)s, in spite of having a wide variety of applications, possess a disadvantage that they are insoluble in most of the common organic solvents owing to their strong chain-chain interaction [1-4]. To overcome the problem of insolubility different tactics are used such as introduction of flexible aliphatic spacers in the main chain, pendent alkyl groups along the backbone, the co-polymerization of different soft groups (aliphatic, alkyl or siloxanes) and composite formation [5-8]. The other approach is supra-molecular modifications/dopant engineering of material employing organic sulfonic acids, organic esters of phosphoric acids, sulfophthalic acid, or various substituted phenols [9]. In addition, charge injection into the conjugated, semiconducting macromolecular chains by doping a suitable metal into a polymer matrix could lead to the enhanced electrical properties. Similarly, polyaniline (PANI) blends can be made as lesser amount is required to improve the conductivity of material [12-17]. However, the chemistry and physics of these polymers in their non-doped semiconducting state are also of great interest because they provide a route to plastic electronic devices. These novel properties enable a number of applications including polymer LEDs, conducting polymers as electrochromic materials, polymer photo-detectors, and photovoltaic cells.

Nowadays these polymers could be designed theoretically employing density functional theory (DFT) calculations by their predicting molecular geometries, energy levels, and absorption spectra. Performing DFT calculations on conducting polymers is challenging due to their size (large number of atoms); however, they can be approximated using oligomeric/repeat unit model compounds. Addition of different sequences to the chain creates wide possibilities for the modification of their properties[17].

To our knowledge, there are only few articles describing the structural elucidation and predictive study of electrical properties (complemented by experimental data) of newly synthesized macro chains [17]. Thus, we report herein, the synthesis and characterization of poly(azomethine)ester (PAME) and a variety of aliphatic/aromatic terpolymers. Structure-property relation in term of electrical conductivity is discussed. G0W3 was employed for 3D electron density mapping of the chains. ΔE along with HOMO/LUMO coefficients were calculated and compared with the experimental data.

Synthesis of monomer, SEM-EDX of neat and doped material is given in the supporting information, whereas, thermal behaviour and molecular weight by laser light scattering will be discussed in our future article.

Results and discussion

The Schiff base containing terminal diol was prepared according to previously published procedure given in supporting information [18, 19]. PAME (PI) was obtained in good yield using low temperature solution phase polycondensation of monomers isophthaloyl chloride and 4-((2-(4hydroxibenzylideneamino)ethylimino)methyl)phenol (SB), scheme 1. A wide variety of terpolymers were prepared by adding different diol-based moieties in the macrochain using one-pot three-reactant reaction in an in situ process to improve the solubility of material, scheme 2. The material was made soluble by protonating with p-sulphonic acid. The reaction was carried out at atmospheric pressure and low temperature to avoid any side reaction and decomposition of thermally sensitive monomers [19]. The FTIR and ^{1}HNMR spectroscopic studies were used to

confirm the functionalities present in the synthesized monomer (SB), polymer (PI) and terpolymers (PIF, PIB, PIH, PIPr, PISi,).

PAMEs were found insoluble in all organic and inorganic solvents owing to the presence of bulky aromatic groups in the main chain [18, 19]. In an attempt to process the material, different commercial diols (Pr, H, Si, B or F, scheme 2) containing aromatic, semi-aromati, silyl and floro moieties were assimilated in the parent polymer chains (PI) to improve their solubility in organic or inorganic solvents [19]. Subsequently, five aliphatic/aromatic terpolymers, were synthesized which were still found insoluble in any solvent. After various attempts, eventually, the material was solubilized by supra molecular modification employing p-toluene sulphonic acid [9]. The macrochains becomes completely soluble in DMSO and sparingly in THF, ethanol and methanol.

The structure of synthesized PI was confirmed by the presence of characteristic absorption peaks in their respective areas. Significant changes were observed in the spectral properties of initial compounds and product as some of the signals disappeared and some new appeared. Stretching vibration for (C=O) and (C-O) appearing in range 1720-1750(s) cm^{-1} and 1101-1200(s) cm^{-1} respectively confirmed the presence of ester linkage in PI. The additional peak around 1600-1645(s) cm^{-1} confirmed the azomethine linkage in the macrochains. Two symmetric peaks in the ester and azomethine region in each terpolymer confirm the successful incorporation of diol moieties in the parent chain. The FTIR spectra showed characteristic peaks related to added diols in addition to the once common in all spectra. The aliphatic absorption band (C-H aliphatic) appeared around 3000-2900 cm^{-1} in the spectra of PIH and PIPr. The characteristic FTIR absorption peaks for (Si-O-Si) group present in silanol containing polymers like PISi appeared as doublet around 1020 cm^{-1} and 2900 cm^{-1}.The presence of aromatic C-H in polymers such as PIF and PIB was confirmed by the appearance of peak around 3100 cm^{-1}. Occurrence of C-Cl in range 780-540 cm^{-1} along with the disappearance of hydroxyl group peak in PAME and its condensation terpolymers revealed that they have acid chloride group at the terminal [18-20].

