Poly(3,4-ethylenedioxyselenophene) and Its Derivatives: Novel Organic Electronic Materials[†]

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CONSPECTUS: Since the discovery of high conductivity in iodine-doped polyacetylene, many interesting conducting polymers have been developed. Of these, polythiophenes have been most studied as electronic materials, with poly(3,4-ethylenedioxythiophene) (PEDOT) and the water-soluble PEDOT−PSS being the most successful commercially used conducting polymers.

The polyselenophene family together with poly(3,4-ethylenedioxyselenophene) (PEDOS) and its derivatives have been shown to have slightly different properties compared to these of polythiophene and PEDOT because of their different electron donating characters, aromaticities (selenophene vs thiophene), oxidation potentials, electronegativities, and polarizabilities (Se vs S). As a result, the polyselenophenes, especially PEDOS and its derivatives, show a lower band gap and higher-lying highest occupied molecular orbital (HOMO) levels compared with those of thiophene and the PEDOT family.

In an organic materials context, the PEDOS family offers some advantages over PEDOT derivatives. This Account draws on computational studies, synthetic methods, electrochemical polymerizations, chemical polymerizations, and the materials properties of PEDOS and its derivatives to demonstrate the importance of these novel materials, which lie at the frontier of conducting polymer research. In particular, we show that (i) PEDOS derivatives have a lower band gap (about 0.2 eV) than the corresponding PEDOT derivatives. Consequently, PEDOS derivatives can absorb the solar spectrum more efficiently compared to PEDOT derivatives and the properties of optoelectronic devices based on neutral and doped PEDOS should be somewhat different from these of PEDOT. (ii) EDOS derivatives have a greater tendency to undergo electrochemical polymerization compared to EDOT derivatives and offer stable and smooth polymer films. (iii) The PEDOS backbone is more rigid than the PEDOT backbone. (iv) PEDOS derivatives are excellent electrochromic materials with high transparency, and have higher contrast ratio and coloration efficiency. (v) The PEDOS/C electrode offers better control over the formation and size of nanoparticles through Se···Pt interactions compared with the PEDOT/C electrode.

In addition to this, we summarize the synthesis, electrochemical polymerization, materials properties, and computational studies of fused polyselenophene analogues, namely, poly(cyclopenta[c]selenophene), and a series of low band gap thieno- or selenolo-fused polyselenophenes and selenolo-fused polythiophene. Additionally, we discuss oxidative and solid state polymerization to obtain conducting PEDOS, and its derivatives, and made throughout comparison with S-analogue where applicable. We found that EDOS-based derivatives have a greater tendency toward solid state polymerization and working at a temperature about 20 °C lower than that required for EDOT-based compounds.

Our results demonstrate the utility of EDOS unit for generating promising materials PEDOS and its derivatives for electronic devices. Consequently, EDOS structure is the basis for many functionalized polymers and copolymers with tunable optoelectronic and redox properties. These interesting properties, which include high conductivity, lower band gap, rigidity, multicolor electrochromism, and rapid redox switching, allow them to be used in a variety of electronic applications.
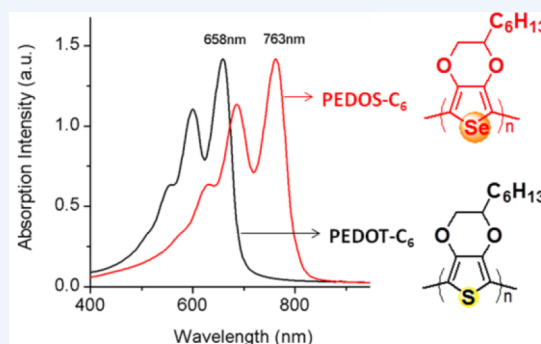
1. INTRODUCTION

Since their discovery, conjugated polymers have been successfully applied as organic electronic materials in photovoltaic cells, organic light emitting diodes (OLEDs), electrochromic devices, chemical sensors, microelectronic actuators, and organic field effect transistors (OFETs), and so forth.[1] Conjugated polymers based on polyanilines, polypyrroles, polythiophenes, polyphenylenes, poly(p-phenylenevinylene)s,

and so forth have attracted the most attention because of their academic interest and industrial applications. Thiophene-based conjugated oligomers and polymers are among the most studied organic materials, and poly(3,4-ethylenedioxythiophene)−poly(styrenesulfonate) (PEDOT−PSS)[2] is the most prominent commercially used material in the conducting and

[†]Dedicated to the memory of Prof. Michael Bendikov.

hole-transport layers for photovoltaic cells and OLEDs. The outstanding properties of thiophene-based materials[2] sparked a search for its heterocyclic analogues, such as furan-,[3] selenophene-,[4,5] and tellurophene-based[6] materials, in the hope that these would offer interesting new properties.

As members of group 16, heavier selenium is similar to lighter sulfur in many respects and many properties of polyselenophenes are similar to these of polythiophenes. The size of the selenium atom is bigger than that of sulfur, and the electronegativity of selenium is weaker than that of sulfur. Thus, selenophene-based materials have possible advantages over thiophene-based materials.[7] (i) Polyselenophene should have a lower band gap than polythiophene due to the lower aromaticity of a selenophene ring contributing larger quinoid structure compared to a thiophene.[8] (ii) Strong intermolecular Se⋯Se interactions should enforce interchain charge transfer.[9] (iii) Selenophenes and polyselenophenes should have lower oxidation and reduction potentials than their thiophene counterparts.[7] (iv) The selenium atom is more easily polarized than sulfur, and therefore, selenophene-based materials should be more easily polarized than thiophene-based materials. Despite the many advantages, the main drawback of Se-containing compounds and selenophenes are toxicity and bad smell, and low valence state selenium compounds are easily oxidized compared to their sulfur counterparts. Regardless, they are promising biomaterials and show potential application as mild-responsive drug delivery vehicles and artificial enzymes.[10]

PEDOT (P1)   PEDOS (P2)
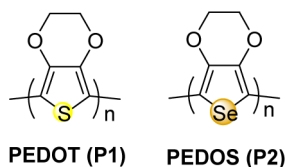
Due to the presence of a fused ethylenedioxy bridge at the 3- and 4-positions of the selenophene ring in 3,4-ethylenedioxyselenophene (EDOS; **2**), the polymer PEDOS shows a lower band gap, and the monomer EDOS and polymer PEDOS have lower oxidation potentials compared with parent selenophene and polyselenophene, respectively. The chemical, electrochemical, and optical properties of PEDOS and its derivatives depend on the degree of conjugation along the backbone and on conformational stability, which in turn may be influenced by the heteroatom properties. It is notable that, in PEDOS, the electron donating ethylenedioxy bridge directly attaches into the π-system, which raises the highest occupied molecular orbital (HOMO) of the polymers. It was also established that the electronic, optical, and solubility properties of PEDOS can be tuned by varying the size of the fused alkylene bridge and by attaching an alkyl chain to the fused bridge.

