Charge transport and transfer phenomena involving conjugated acenes and heteroacenes

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Abstract. Conjugated acenes are very promising for their applicability in different optoelectronic devices. In particular, pentacene (PCn) shows some distinct behaviours, namely high optical absorption and remarkably high carrier mobility which makes it as a landmark semiconductor for use in field-effect transistors or hole transporting materials in organic photovoltaics. During the last few decades, a large number of theoretical and experimental researches has been performed showing the practical applicability of different acenes and heteroatom-doped acenes (heteroacenes). Few reviews are also made in this regard. However, correlating the molecular properties arising from their intrinsic electronic structures with their charge transfer (CT) and transport characteristics is really scattered. Furthermore, very recent understandings on the nanojunctions made of acenes along with suitable electrodes need to be reviewed for further development of their performances in electronic devices. At the same time, the photovoltaic applicability of acenes and heteroacenes has recently been shown as an interplay of the dynamics of CT states as well as the intrinsic charge separation within the molecules or composites. The present review aims to point out those recent observations so as to draw more attention for further development in the area of acene- and heteroacene-based optoelectronic devices. We concentrate more on the structure–property relationships which could guide the device performance. As the subject area is so vast, we put emphasis on the very recent studies on PCn and some lower S,N-heteroacenes.

Keywords. Acenes and heteroacenes; optoelectronics; transport properties; photovoltaic activities.

1. Introduction

Over the last few decades, π -conjugated small organic molecules have drawn tremendous attention for their use in different optoelectronic devices such as logic gates, field-effect transistors (FETs), memory storage devices, organic photovoltaic cells (PVCs), etc. [1–7]. The solution processability and tunable electronic structures of these conjugated organic molecules make them attractive for such applications [4–7]. The tunable electronic structures of those molecules could easily be realized by functionalizing their aromatic rings by different electron donating or withdrawing groups. Thus, with the help of sophisticated organic synthetic protocols, those molecules are implemented in molecular or organic electronics as per the requirement. Acenes are such a class of π -conjugated molecules which can be considered as one-dimensional (1D) strips of graphene and they have been identified as potential materials to be used in the next generation of electronic devices [8,9]. One of the most attractive features of acenes is their exceptionally narrow band-gap, which leads to a higher conductivity than that of other similar organic molecules. Pentacene (PCn) is the most popular example amongst the acene family which is supposed to be a benchmark semiconductor in organic electronics [10,11].

This is mainly due to its high field-effect mobility and at the same time, it has also some unique features like high carrier mobility, high amenability to thin film formation, etc. [12–17]. Single molecular contacts using PCn or heteroatom-doped PCn are an interesting issue in this regard and hence, PCn-based molecular junctions using various metallic contacts have been widespread studied theoretically as well as experimentally [11,13,18–21].

PCn–Au nanojunctions are studied for various electronics measurements [21–24]. However, during the last couple of years, carbon-based materials, such as carbon nanotubes (CNTs), graphene, etc. are also employed for such junction studies. Even, these materials are sometimes proved to be better than metal contacts because they are directly synthesized at the contact region by using a chemical vapour deposition method and can be patterned by lithographic technique [25–28]. Furthermore, recent advancements in material growth and designing techniques have made two-dimensional (2D) graphene and its lower-dimensional analogue, graphene nanoribbon (GNR) possible to be synthesized in different orientations. Few-layered graphene surfaces have also been used as electrodes for measuring electron transport through molecular films or single molecular nanojunctions [29,30]. The high conductivity and transparency of graphene

electrodes have been utilized in organic FETs or organic PVCs [31–33].