^{1}H NMR spectroscopy was also used for the structural analysis of PAMEs. The study was performed after protonation of samples with p-toluene sulphonic acid (dopant engineering), in DMSO, using TMS as internal reference. ^{1}H NMR studies showed the presence of all types of proton expected for the proposed structures. Resonance in the range 8.5-7.7 ppm, common in all spectra was attributed to the presence of HC=N proton whereas the signal that appeared in the range 6.9 to 7.9 ppm showed aromatic protons. In addition to these signals which were common in all the spectra, the polymer having aliphatic diols (Pr, H) showed multiplet signal in the range 0.7 to 2.3 ppm (aliphatic –CH). The polymer (PIB) showed additional signals in the range 7.0 to 8.0 ppm (additional aromatic rings of added diols) and 2.3 ppm (-CH$_3$ present in bisphenol A). PIF showed resonance around 7.4 to 8.1 (aromatic rings), slightly deshielded owing to the presence of electronegative F (CF$_3$)in the diol added. Silanol based material exhibited additional resonance peaks at 1.9 to 2.1 (CH$_3$ attached to Si). The signal present in the range 2 to 2.5 (–CH$_3$) and 2-2.2 (OH) confirm the protonation in the main chain. The OH group appeared at the lower field owing to the magnetic anisotropy of the aromatic ring present in the p-toluene sulphonic acid group [18-20].

The calculations for the elemental analysis of polymers were made on the basis of structure of repeat units present in the polymer chain.The data for C, H and N contents in polymers were found in relative good agreement with the presumed structure for the condensation terpolymer. The Si in the copolymers having (dimethylsiloxane) reacts with C at high temperature to make

ceramic material. Therefore their elemental analysis was not possible [19, 20] and such polymers are currently investigated as precursor to ceramic materials.

Conductivity Measurements:

The material was pressed in the pellets of equal dimensions to study the improvement in their conducting behaviour after doping and blending. It is known that the valence electrons bound in sp^3 hybridized sigma-bonds have low mobility and do not contribute to the electrical conductivity of the material. However, in conjugated materials, the situation is completely different as they have backbones of connecting sp^2 hybridized carbon centres. One valence electron on each centre resides in a p_z orbital. When the material is doped by oxidation, it removes some of the delocalized electrons which have high mobility. Thus, the conjugated p-orbitals form a partially empty one-dimensional electronic band having mobile electrons. Electrical conductivity of neat macrochains, polymer/PANI blends and silver doped material at room temperature was measured and the data is given in table 1.

The influence of the structure on the electrical properties in the case of condensation terpolymers was also studied. The material having continuous conjugation in the chain (PI and PIB) showed maximum conductivity, however PIF have relatively low conductivity owing to the presence of highly electronegative hexaflouroisopropylidine group in the macrochain. The polymers based on methylene and silyl spacers have lowest conductivity among the all which might be due to the suspension of conjugation in the chains due to the presence of these moieties. The study also showed the lower conductivity of the neat material as the undoped polymers usually have energy gap > 2 eV, which is too high for conduction [11-13]. Since most organic polymers do not have intrinsic charge carriers, the required charge carriers could be introduced in the material either by partial oxidation (*p*-doping) with electron acceptors (*e.g.* I$_2$, AsF$_5$) or by partial reduction (*n*-doping) with electron donors (*e.g.* Na, K). Through a doping process, charged defects (*e.g.* polaron, bipolaron and soliton) could be introduce in the structures, which then serve as charge carriers. For the presented work, all the polymers were doped with silver involving removal of electrons from the HOMO of poly(azomethine)esters and thus forming positive hole and counter anions. Elimination of two electrons from same energy level form bipolaron which cause decrease in the band gap and thus, increase in conductivity of the material [12,13].

Polymer matrix was also blended with PANI. The trend of conductivity was found same as was in neat material however the material blended with PANI was found to be more conducting as compare to silver doped one which was in accordance to the literature, table 1.
In spite of intensive research, the relationship between morphology, chain structure and conductivity is still poorly understood. However it is assumed that conductivity should be higher for the higher degree of crystallinity and better alignment of the chains; however this could not be confirmed for PANI, which is amorphous in nature. To explain whether the trend observed in conductivity can be explained theoretically considering the molecular properties, DFT calculations were carried out.

Table 1 Conductivity measurement of neat, doped and blended material at room temperature