In this Account, we will focus our attention on discussing the advantages of PEDOS and its derivatives over PEDOT and the differences between them. The Account covers the synthesis, electrochemical and chemical polymerizations of EDOS and its derivatives. We also demonstrate the optical, electrochemical, and chemical properties of PEDOS and its derivatives as revealed by computational studies. Comparison is made with the PEDOT analogue throughout. In parallel, we try to estimate the scope and possible applications of PEDOS and its derivatives that will enable them to become important and useful members of the organic electronic materials family. Since the field of PEDOS is new, this Account is intended to be comprehensive. We apologize for any omissions.

2. COMPUTATIONAL STUDIES

2.1. Band Gap and Twisting Energy

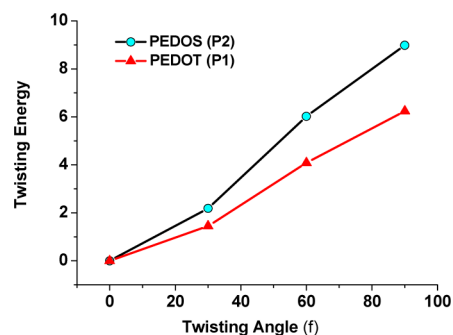The calculated band gap (at PBC/B3LYP/6-31G(d)) of polyselenophene is 1.86 eV, which is about 0.18 eV lower

Figure 1. (a) Twisting potentials (per ring) vs twisting angle calculated at the PBC/B3LYP/6-31G(d) for **P1** and **P2** (redrawn from data in ref 12).

than that of polythiophene (2.04 eV).[8] Similarly, the calculated band gaps of PEDOS and PEDOT are 1.66 and 1.83 eV, respectively. The band gap of PEDOS is about 0.17 eV lower than that of PEDOT because of the combined effect of a 0.11 eV lower-lying lowest unoccupied molecular orbital (LUMO) and a 0.07 eV higher-lying HOMO in PEDOS compared to PEDOT.

The twisting of oligo- and polyselenophenes requires more energy than the twisting of oligo- and polythiophenes because of the shorter inter-ring C−C bond in selenophene derivatives and the larger contribution of the quinoid structure in oligo- and polyselenophenes.[11] PEDOS and PEDOT show a similar trend of increasing twisting energy with increasing twisting angle, although PEDOS requires a greater twisting energy than PEDOT (Figure 1).[12] For example, PEDOS requires 0.6 and 9.0 kcal mol^{-1} energy for 15° and 90° twists, respectively, while PEDOT requires 0.4 and 6.2 kcal mol^{-1} for such twists, respectively. The higher twisting energy of PEDOS is due to lower aromaticity of selenophene ring, which leads to larger contribution of quinoid structure and consequently to higher degree of planarity. Therefore, PEDOS might be an excellent choice for controlling planarity in conjugated polymers and more substituents can be introduced onto PEDOS backbones than onto those of their PEDOT derivatives without reducing the extent of conjugation.

A computational study indicated that polyselenophenes can accept a greater degree of doping than polythiophenes.[11] Furthermore, conjugation in polyselenophenes is expected to be stronger than that in polythiophenes because of the larger contribution of the quinoid structure and strong intermolecular Se⋯Se interactions in bulk polyselenophenes. As a result, the conductivity of PEDOS derivatives is expected to be of the same order of magnitude or even higher than that of PEDOT derivatives.

3. SYNTHESIS OF EDOS AND ITS DERIVATIVES

3.1. EDOS

Unlike PEDOT, the PEDOS family remained practically unexplored due to unavailability of synthetic methodologies for the preparation of EDOS monomer. The most common and industrially applied route for preparation of EDOT is the

Scheme 1. Synthesis of EDOS[13]
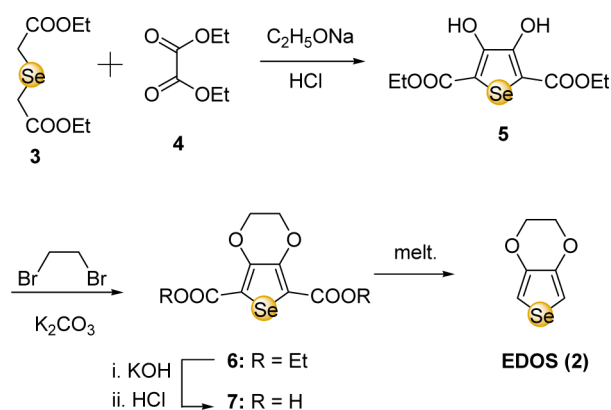
Scheme 2. Synthesis of EDOS[14]
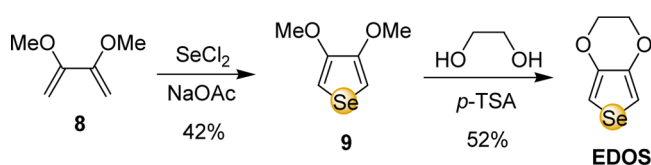
Scheme 3. Synthesis of EDOS[15]
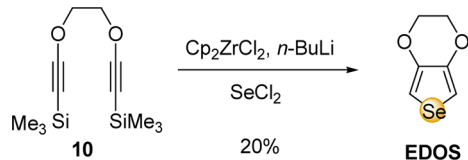
five-step synthetic methodology.[2a] Aqad et al. reported synthesis of EDOS using a similar synthetic strategy as shown in Scheme 1.[13] The condensation of **3** with **4** followed by acidification gave **5**. Compound **7** was achieved by etherification of **5** with 1,2-dibromoethane to yield **6**, and then hydrolysis and subsequent acidification. Decarboxylation of **7** by melting provides EDOS as a colorless liquid.[13]