Compared to 2D graphene, which is a zero-gap semiconductor, 1D nanoribbons (GNRs) are distinct by their electronic and optical properties. The electronic properties of GNRs are sensitive to many factors, edge modification being one of the main controls over them [25,34–37]. It has been shown that the zigzag-edged GNRs (zGNRs) are mainly low band-gap semiconductors in their ground state antiferromagnetic spin configurations [36]. However, they become half-metallic under the application of an external electric field [38,39]. The origin of magnetism in zGNRs stems from the localized edge states where the magnetic centres are ferromagnetically coupled. However, the two magnetic edge states couple antiferromagnetically resulting in poor magnetic moment in the ground state [40,41]. There have been numerous experimental and theoretical research studies on the charge and spin transport properties of zGNR heterojunctions [42–48] which show negative differential resistance (NDR), spin filtering effect, etc. These exciting properties make those materials highly promising to be used in different magnetoelectronic and spintronic devices [11,49]. On the other hand, armchair-edged GNRs (aGNRs) exhibit semiconducting properties, where the band-gap decreases with increase in ribbon width [36,37,50]. This restricts the usability of aGNRs as conducting electrodes in molecular nanojunctions. However, defect formation or proper doping of heteroatoms like N or B shifts the Fermi level of aGNRs resulting in their metallic nature and thus, they have been properly used as the contact leads [34,51–56].

Charge transport properties of PCn–GR (graphene flakes) nanojunctions have recently been studied theoretically by employing density functional theory (DFT) in conjunction with the non-equilibrium Green's function formalism [11,19]. Pshenichnyuk *et al* [19] have demonstrated how the transport properties of these nanojunctions are mediated by PCn–GR coupling pattern and energy level sequences. Efforts have been made to tune the molecular energy levels of PCn by the influence of electron donating or withdrawing functional groups, which in turn affect the charge transport properties. Additionally, the particular effects of spin channels, which are crucial for zGNR leads, have also been resolved recently [11]. Thus, the current–voltage ($I-V$) characteristics of differently functionalized PCn–GR/GNR nanojunctions show various types of spin resolved transport properties which are of prime interest for designing spintronic devices. Although the higher acenes are predicted to be less stable, recently, platelet-shaped crystals of hexacene have been prepared and an FET made of hexacene single crystal has shown a hole mobility much higher than that of PCn [18]. Other oligoacenes and even oligothiophenes are also reported to show high charge transport properties. The planar, rigid molecular backbones arising due to highly conjugated structures of those molecules are mainly responsible for their high conductivity [20]. Apart from acenes, a large number of heteroatom-doped acenes (heteroacenes) are also synthesized for their possible applications

in organic electronics and photovoltaics. Recently, novel low band gap-fused thiophene–pyrrole-based heteroacenes (S,N-heteroacenes, SN_n (n = number of fused aromatic rings)) have been successfully used as hole transporters in perovskite-based solar cells [20,57–60]. Owing to their high conducting nature, such materials have been shown to improve the photocurrent efficiency (PCE) of the solar cells to a great extent [58].

Noteworthy, such kind of organic semiconductor molecules can be categorized into two main groups. In the molecules, p-channels are introduced into the composite nanojunction, i.e., if holes are generated at the highest occupied molecular orbital (HOMO) levels, they are termed as hole transporters; on the other hand, if electrons are injected into the lowest occupied molecular orbital (LUMO) levels, thereby introducing n-type of effect, they are termed as electron transporters. Most of the stable known organic semiconductor materials are of p-type mostly because they are found to be stable only under ambient conditions [61]. The reported carrier mobilities of p-type materials are also higher in comparison with that of n-type materials [5,62]. The major cause behind the unavailability of high performing n-type organic semiconductor materials is the unavailability of suitable electron withdrawing functional groups which could stabilize the materials with the desired electronic energy levels [63]. Injecting an electron into the LUMO of an organic semiconductor is equivalent to the electrochemical reduction at the cathode. Furthermore, the injected electron at the LUMO (which is generally high energetic) is highly susceptible to react with aerial O_2 and H_2O under ambient conditions, finally leading to the annihilation of electron transport. Thus, the primary criterion for realizing a stable electron transporting material is the stabilization of its LUMO level to sufficient extent [63–66].