Codes	ΔE eV	Holes	LUMO Coefficients
PI [a]N=4.1x10⁻¹⁴ [b]S.D=3.44x10⁻⁵ [c,d]PB=1.54x10⁻³	LUMO=-0.0824 HOMO=-0.1949 ΔE=0.11	41	-0.032(3C),0.033(11c)-0.046(13C),0.030(15C),-0.021(16C),0.35(37O),0.002(37O) -0.0002(38O),-0.04(41H),-0.79(42H),-0.71(43H),-0.64(44H),-0.15(45H),0.0033(47H),- 0.0008(48H),0.016(49H)
PIF [a]N=4x10⁻¹⁴ [b]S.D=3.4x10⁻⁴ [c,d]PB=3.5x10⁻³	LUMO=-0.02051 HOMO=-0.09950 ΔE=0.08	69	-0.012,(410),-0.0008(49H),0.0089(50C),0.077(51,C),-0.056(53C),-0.11(62C),0.35(64C),-0.11(66C).- 0.09(71O),0.58(73C), -0.13(76F),-0.3(77F),0.27(78F), 0.03(79C), 0.076(81F), -0.012,(410),- 0.0006(49H),0.009(50C),0.077(51,C),-0.05(53C),-0.104(62C),0.38(64C),-0.103(66C).-0.09(71O),0.5(73C),- 0.16(74C),-0.39(76F),-0.29(77F),0.25(78F), 0.033(79F),0.16(81F)
PISi [a]N=5x10⁻¹⁵ [b]S.D=4.5x10⁻⁷ [c,d]PB=4.0x10⁻⁶	LUMO= -0.13330 HOMO=- 0.171254 ΔE=0.04	113	0.35(11,C),0.37(13,C),0.38(15,C),0.12(16,C),0.002(H,19),0.004(21,C),0.0045(22,C),0.0006(23,C),0.01(24,C), 0.00105(25,C),0.00105(25,C),0.20(26,C),0.0006(27,H),0.002(28,H),0.0022(29,H),0.005(30,H),0.8(31,C),0.02 1(32,C),0.78(34,C),0.02(35,C),.0.0025(36,C),0.137(37,N)0.363(38,N),0.005(39,O),0.2(40,O)
PIPr [a]N=5.9x10⁻¹⁶ [b]S.D=6.4x10⁻⁸ [c,d]PB=6.1x10⁻⁷	LUMO=--0.09850 HOMO=--0.14642 ΔE=0.05	53	-0.005(11C),-0.007(12C),0.02(13C),-0.05(14C),0.03(15C),-0.016(16C),-0.007(17H),-0.005(18H),0.01 (19H),- 0.0077(20H), 0.01(21C),0.44(22C), -0.34(23C),0.23(24C),0.32(25C)-0.56(26C), -0.009(27H),0.0049 (28H), 0.005(29H), 0.04(30H), 0.29(31C), 0.16(32C),
PIH [a]N=4.1x10⁻¹⁵ [b]S. D=5.4x10⁻⁶ [c,d]PB=5.x10⁻⁷	LUMO=0.0012 HOMO=-0.04434 ΔE=0.042	57	0.016(50C),0.002(51H),0.0013(52H),0.002(53H),-0.00143(54H),-0.002(55H),- 0.009(56H),0.0091(57H),0.0032(58C),-0.0020(59C),0.00064(60C),-0.0005(61O), -0.0001 (62H),-0.00043 (63H),-0.0003(64H), 0.0006(65H),-0.0006(66H),0.00116(67H),-0.00028(68H),-0.00055(69H), 0.00013,- 0.049(70C)
PIB [a]N=1.5x10⁻¹³ [b]S. D=1.9x10⁻⁴ [c,d]PB=1.5 10⁻²	LUMO=-0.09312 HOMO=-0.12752 ΔE=0.04	75	-0.00003(1C)-0.0037(2C),-0.003(3C),-0.0036(4C),-0.00036(5C),0.0036(6C),-0.00006(7H),0.00013(8H),- 0.00062(9H),-0.00014(19H),-0.0004(11C),-0.0004(12C),-0.003(13C),0.115(21C),-0.064(22C),- 0.005(23C),0.05(24C),-0.038(25C),-0.025(26C), 0.00145(27H),0.00063(28H),0.00034(29H),0.0054(30C),- 0.0082(31C),0.004(32C),0.001(33C),-0.07(34C),-0.00004(N),- 0.0007(36N),0.02(38O),0.055(39O),0.103(40O),-0.011(41O), - 0.002(44H),0.00135(45H),0.00132(46H),0.0003(48H),0.0031(49H),-0.1 (51C),-0.114(52C)

[a] Neat [b] Silver doped [c] Polymer blends [d] Conductivity of PANI at R.T is 1(Scm⁻¹)

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3.2 DFT calculation results

Objective of this study was to apprehend the relation-ship between the chemical structure and conduction properties of the polymers which could help to design material with the desired properties. Quantum chemical calculations offer good understanding of the connection between the molecular properties and conductivity of material. All valence MO calculations, for the repeat unit of each poly(azomethine)esters, were carried out to predict the various parameter in the π-conjugated system to explain the conductivity trend observed. It is assumed that electrical properties (conductivity) in the polymer is correlated to the difference of energy (ΔE) between highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) [16, 16-23]. The electron(s) from the highest occupied molecular orbital (HOMO) have ability to populate the lowest unoccupied molecular orbital (LUMO) in the excited state resulting in the process of conduction. The variation in electrical conduction of the polymers with the calculated band gap is in the order PIB>PI~PIF>PISi>PIH>PIPr, however, the band gap, ΔE does not seems to obey the same trend, table 1. These results showed that the band gaps solely could not explain the observed conductivity results, subsequently other parameters need to be investigated.

Based on literature, in addition to the ΔE, carrier movement and movement of holes are also involved in the conduction process. Where holes (theoretically) are related to regions where there is no electron density and the coefficients (mixing ratio) of atoms involved in HOMO are zero. In addition, the coefficients of atoms involved in LUMO are also important as they facilitate the carrier movement up to the point and it is also known that higher the coefficient, greater is the electron density on excitation. Zero or very low LUMO coefficients are visualized as impaired carrier movement.

To explain the results, the coefficients of the atoms involved in HOMO were examined to study the role of intrinsic holes (zero coefficient shows presence of hole) as they seem to contribute in the conduction process. Since there is significant involvement of LUMO in conduction so these coefficients were also investigated, table 1.