The multistep synthetic route for EDOS suffers from several drawbacks such as high temperature, pressure, and potential run-away reaction conditions. Our group developed a new and efficient synthetic route for the preparation of EDOS (Scheme 2) in two steps from commercially available 2,3-dimethoxy-1,3-butadiene (**8**).[14] 3,4-Dimethoxyslelenophene (**9**) was obtained by the cycloaddition of **8** with SeCl$_2$. Compound **9** is a crucial

precursor to development of EDOS and its derivatives (see Scheme 4). Finally, transetherification of **9** with ethylene glycol in the presence of p-toluenesulfonic acid (p-TSA) produced EDOS as a colorless oil. The resulting EDOS exhibits adequate stability under ambient conditions and is stable for a few years under refrigeration at 4 °C.[14]

Das et al. reported the synthesis of EDOS from compound **10** by a zirconocene-dichloride-mediated cyclization reaction of **10** followed by treatment with SeCl$_2$ (Scheme 3).[15]

3.2. Alkyl Substituted 3,4-Ethylenedioxyselenophenes (EDOS-C$_n$) Derivatives

We reported, a series of alkyl substituted EDOS-C$_n$ (**11a–e**)[16,17] compounds synthesized by transetherification of **9** with 1,2-alkyldiol (Scheme 4). It is noteworthy that the yield of EDOS-C$_n$ increases significantly as the length of the 1,2-alkyldiol chain increases, from about 52% for EDOS to 95% for EDOS-C$_{12}$.

3.3. Heteroatom Analogues of EDOS

We reported, a series of new heteroatom derivatives **12–14** of EDOS, in which one or both oxygen atoms in the ethylenedioxy bridge (peripheral ring) were replaced with sulfur.[12,18] Compounds **12–14** were prepared by trans-etherification of **9** (Scheme 4).

3.4. 3,4-Phenylenedioxyselenophene (PheDOS) Derivatives

These are a series of new flat polyselenophenes **P15–17**[19] that, in the 3,4-positions of the selenophene ring, have oxygen or sulfur substituents bridged by a phenylene moiety. The monomers **15–17** were prepared by transetherification of **9** with catechol, 2-hydroxythiophenol, and 1,2-benzenedithiol, respectively (Scheme 4).

3.5. 3,4-Propylenedioxyselenophene (ProDOS-C$_n$) Derivatives

Kim et al.[20] synthesized 3,4-propylenedioxyselenophene (ProDOS; **18a**) by transetherification of **9** with propane-1,3-diol. Recently, Cihaner and co-workers[21,22] used 2,2-dialkyl-propane-1,3-diol to synthesize three monomers ProDOS-C$_n$ (**18b–d**) based on ProDOS. These monomers have a long alkyl chain-substituted propylenedioxy bridge instead of the ethylenedioxy bridge (Scheme 4).

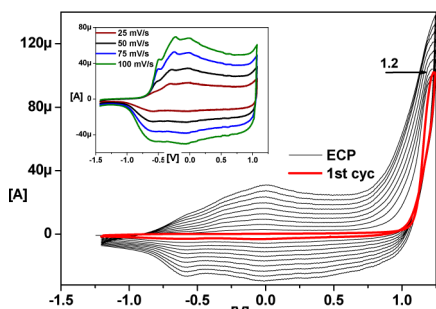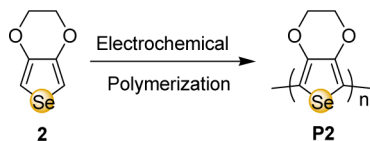**Scheme 4. General Synthetic Strategy for the Synthesis of EDOS Derivatives**
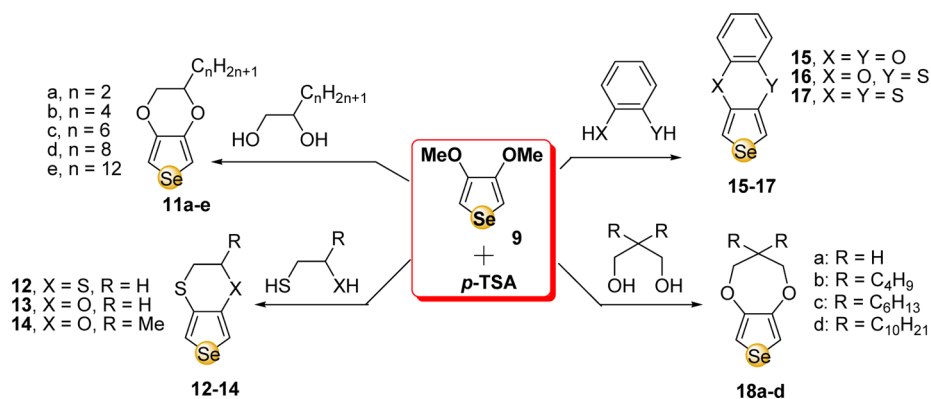
Scheme 5. Electrochemical Polymerization of 2

Figure 2. Electrochemical polymerization of EDOS; (inset) CV of PEDOS. Reproduced with permission from ref 14. Copyright 2008 American Chemical Society.
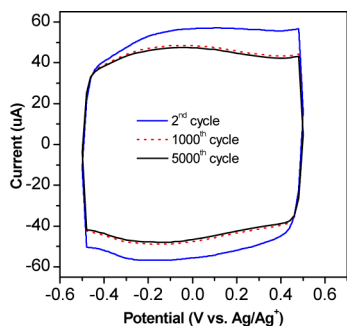

Figure 3. CV of PEDOS film after 2nd, 1000th and 5000th cycle. Reproduced with permission from ref 14. Copyright 2008 American Chemical Society.
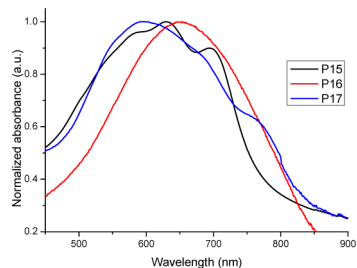

Figure 4. Normalized absorption spectra of polyselenophene films **P15−17** (redrawn from data in ref 19).

Figure 6. Twisting potentials (per ring) versus twisting angle (redrawn from data in ref 12).

Figure 7. Spectroelectrochemical for a PEDOS-C_6 film; (inset) photos of a PEDOS-C_6 film on ITO-coated glass in the doped state and neutral state. Reproduced with permission from ref 17. Copyright 2009 John Wiley and Sons.