Although n-type organic semiconductors are rare, they are of complementary interest for the fabrication of p–n junctions as well as other logic circuits [51,67]. Stable n-type organic semiconductors have recently been realized by introducing electron withdrawing groups into thiophene- or acene-based oligomers which are intrinsically hole-transporting materials [68–72]. Such kind of carrier switching may also occur through stereo-electronic changes inside a molecule [73,74]. However, in any case, the conformational change or incorporation of an electron-withdrawing group practically lowers the LUMO levels of the molecules, thereby provoking the crossing of the energy barrier for electron conduction [74–78]. Obtaining or predicting such electron conducting materials, even *in silico*, is still really demanding. Two methods have been singled out for converting a hole conducting material to an electron conducting; one is increasing the degree of polymerization and the other is chemical functionalization with a suitable electron withdrawing group as already discussed. Various experimental techniques, such as atomic force microscopy, scanning tunnelling microscopy (STM) in combination with the molecular break junction (BJ) method have been designed which can characterize the carrier type

either through Hall measurement or through the detection of Seebeck coefficient. In the experimental set-up, the molecule is selectively placed in between a static metal surface and a movable STM tip [79–81]. Theoretically, one can intuitively predict the carrier type by proper and accurate molecular orbital (MO) analysis and following the transmission eigenchannels projected over the molecular states [69,74,76].

Besides the spin and charge transport properties of acenes and heteroacenes, a large number of studies have also been devoted to show their photovoltaic activities [82–85]. Here also, PCn plays a leading role. Although solution processability of PCn is severely limited due to its poor solubility in water, design and synthesis of functionalized PCn are of recent interest with the aim of fabricating low cost solar cell devices. In a recent work, Pramanik *et al* [82] have synthesized a water-soluble PCn derivative with a low optical band-gap of 1.95 eV which shows a moderate PCE, while fabricating a bilayer solar cell with C₆₀ as an acceptor. Besides, differently functionalized PCn thin films are also reported to show intense optical absorption bands in the visible region, showing their promise in solar energy harvesting processes [86]. In this context, PCn–C₆₀ nanoadducts are important model systems to be studied theoretically as well as experimentally.

Among other different π -conjugated systems, oligothiophenes comprising donor–acceptor (D–A) or A–D–A types of architecture are well developed and are proved to show high performances in vacuum or solution-based organic solar cells [87–90]. As already discussed, the rigid and co-planar backbones of those systems easily suppress the conformation disorder which reduces the reorganization energy, finally enhancing their intrinsic charge mobility [91]. Similarly, SN n and their derivatives of similar nature have also been reported to show good photovoltaic performances [59]. N-alkylated S,N-PCn (SN5) molecule was synthesized a few years back as a component of fused thiophenes [92]. However, for their applicability in organic solar cells, different acceptor group functionalized SN5 derivatives have recently been studied. These derivatives in conjugation with different fullerene acceptors achieve remarkable PCE in vacuum-processed or solution-processed solar cells [20,57]. Even, some of these materials show up to 10.3% of PCE when applied as a hole transporter in perovskite-based solar cells [58]. Dicyanovinyl (DCV)-substituted SN5 (DCV-SN5) has been shown to produce PCE up to 5.64% which is higher than that of SN6 analogue (PCE = 3.02%) with C₇₀ as the counter composite [93]. A higher PCE has also been achieved with further modifications at the edge terminations of the molecules or by applying thermal annealing and subsequent solvent vapour annealing techniques [93–96]. As for example, Wetzel *et al* [96] have developed a DCV-SN6-based vacuum-processed planar-heterojunction with an excellent PCE of 7.1% with C₆₀ as an acceptor. In the meantime, the same group has extended the synthetic protocol up to SN10 [60]. As extended delocalization in SN n shows better visible region optical absorption properties, it is expected that

such systems may produce even better PCE. Very recently, on the basis of systematic *ab initio* simulations, our group has studied the optoelectronic properties of such materials in view of their potential applications in small molecule-based solar cells [85]. It has been demonstrated that there has been an even–odd parity in the intramolecular charge separation process, which is again reflected in generating charge transfer (CT) states while making composite systems. As a matter of fact, the odd SN n molecules show faster CT rates, thereby showing better photovoltaic performances [85].