Highest conductivity observed in polymer, PIB can now be explained by considering its low band gap, number of HOMO (holes) and contribution of LUMO. Both PI and PIF have approximately same conductivity although both differ in their band gaps. The good electrical conductivity of these polymers may be due to the presence of holes in HOMO and significant LUMO electron density at the connecting atoms (centers).The polymer PISi showed less conductivity although it has ΔE value of 0.04 which might be due to the presence of low electron density at some centers in the chain. Thus low eigen values are responsible for the lower conductivity of polymer PISi compared to others as expected. The polymers PIPr and PIH has low ΔE (0.05a.u, 0.04a.u, respectively) which indicates easier excitation of electrons from HOMO to LUMO. However, the conductivity of these polymer were low, i.e., 5.9×10^{-16} and 4×10^{-15} respectively as compare to the PIB [22,23].

Our calculations showed that low band gap does not ensure facile conduction as no correlation was found in band gap and conductivity. The results suggest that presence of intrinsic holes as well as significant contribution from atoms in LUMO also contribute to conductivity.
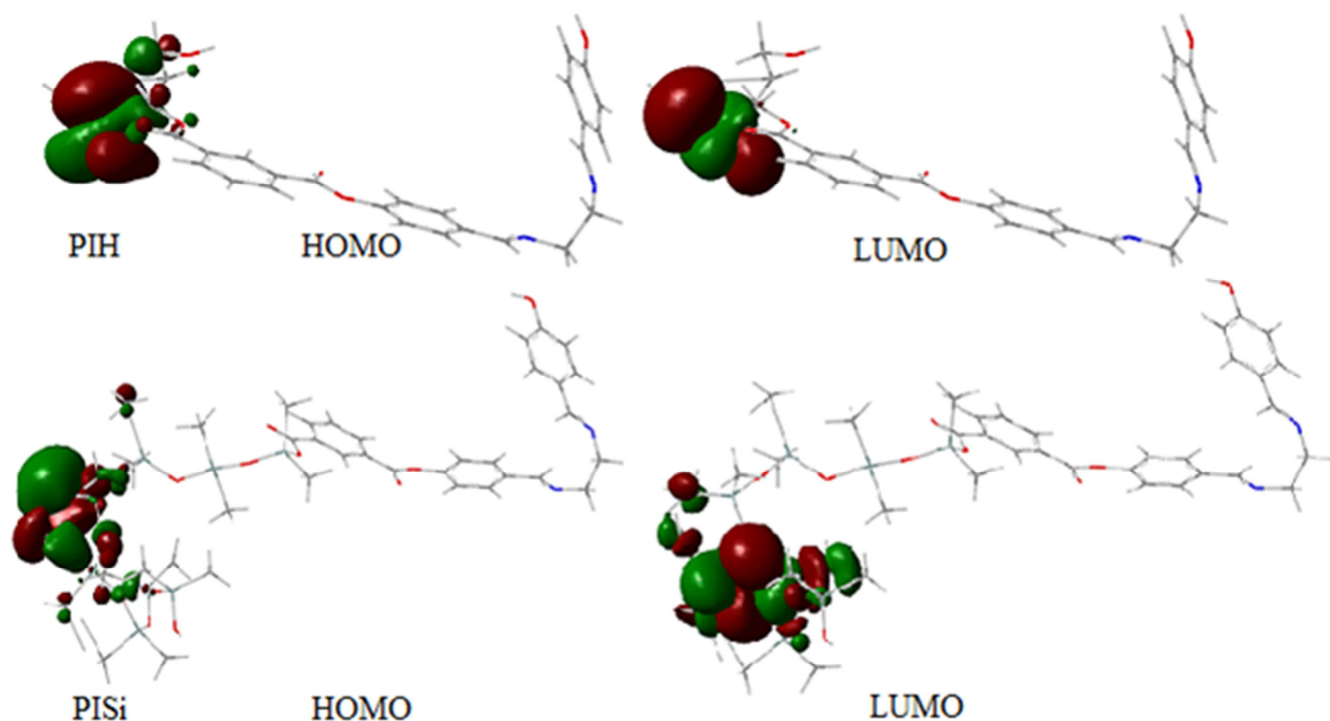
PI