Figure 8. Absorption spectra of PProDOS-C_{10} (**P18d**) at various applied potentials. Inset: colors of PProDOT-C_{10} in (a) the neutral state, (b) an oxidized state, and (c) dissolved in dichloromethane. Reproduced with permission from ref 21. Copyright 2011 Royal Society of Chemistry.
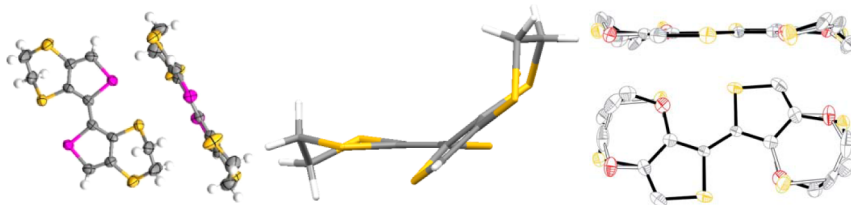

Figure 5. Crystal structure of (left) **25** showing its unique planarity (Reproduced with permission from ref 18. Copyright 2009 John Wiley and Sons); (middle) **26** showing it to be twisted by 45° (Reproduced with permission from ref 26. Copyright 2005 American Chemical Society); (right) **27a−b** showing planarity around the interring bond (Reproduced with permission from ref 12. Copyright 2011 Royal Society of Chemistry).
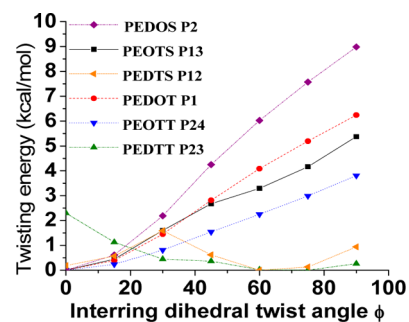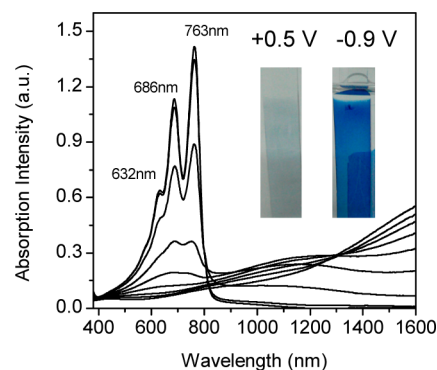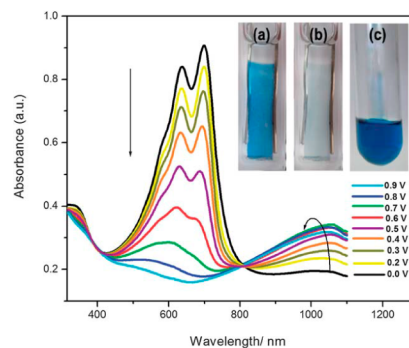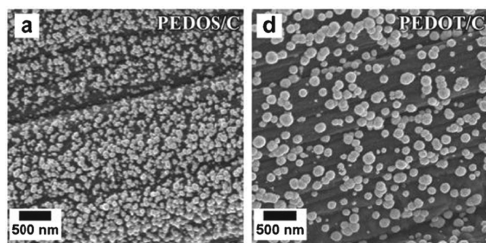
Figure 9. SEM image of Pt nanoparticles on (left) PEDOS/C and (right) PEDOT/C surfaces. Reproduced with permission from ref 29. Copyright 2012 Royal Society of Chemistry.

4. ELECTROCHEMICAL AND OPTICAL BEHAVIOR OF PEDOS DERIVATIVES AND THEIR PROPERTIES

4.1. EDOS

The EDOS monomer shows two irreversible oxidation peaks at 1.22 and 1.75 V (vs Fc/Fc$^+$ = 0.34 V) in cyclic voltammetry (CV).[14] In comparison, the first oxidation potential for EDOT is 1.44 V, which is higher than that of EDOS under the same experimental conditions. EDOS monomer undergoes smooth electrochemical polymerization to produce an insoluble PEDOS film (Scheme 5; Figure 2).[14] Due to its lower oxidation potential, the EDOS has a greater tendency to undergo electrochemical polymerization compared to EDOT.

The PEDOS film is very stable during spectroelectrochemical measurements.[14] Polaron and bipolaron peaks were observed at around 1050 and 1600 nm respectively, where as a similar polaron peak for PEDOT at around 900 nm. The color of the PEDOS film ranges from pure deep-blue in the neutral state to transmissive gray in the doped state. The optical band gap of PEDOS is 1.4 eV (onset 876 nm) and λ_{max} is 673 nm, which is 0.2 eV lower than that of PEDOT.[2,14] The stability of the PEDOS film was established by running it through CV cycles (Figure 3).[14] The total charge decrease between the initial and 5000th cycle was less than 17%, while only a 1% decrease in total charge between the 1000th and 5000th cycles. The high stability of the PEDOS films is comparable to that of PEDOT films.

4.2. Flat Conjugated PEDOS Derivatives

A low HOMO energy level is important for polymer stability, while a low band gap is necessary in more efficient solar spectrum absorption capabilities.[23] The introduction of substituents onto the conjugated polymer backbone is necessary to improve solubility and other desired properties. However, such substitution often causes the polymer to twist significantly, which impairs conjugation and consequently increases the band gap. The incorporation of a flat phenylene ring into the monomer unit may provide a potential solution to this problem. Such incorporation eliminates the problems of out-of-plane substituents and stereoisomers and potentially enables better ordering and packing. Flat conjugated polythiophenes such as poly(3,4-phenylenedioxythiophene) (PPhe-DOT; P20) and its alkyl derivative 19, a phenylene-extended analogue of PEDOT, have been reported previously to overcome these problems.[24,25]