HOMO

LUMO

PIB

HOMO

LUMO

PIF

HOMO

LUMO

PIPr
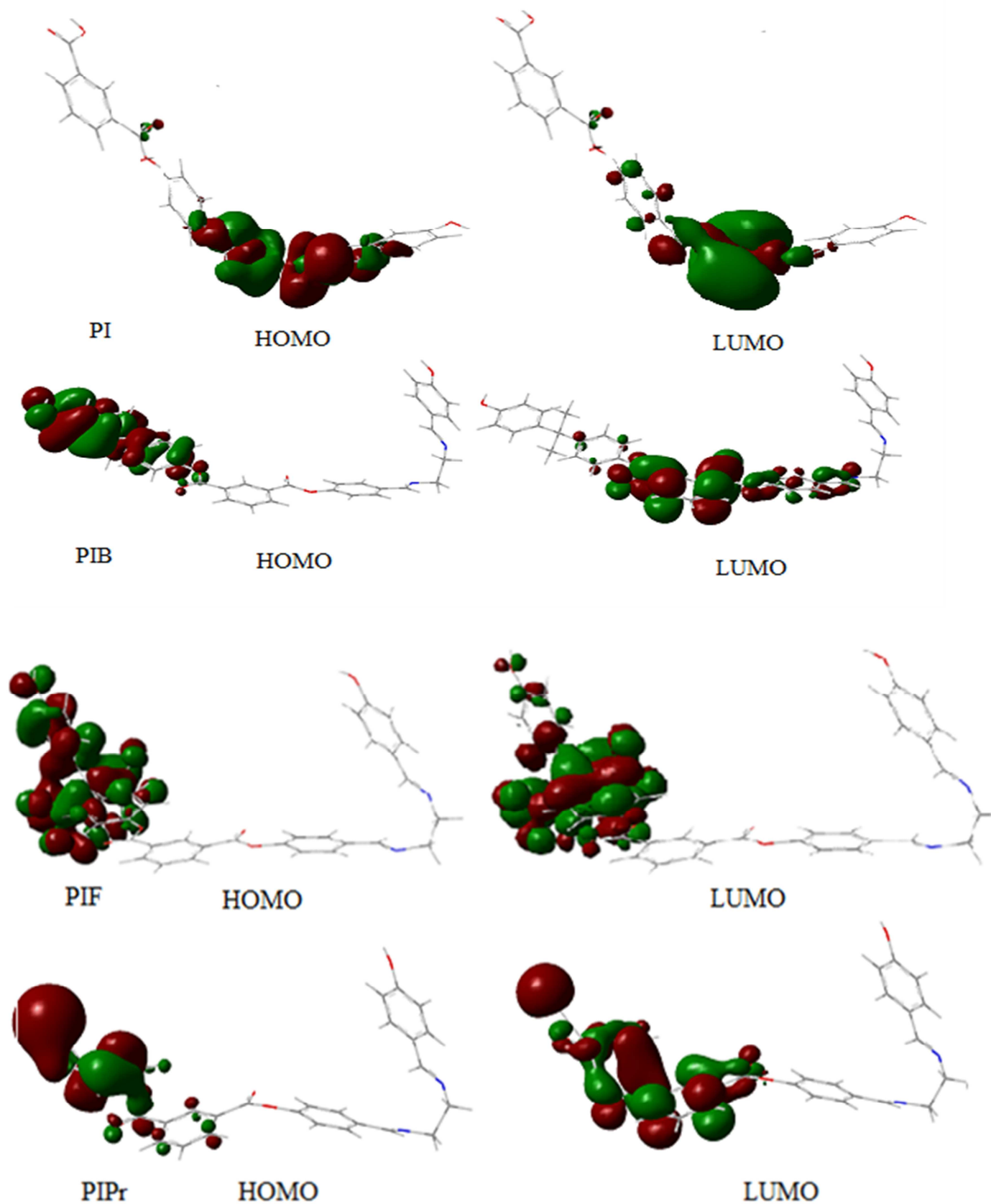
HOMO

LUMO

Figure 1 3D HOMO/LUMO orbitals of Synthesized Material

The electrostatic potential V(r) maps are well known for identification of one specie by the other, thus, this methodology can be used to evaluate the electronic distribution around molecular surface for the macrochains. The electrostatic potential has been used primarily for predicting sites and relative reactivities towards electrophilic attack, and in studies of biological recognition and hydrogen bonding interactions. It can be seen that the macromolecules are stable having almost uniform distribution of charge density. The oxygen and nitrogen atoms are surrounded by a greater negative charge surface, making these sites potentially more favorable for electrophilic attack (red). Among these two sites, the nitrogen atoms having higher values are more susceptible for the attacks which support the H bonding of p-toluene sulphonic acid in the dopant engineering. Similarly those with minimum electron density are prone to nucleophic (blue color), figure 2. The representative electrostatic potential data for PI is given in table 2. [20-23].
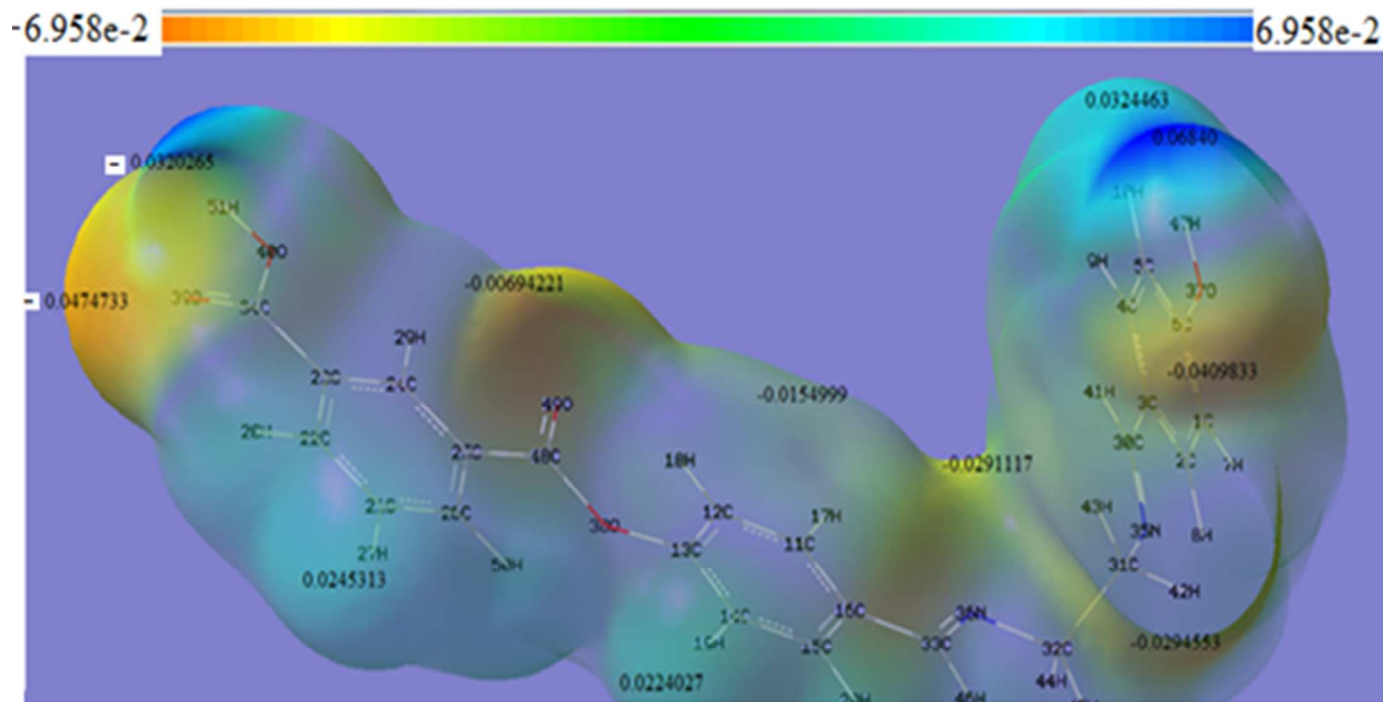
Figure 2 Electrostatic Potential Map, PI; Yellow color around N and O atoms indicate electron rich area prone to the electrophillic attack

Table 2 Electrostatic Potential data for PI

Atoms	Electrostatic Potential	Atoms	Electrostatic Potential	Atoms	Electrostatic Potential
C34	0.0027	C14	-0.0005	C13	-0.0065
O39	-0.026	C15	-0.007	O49	0.002
O40	-0.007	C16	-0.015	N32	-0.02
H51	0.0165	C11	-0.0174	H44	-0.028
C23	-0.0013	C12	-0.0106	C48	0.007
C21	0.0038	H18	-0.012	N36	-0.0065
C26	0.001	H17	-0.0174	H50	0.009
C25	-0.00162	H19	0.0074	H46	-0.00023

| C29 | -0.0025 | H20 | 0.0055 | H27 | 0.0138 |
| H28 | 0.0072 | C33 | -0.010 | | |

Experimental

Isophthaloyl chloride (m.p=43-44°C), 4-hydroxybenzalde (m.p= 112-114°C), 4-aminophenol (m.p=188-190 ^{o}C, Fluka), 1,2-ethylenediamine(206°C, Sigma Aldrich), p- toluene sulphonic acid (monohydrated, m.p=98-102 ^{o}C, Fluka), 1,3-propan-diol (211-217°C, Sigma Aldrich), 1,6-hexan-diol (250°C, Sigma Aldrich), poly(dimethylsiloxane), hydroxyl-terminated (n=550) (Sigma Aldrich), (1,1,1,3,3,3-hexaflouro)bisphenol propane (160-163°C, Sigma Aldrich) and bisphenol A (158-159°C, Sigma Aldrich) were used as received. The solvents dichloromethane, ethanol (Sigma Aldrich), and dimethyl sulfoxide (Sigma Aldrich) used were purified according to the standard reported method [24].

2.1 Computational Details

All MO calculations for the studied compounds were carried out for a repeat unit of each polymer. An exchange functional proposed by Becke in 1988 using a gradient-corrected correlation functional of Lee, Yang and Parr was employed (B3LYP) using minimal basis set 6-31G considering the computational cost due to large size of repeat unit. Gaussian 03 program package was used to evaluate some of the useful molecular descriptors.

Methods

Synthesis of 4-((2-(4hydroxibenzylideneamino)ethylimino)methyl)phenol (SB)

4-((2-(4hydroxibenzylideneamino)ethylimino)methyl)phenol (SB) was prepared according to the reported procedure[18,19].

Polycondensation
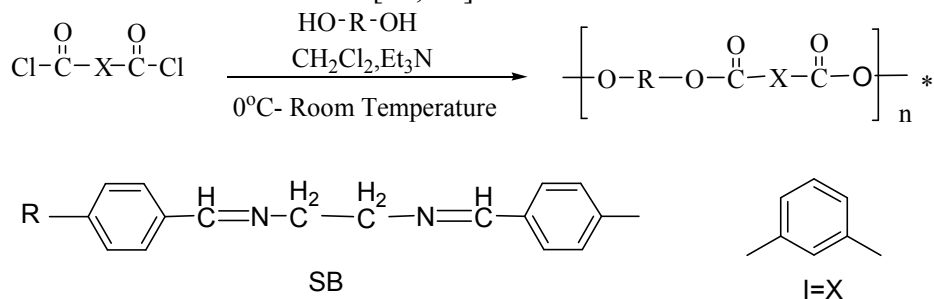
Synthesis of Polymers: (PI)

Stoichiometric amount (1:1) of SB was added to 50mL dried dichloromethane in a two necked round bottom flask fitted with reflux condenser, magnetic stirrer, hot plate and gas inlet. The temperature of the reaction mixture was maintained at 0°C using ice bath. Isophthaloyl chloride (I) was added to the flask followed by the addition of 3-4 ml triethyl amine with constant stirring. The reaction mixture was stirred for 24 hs at room temperature and then refluxed for one h. Yellow colored precipitates of polymer obtained were filtered, washed several times with water, ethanol, dried in air and weighed, scheme 1[18,19].