In this context, flat polymers P15−17 were designed that combine the advantages of polyselenophenes with phenylene-bridged substitution of the peripheral ring to form planar polymers with a low band gap and lower HOMO level compared with PEDOS.[19]
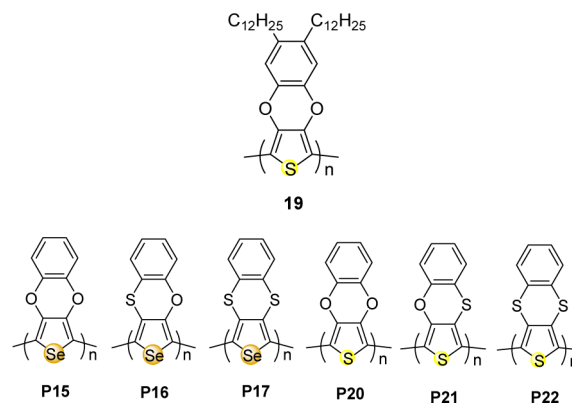
Interestingly, due to the lower oxidation potentials of monomers 15−17 phenylene-bridged 3,4-selenophenes undergo polymerization relatively smoothly compared with their thiophene analogues[12,19] The oxidation onset potentials of phenylene-bridged polyselenophenes P15−17 are significantly positively shifted compared with those of ethylene-bridged PEDOS, which indicates that they have lower HOMO energy levels. However, their HOMO energy level is slightly higher than that of their polythiophene analogues P20−22.

The optical band gaps (1.49−1.57 eV) of electrochemically synthesized phenylene-bridged polyselenophenes P15−17 vary only slightly as a function of the heteroatom substituent at the 3,4-position (Figure 4) and are somewhat higher than that of PEDOS (1.4 eV).[19] However, the band gaps of phenylene-bridged polyselenophenes P15−17 are lower than those of their polythiophene analogues P20−22. Thus, while the HOMOs of polymers P15−17 vary in the range of 0.34 eV, variations in their band gaps are much smaller at about 0.08 eV. A comparison shows that polyselenophenes P15−17 benefit from a lower band gap, and greater rigidity and that they create better quality polymer films under electrochemical polymerization compared to polythiophenes P20−22.

The calculated band gaps of flat phenylene-bridge polyselenophenes P15−17 are consistently about 0.2−0.4 eV higher than the experimentally obtained band gaps. All the minimal energy structures of the polymers P15−17 and their polythiophene analogues P20−22 have planar conformations, in contrast to the analogous ethylene-bridge structures, some of which have nonplanar minimal energy structures (see detailed discussion in next section). Interestingly, the twisting potentials of these polymers P15−17 and P20−22 show significant differences, with twisting of selenophene-based polymers always requiring more energy compared to thiophene-based polymers.[19]

4.3. Planarity and Rigidity of EDOS Derivatives

PEDOT is believed to be planar; however, its sulfur analogue in which the two oxygen atoms in the ethylene bridge are replaced by sulfur atoms, poly(3,4-ethylenedithiothiophene) (PEDTT; P23), is assumed to be twisted. This observation is reflected in the significantly higher band gap of PEDTT (2.2 eV experimentally and 2.06 computationally) compared with PEDOT (1.6 eV experimentally and 1.84 eV computationally). In contrast to PEDTT, PEDTS (P12) has a significantly (0.6−0.8 eV) lower experimentally obtained optical band gap than PEDTT, and one that is comparable to the optical band gap of PEDOS, which can be attributed to its planarity.[18]

Interestingly, this observation is supported by crystal structures of their dimers 25−27. The crystal structure of bis-

**PEDTS (P12)**   **PEOTS (P13)**   **PEDTT (P23)**   **PEOTT (P24)**
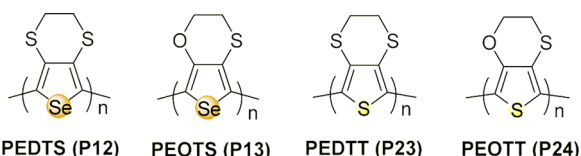
3,4-ethylenedithioselenophene (bis-EDTS; **25**) (Figure 5) reveals that it has a planar structure around the inter-ring C—C bond. This is in agreement with DFT calculations but in complete contrast to the crystal structure of bis-EDTT (**26**), which has an inter-ring twist angle of 45° (Figure 5).[26] By contrast, the crystal structures of **27a**−**b** (a mixture of isomers) are planar, apparently because the amount of isomer **27b** is small and the overall crystal packing forces are stronger than the twisting potential of the mixture of dimers.[12]

bis-EDTS (25)   **bis-EDTT (26)**   **27a**   **27b**
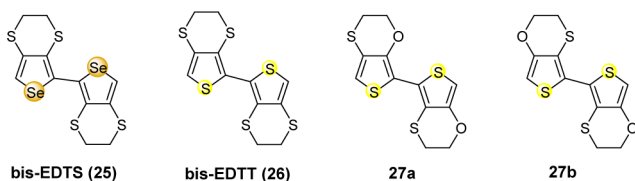
The difference in planarity found among these dimers **25**−**27** is strongly related to the band gap of the corresponding polymers. The spectrochemically measured band gap values show that PEDOS, PEOTS (**P13**), and PEDTS have lower band gaps than the corresponding PEDOT, PEOTT (**P24**), and PEDTT respectively.[12] According to DFT calculations performed on the thiophene-based polymer PEDTT, the minimal energy structure is not planar, while in the case of the selenophene-based polymer PEDTS, there are two minima, one planar and one twisted (Figure 6). Thus, polymer PEDTS comprises both planar and twisted fragments, while PEDTS is more planar than PEDTT but less rigid than PEDOS.[12]

4.4. Electrochromic Properties of PEDOS Derivatives

Polythiophenes, especially PEDOT, and their derivatives are the most promising conjugated polymers for electrochromic (EC) devices because of their unique optical and electronic properties. Recently, we found that PEDOS derivatives have excellent electrochromic properties.[16,17] The absence of an absorption band between 400 and 500 nm in PEDOS results in a pure blue color, which makes it a promising candidate for electrochromic devices.[16,17] Thus, PEDOS exhibits a high contrast ratio of 55% at 666 nm (λ_{max}) and a coloration efficiency of 212 cm^2 C^{-1} compared to PEDOT which has a contrast ratio of 54% and a CE of 137 cm^2 C^{-1} at full switching.[17]

a, n = 2
b, n = 4
c, n = 6
d, n = 8
e, n = 12
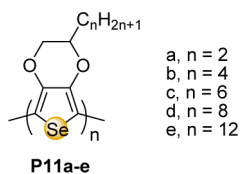
P11a–e

In an effort to improve the electrochromic properties of PEDOS derivatives, PEDOS-C_n (**P11a**−**e**) were synthesized in which alkyl chains were introduced onto the ethylenedioxy bridge. PEDOS-C_n films show significantly better electrochromic properties compared with unsubstituted PEDOS. Thus, PEDOS-C_n films show both a high contrast ratio and high coloration efficiency with a low switching voltage, fast switching time, and remarkable stability. The red-shift of the

λ_{max} of PEDOS-C_n films compared to PEDOT and its derivatives leads to the near-absence of absorption (complete transmittance) between 400−500 nm and, as a result, the PEDOS derivatives have a pure blue color. The contrast ratio of PEDOS-C_6 (**P11c**) films achieves a maximum of 88−89% at 763 nm and a coloration efficiency of 686−773 cm^2 C^{-1} compared to PEDOT-C_6 film has a contrast ratio of 83% and a CE of 491 cm^2 C^{-1}. Thus, PEDOS-C_6 films exhibit the unusual combination of both the contrast ratio and the CE are among the highest reported with fast switching time and excellent long-term stability making it a unique EC material.