IP; 398, yellow powder, 88%, FTIR(cm^{-1}, KBr) 3124 (arom-CH), 2956(aliphatic C-H) 1763 (-CO-), 1634 (-N=CH-), 1076 (-C-O-), 747 (C-Cl). ^{1}HNMR [δ, deuterated dimethyl sulfoxide (DMSO-d$_6$)] δ (ppm) (protonated): 8.42 (2H,s azomethine), 7.4-6.8 (m, aromatic-H), 2.3 (6H, m, methylene), 2.01 (2H, s, alcohol), 1.8-1.2(1H,s methylene). Elemental analysis; Calcd (C 72.61, H 4.52, N 7.03) found; (C 72.51, H 4.32, N 7.10).
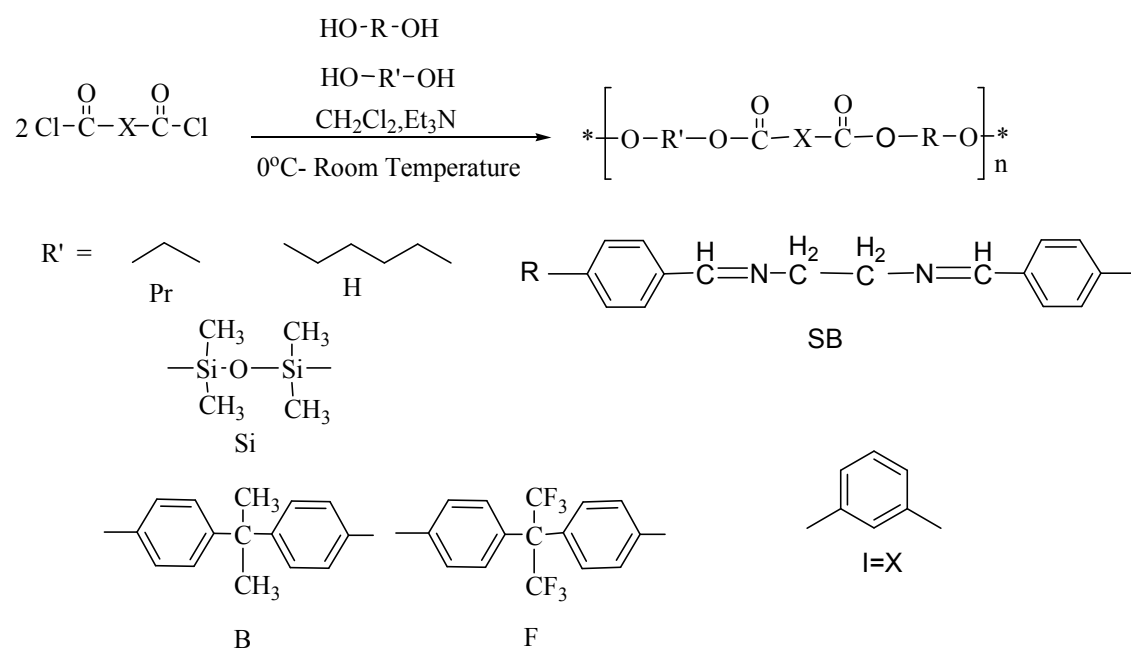
Synthesis of Terpolymers: (PIF, PIB, PISi, PIH, PIPr)

The monomer SB and the commercial diol (R= 1,3-propan-diol, 1,6-hexan-diol, poly(dimethylsiloxane), hydroxyl-terminated (M$_n$=550, (1,1,1,3,3,3-hexaflouro)bisphenol propane or bisphenol A) were taken in two-necked round-bottom flask under inert atmosphere (N$_2$), scheme 2. 50ml dried dichloromethane (CH$_2$Cl$_2$) was added to the flask followed by 5 ml triethylamine (Et$_3$N) at low temperature using ice bath with constant stirring. Then the diacid chloride, I was added to the reaction mixture under same reaction conditions. The reactant ratio was 1:1:2 for SB, the diol (R) used, and I. After 24 h the reaction mixture

was refluxed for 1 h and then poured into water for removing triethylammonium chloride salt (Et$_3$NHCl) from the organic layer. Polymers were obtained as precipitate which were then washed several times with water, ethanol and then dried in air [18, 19] scheme 2

Scheme: 1 Synthesis of the Poly(azomethine)ester (PI)

Scheme: 2 Synthesis of the Ter-poly(azomethine)ester terpolymers (PIF, PIB, PIH, PIPr, PISi).

PIF; 712, Light yellow powder, 92%, FTIR (cm^1, KBr): 3212 (arom-CH), 2989 (aliphatic CH) 1752 (-CO-), 1756 (-CO-), 1085 (-O-), 1088 (-O-), 1643 (-N=CH-), 751 (C-Cl). ^{1}HNMR [δ, deuterated dimethyl sulfoxide (DMSO-d$_6$)] δ (ppm) (protonated): 8.7 (2H, s, azomethine), 7.8-7.4 (aromatic, m), 2.6-1.7 (m, methyl, methylene, alcohol). Elemental analysis, calcd; (C 65.4, H 3.6, N 3.9), found; (C 65.7, H 3.69, N 3.91)

PIB; 608, Light yellow powder, 90%, FTIR (cm^1, KBr): 3109 (arom-CH), 2985(aliphatic-CH), 1732, 1737 (C=O), 1076, 1081(-CO-), 1609 (-N=CH-), 749 (C-Cl). ^{1}HNMR [δ, deuterated dimethyl sulfoxide (DMSO-d$_6$)] δ (ppm) (protonated): 8.6 (2H, s, azomethine), 7.4-7.1 (aromatic, m), 2.3-1.4(m, methyl, methylene, alcohol). Elemental analysis, calcd; (C 77.01, H 5.69, N 4.6); found; (C 77.0, H 5.69, 4.67).

PIH; 498, Light yellow powder, 90%, FTIR (cm^1, KBr): 3173 (arom-CH), 2967 (aliphatic-CH), 1730, 1735 (C=O), 1033, 1035 (-CO-), 1654(-N=CH-), 743 (C-Cl). ^{1}HNMR [δ, deuterated dimethyl sulfoxide (DMSO-d$_6$)] δ (ppm) (protonated): 8.23 (2H, s, azomethine), 7.5-6.8 (m, aromatic), 2.6-1.7 (m, methylene, methyl, alcohol). Elemental analysis; calcd; (C 72.30, H 6.02, N 5.62) found; (C 72.2, H 6.16, N 5.62).

PIPr; 456, Light yellow powder ,92%, FTIR (cm^1, KBr): 3193 (arom-CH), 2989, 1732, 1735 (C=O), 1042, 1047 (-CO-), 1654 (-N=CH-), 741(C-Cl). ^{1}HNMR [δ, deuterated dimethyl sulfoxide (DMSO-d$_6$)] δ (ppm) (protonated): 8.3 (2H, s, azomethine), 7.5-7.2 (aromatic, m), 2.4-2.0 (m, methyl, methylene, alcohol). Elemental analysis; calcd. (C 72.01, H 5.26, N 6.14); found; (C 72.1, H 5.34, N 6.23)

PISi; Light yellow powder, 89%, FTIR (cm^1, KBr): 3212 (arom-CH), 2989(aliphatic-CH), 1752, 1756 (C=O), 1085, 1088 (-CO-), 1643 (-N=CH-), 747 (C-Cl). ^{1}HNMR [δ, deuterated dimethyl sulfoxide (DMSO-d$_6$)] δ (ppm) (protonated): 8.2 (2H, s, azomethine), 7.2-6.6 (m, aromatic), 2.1-1.6 (m, methyl, methylene, alcohol).

Doping and Blending:

Silver was incorporated (by wt %) into the matrix of PAMEs and their terpolymers according to the reported method [16]. EDX analysis was carried out qualitatively to check the silver incorporated in the polymer matrix.

PANI was prepared as reported previously [16, 17]. PAME/PANI was taken in the weight ratio percentage 9:1. The powder was ground, blended in a crucible for homogenous mixing, dried in oven at 40°C for 6 h. The material doped with silver or blended with PANI was compressed into pallets under 5 ton load for conductivity measurements at room temperature [16, 17].

Instrumentation

Melting point was determined on a Mel-Temp. (mitamura Riken Rogyo, Inc.) using open capillary tubes. FTIR spectra in KBR pellets were recorded in Bio-Rad FTS-60A series FTIR spectrophotometer. Nuclear magnetic resonance was carried out by using Brukeravance 300 digital NMR in DMSO-d$_6$ as solvent and tetramethylsilane as an internal standard. Elemental analyses were obtained on a Vaio-EL instrument. X-ray diffraction was carried out on Philip X-Pert PRO 3040/60 diffractometer equipped with Cu Kα radiation source (λ=1.54 A) operated to characterize the solid samples. SEM-EDX studies were carried out by using model JSM 6460, EDX OXFORD model 7573. Electrical conductivity was measured by Keithley 2400 at room temperature. G03W was employed for density function theory (DFT) calculations at the 6-31G/B3LYP level to evaluate the energies of highest occupied molecular orbital (HOMO), lowest unoccupied molecular orbital (LUMO) and to locate charge distribution and generate electron density maps [15].

Conclusions

The electrical properties of a newly synthesized, conducting PAME and its terpolymers comprising various soft and hard moieties in the chain were evaluated successfully. The polymers were doped with silver and blended with PANI and it was found that lesser amount of PANI is required to increase the conductivity of the material. Contrary to some approaches which attempts to lower the band gap by increasing aromaticity of backbone, we showed that being aromatic in it does not ensure low band gap. However, the data could help to design material with small band

gaps, more electron density and holes resulting in significant technological progress in next generation organic light emitting diodes (OLEDs) and flexible photovoltaic material**.**

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Notes and references
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