4.5. Soluble Electrochromic Polyselenophenes

PEDOS and its derivatives, including alkyl-substituted polymer films prepared by electrochemical polymerization, are insoluble, which might hinder their use in optoelectronic devices. It has been reported that the presence of alkyl chains attached to poly(3,4-propylenedioxythiophene) (PProDOT; **P28a**) units (where the ethylenedioxy bridge in the EDOT unit is replaced with a long alkyl-substituted propylenedioxy bridge) would also increase the solubility and the processability of the corresponding polymers.[27] Recently, soluble electrochromic polymers based on poly(3,4-propylenedioxyselenophene) (PProDOS, **P18a**) was reported.[21,22]

Electrochemical polymerization of the monomers **18b**−**d** was unsuccessful in dichloromethane because the resulting polymers were highly soluble.[21,22] Electropolymerization in a mixture of solvents (dichloromethane and acetonitrile) produced insoluble polymers films **P18b**−**d** and the oxidation potentials of those polymers are lower than that of the corresponding polythiophene-based polymers **P28b**−**d**, which reflects the higher HOMO level of PProDOS-C_n.[21,22]

a: R = H
b: R = C_4H_9
c: R = C_6H_{13}
d: R = $C_{10}H_{21}$

P18a-d   **P28a-d**
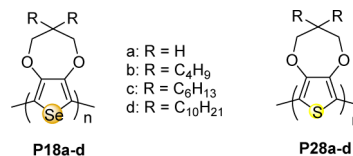
The optical band gaps of these polymers PProDOS-C_n (**P18a**−**d**) vary from 1.55−1.65 eV, which is lower than that of polythiophene analogues PProDOT-C_n (**P28a**−**d**).[20,21] In comparison, the band gaps of polymers **P18a**−**d** are higher than those of PEDOS and comparable with those of the alkyl derivatives of PEDOS-C_n. PProDOS-C_n polymers show excellent electrochromic behavior and a color change from pure blue to a highly transparent state during oxidation (Figure 8) with high coloration efficiencies (328−864 cm^2 C^{-1}) when compared with their thiophene analogues **P28b**−**d**.[22]

The polyselenophene films **P18b**−**d** are quite stable and robust, retaining 82−97% of their electroactivity even after 5000 cycles.[22] The PProDOSC$_{10}$ film[21] shows the highest stability and retained 97% of its electroactivity, even after 40 000 cycles and somewhat more stable than PEDOS.[14]

4.6. Controlling Nanoparticle Formation Through Se···Pt Interactions

Controlling the formation of nanoparticles and their size of conducting polymers is crucial for their application, and especially for their use in catalysis. PEDOT has been used for this purpose[28] and has been shown to be an excellent material for direct methanol fuel cell applications.

Interestingly, the nanoparticles formed on a PEDOS/C electrode are smaller-sized than these deposited on a PEDOT/
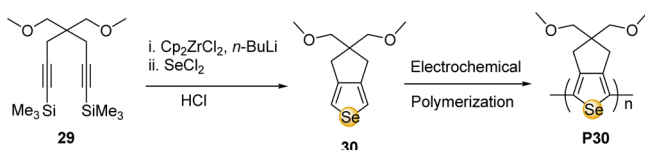
C electrode (Figure 9).[29] A uniform distribution of Pt nanoparticles having an average diameter of 79 ± 15 nm was observed on the PEDOS/C electrode surface, whereas the nanoparticles formed on the PEDOT/C electrode were larger in size (average diameter of 110 ± 33 nm).[29] This is due to the Pt···Se interactions between the Pt atom and the PEDOS/C surface being stronger than the Pt···S interactions between the Pt atom and the PEDOT/C surface. The average roughness of a PEDOS/C electrode is slightly larger than of a PEDOT/C electrode, which may offer more nucleation centers, which might lead to a greater degree of dispersion of Pt nanoparticles on the PEDOS/C electrode. Indeed, DFT calculations (at the M06L/SDB-cc-pVDZ//M06L/SDD level of theory) showed that Pt···Se interactions are 4−6 kcal mol^{-1} stronger than Pt···S interactions for the optimized geometry.[29] The Pt−PEDOS/C electrode is much better for electrocatalytic methanol oxidation by Pt nanoparticles than a polymer support-free bare Pt/C electrode and at least as good as using the Pt−PEDOT/C electrode.[29] Formation of Pt nanoparticles of smaller size and the greater surface coverage of the PEDOS/C electrode can have important implications for catalysis.

Photothermal effect of doped and dedoped PProDOS polymeric films were reported and found better performance compared to PEDOT mainly because of the larger NIR absorbance of PProDOS.[20] Electrocatalytic activity of electrochemical polymerized PEDOS film has been found and comparable to PEDOT.[30]

5. FUSED POLYSELENOPHENES

Zade et al. reported an efficient synthetic route for cyclopenta-[c]selenophene-(CH$_2$OMe)$_2$ (30) from 29 (Scheme 6).[31] The

Scheme 6. Synthesis and Electropolymerization of 30[31]

monomer 30 presents irreversible oxidation peaks at 1.56 and 1.79 V (Fc/Fc$^+$ = 0.34 V), which are much higher than the

oxidation peak of EDOS (1.2 V), but lower than that of the corresponding thiophene analogue cyclopenta[c]thiophene (1.80 V). During electrochemical polymerization, monomer 30 is transformed into an insoluble deep blue polymer film P30. The optical band gap of polymer P30 is about 1.65 eV, which is 0.25 eV higher compared to PEDOS.[31]

Thiophene-based fused polymers and their derivatives P31−33 have attracted significant attention as low band gap polymers.[32,33] Recently, soluble derivatives of thieno[3,4-b]thiophene building blocks (such as 34a,b and 35a,b) were used as attractive units in polymers for solar cell applications. In particular, the copolymer having 34 or 35 chromophore offer much better performance in solar cell applications and achieve a maximum 9.2% power conversion efficiency (PCE) in an inverted device structure.[34]
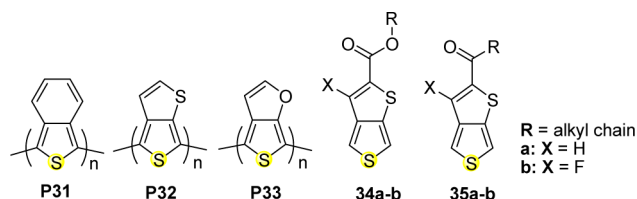
Recently, selenophene-based polymers P37−39, especially P38, have attracted significant attention for use in organic solar cells due to their high PCE.[35] Interestingly, selenophene-based polymers show significantly higher PCE values than their sulfur analogues. Indeed, P38 achieved a PCE of 6.87% when blended with PC$_{71}$BM, which is an almost 21% increase in PCE compared to the corresponding thiophene analogue (5.66% for P36).[35]
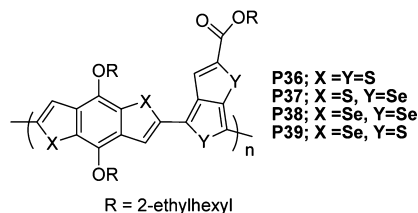
Our group reported a new low band gap selenolo-fused polythiophene P40 prepared by electropolymerization from 40 (Scheme 7).[36] Other thieno- and selenolo-fused polyselenophenes P41 and P42 were obtained by both electropolymerization and solid state polymerization from 41 and 42 respectively.[36] The monomers 40−42 were prepared by the lithiation of 43 or 44 followed by the addition of sulfur or selenium (Scheme 7).[36]

Scheme 7. Synthesis and Electrochemical Polymerization of Monomers 40−42[36]
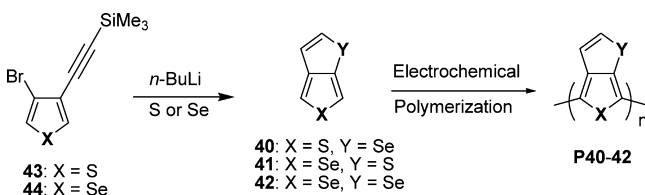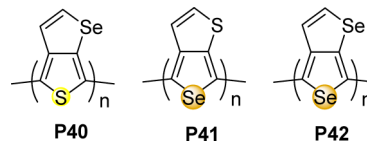

Table 1. Calculated HOMO and LUMO Energies (at PBC/B3LYP/6-31G(d)), and Experimental Optical Band Gaps for P32 and P40−42

polymers	HOMO (eV)	LUMO (eV)	band gap (eV) calcd	band gap (eV) expt
P32	−4.02	−3.06	0.96	0.85
P40	−4.07	−3.00	1.07	0.96
P41	−3.92	−3.23	0.69	0.72
P42	−4.00	−3.17	0.83	0.76

All the monomers 40−42 show an irreversible anodic peak corresponding to their oxidation. The CVs of polymer films P40−42 were revealed that films prepared from thiophene-based monomer 40 are more stable compared with the polymers films prepared from selenophene-based monomers 41−42. This may be due to the very low band gap of selenophene-based polymers P41 and P42 compared to thiophene-based polymer P40, as found in spectroelectrochemical studies (Table 1).[36]
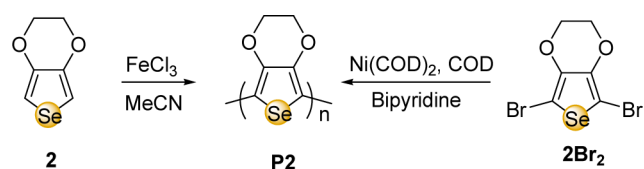
The optical band gap of **P40**, which has a polythiophene backbone and a selenium atom in the peripheral ring, is 0.96 eV (~1290 nm). For comparison, the optical band gap of **P32**, in which the heteroatom in the peripheral ring is sulfur, is 0.85 eV.[33] Polyselenophene based polymers **P41−42** exhibit very low band gaps of 0.72 and 0.76 eV, respectively compared to **P32** and **P40**. This is due to the lower aromaticity of a selenophene ring compared to a thiophene ring in polymer chain, which stabilized the quinoid structure. The calculated band gaps of these polymers nicely fit with the experimental band gaps (Table 1).

## 6. CHEMICAL POLYMERIZATION TO OBTAIN PEDOS AND ITS DERIVATIVES

6.1. Oxidative Polymerization

Chemical polymerization of EDOS using 4 equiv of $FeCl_3$ led to formation of a completely insoluble black polymer (Scheme

Scheme 8. Synthesis of PEDOS by Chemical Polymerizations[14]

Scheme 9. Solid State Synthesis of PEDOS[14] and PEDTS[12]

2Br₂: X = O, Y= Br
2I₂: X = O, Y= I
12Br₂: X = S, Y= Br
12I₂: X = S, Y= I

PEDOS (P2), X= O
PEDTS (P12), X=S
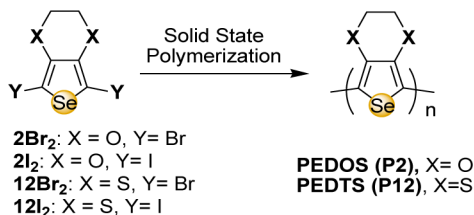
8).[14] Unlike chemically synthesized PEDOT, PEDOS prepared by oxidative polymerization shows a low conductivity of about 0.002 S cm⁻¹.[14] Thus, oxidation of EDOS with $FeCl_3$ is not an effective method for the preparation of conductive defect-free PEDOS chain due to chemical modification of some of the selenophene rings caused by oxidation. PEDOS was also prepared by transition metal-mediated polymerization of 2,5-dibromo-3,4-ethylenedioxyselenophene (DBEDOS; **2Br₂**), leading to the formation of a completely insoluble black polymer (Scheme 8) with a low conductivity similar to that of chemically synthesized PEDOS using $FeCl_3$.[14]

6.2. Solid State Polymerization (SSP)

To obtain a well-defined polymer structure, the polymerization should be carried out under pure chemical polymerization conditions, without using any catalysts. SSP of structurally preorganized monomers has the potential to provide such a method and, indeed, was developed for synthesis of highly conducting PEDOT.[37] Recently, conducting PEDOS and its derivatives[12,14] were prepared by SSP. DBEDOS easily polymerized within 5−6 h under slight heating or within several days at room temperature (Scheme 9).[14] It is found that the SSP of DBEDOS required at a temperature about 20 °C lower compared to DBEDOT (**1Br₂**) (Table 2).[14] During SSP, the structure of DBEDOS crystal was destroyed due to evaporation of bromine, and the resulting bromine doped

PEDOS is completely insoluble in organic solvents and has a strong ESR signal. As obtained, bromine doped PEDOS has a high conductivity of about 3−7 S cm⁻¹ and comparable to the conductivity value of similarly prepared PEDOT.[14] Similarly, PEDOS prepared from DIEDOS (**2I₂**, Scheme 9; Table 2) shows an even higher conductivity compared with bromine doped PEDOS.[14] It is found that neutral PEDOS is more easily doped by oxygen when exposed to air compared to PEDOT.[14] DBEDTS (**12Br₂**) and DIEDTS (**12I₂**) were easily polymerized by SSP upon heating, and the resulting doped PEDTS shows a conductivity of about 3 S cm⁻¹ (Scheme 9, Table 2).[12]

Low band gap fused polyselenophenes **P41−42** were also obtained by SSP under slight heating of the monomers (**41−42)Br₂** respectively (Table 2).[36] The doped polymers **P41−42** have relatively low conductivities of ca. 0.01 and 0.22 S cm⁻¹, respectively, in contrast to polythiophene **P32** (6.0 S cm⁻¹) prepared by SSP from **32Br₂** (Table 2), which has a relatively high conductivity.[36] The SSP results clearly indicate that DBEDOS and its derivatives have a greater tendency toward solid state polymerization than DBEDOT derivatives.[14,36]

7. CONCLUSION

In this Account, we compared the synthesis, polymerization and optoelectronic properties PEDOS and its derivatives with PEDOT. PEDOS derivatives have significant advantages like low band gap, rigidity, lower aromaticity, more quinoid structure, and strong intermolecular Se···Se interactions over PEDOT derivatives. Indeed stable, highly conducting, and well-behaved PEDOS have been obtained that possess superior bulk conductivity, transparency, and electrochromic properties compared to PEDOT. Recently, significant progress has been achieved in the fields of polyselenophenes for photovoltaics and OFETs applications. Lower band gap and strong intermolecular Se···Se interactions of EDOS-based polymer were benefits for further improvement for PCE and mobility. Despite the many advantages, the major drawbacks of PEDOS and Se-containing compounds are bad smell and toxicity, and low valence state selenium compounds are easily oxidized compared to sulfur analogues.

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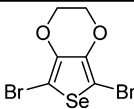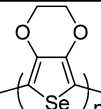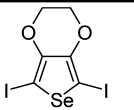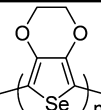
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Notes
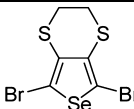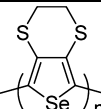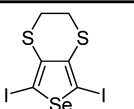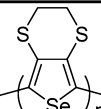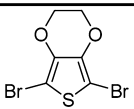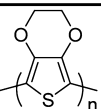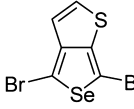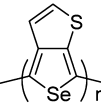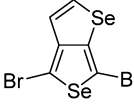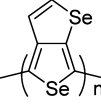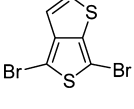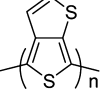
Biographies

Asit Patra received his B.Sc. and M.Sc. degree from Vidyasagar University and then he joined the group of Prof. Dipakranjan Mal at the Indian Institute of Technology, Kharagpur, to undertake a Ph.D. degree. In 2006, he joined Prof. Michael Bendikov's group for postdoctoral research at the Weizmann Institute of Science, Israel. Then he moved to UCSB working with Prof. G. C. Bazan. After a Marie Curie fellowship at the University of Cambridge, U.K. with Prof. J. R. Nitschke, he joined as a senior scientist the CSIR-National Physical Laboratory, New Delhi in October, 2012. His current research interests are π-conjugated systems for application in organic electronics namely photovoltaic.

Michael Bendikov received a B.A., M.Sc., and Ph.D. in Chemistry from the Technion - Israel Institute of Technology under the direction of Prof. Y. Apeloig. In 2001, he joined the group of Prof. F. Wudl at UCLA as a postdoctoral researcher. Since June 2004, he had been a

Table 2. Conditions for SSP and Conductivities of the As Prepared Polymers

Entry	Monomers	Polymers	SSP	Scm^{-1}
1	2Br$_2$	P2	55°C for 5-6h	3-7
2	2I$_2$	P2	80°C for 3 days	30
3	12Br$_2$	P12	50°C for 24h	3
4	12I$_2$	P12	110°C for 3 days	3-4
5	1Br$_2$	P1	60°C for 24h	18
6	41Br$_2$	P41	45°C for 4-5h	0.01
7	42Br$_2$	P42	45°C for 6-8h	0.22
8	32Br$_2$	P32	50°C for 2 days	6

faculty member of the Department of Organic Chemistry at the Weizmann Institute of Science, Israel. He is a recipient of the 2007 DuPont Young Professor Award, the 2009 Israel Chemical Society Outstanding Young Scientist Prize, and the 2010 Journal of Physical Organic Chemistry Award for Early Excellence in the field of Physical Organic Chemistry. He untimely passed away on 2nd July, 2013.

Suresh Chand received M.Sc. and Ph.D. in physics from the Delhi University. In 1981, he joined as a postdoctoral fellow and since 1982 has been a scientist at CSIR-National Physical Laboratory, New Delhi. Currently, he is a chief scientist and head of Physics of Energy Harvesting Division. He is a recipient of CSIR-NPL outstanding scientist award for his contributions made in the area of organic electronics and development of polymer based solar cells.

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