Suitable electron acceptors also play an essential role in the performance of solar cell devices. Although semiconductor metal oxide surfaces like TiO₂ and ZnO are well known materials in this regard [97–109], C₆₀–fullerene and its derivatives are now being utilized as excellent electron acceptors because of their charge capturing ability originating from their unique structural rigidity and high degree of symmetry [110–113]. The suitable reduction potentials and the small reorganization energy during the electron-transfer processes are also very important for their successful implementations in bulk-heterojunction (BHJ) solar cells [114,115]. Fullerene derivative, particularly, phenyl-C₆₁-butyric acid methyl ester (PC₆₁BM) is the mostly used acceptor counterpart in this regard [116]. It is known that the injection of photoexcited electron from D to the A counterpart is the most crucial step in an organic photovoltaic device. To facilitate such process, it is required that the LUMO level of D must lie above the LUMO or conduction band of A. On the other hand, the HOMO level of D should be at lower energy position with respect to the chemical potential of the counter conductive electrode so as to facilitate the regeneration of the oxidized dye [117,118]. As a whole, a type-II band energy alignment is desired to have a good photovoltaic performance [111,112]. The energy alignment of PC₆₁BM, in most of the cases, provides such favoured situation, thereby enhancing the power conversion efficiency of the devices [113]. It has been demonstrated that in many cases, acene–C₆₀ D–A type of composites show ultrafast CT dynamics and slow recombination dynamics [85,119–125].

The above literature briefly outlines the prospects of acenes and heteroacenes in different optoelectronic devices which involve charge transport or CT through such molecular nanojunctions or nanocomposites. The present review aims to point out some interesting prospects of acenes and heteroacenes for favouring the CT and charge transport phenomena. Electron transport being a junction property, we will outline some important aspects of molecular nanojunctions comprising individual acene/heteroacene molecules and graphene or gold surfaces. The photovoltaic properties of the molecules would be discussed on the basis of molecular heterojunctions with fullerenes and their derivatives. The CT dynamics of such composite systems would be discussed on the basis of Marcus theory of electron transfer [126,127] and also with the help of time-dependent DFT (TDDFT) analysis.

Figure 1. Optimized ground-state geometries of the single PCn molecule (left) and PCn-DA- C_{60} composite system (right) [84]. The bond lengths are presented in Å.

2. Geometry and electronic structure

2.1 Pentacene and its derivatives

In general, the π -conjugated aromatic molecules are planar in nature up to a certain extent of ring fusion. However, the planarity in the molecular backbone decreases with increase in molecular length. Likewise, PCn is planar in its ground state with a D_{2h} symmetry. The generalized gradient approximation (GGA)/PBE calculations report that in-plane perpendicular C–C bond distances of PCn vary from 1.43 to 1.46 Å, while entering from edge to the centre of the molecule (figure 1) [84]. The zigzag C–C bond lengths also vary within the range from 1.38 to 1.44 Å, however, the sum of two such bonds in a hexagon is maintained at 2.82 Å [11,128,129]. Now, in the case of substituted PCn, the substituent groups (NO_2 , NH_2) are essentially in the same molecular plane thereby facilitating the extended delocalization. In that case, the symmetry as well as the C–C bond distances are changed to some extent. For practical implementation in solar cells, the solubility of PCn needs to be increased [82] and in view of this, carboxylic acid derivatives are prepared. The carboxylic acid groups also play the role of anchoring group for making composite system with C_{60} . It has been reported that the water soluble PCn diacids (PCn-DA) and their salts are relatively robust in the context of solar cell applications. They possess a higher degree of thermal stability as well as superior resistivity towards aerial oxidation [82].

Back to back experimental and theoretical studies have been performed on the geometry and optoelectronic properties of a series of substituted PCn derivatives. All of the derivatives, **1–12** (figure 2) were synthesized, purified

and then characterized by various spectroscopic and cyclic voltammetric (CV) methods [130]. The theoretically calculated HOMO–LUMO gap of PCn is reported to be 1.1 eV [11,128] which is somewhat less than the experimental value (1.82 eV) reported from ellipsometric spectra of thin PCn films [131]. Such a discrepancy between the theoretical and experimental band gap values may be attributed to the use of GGA in exchange correlation functional [11,84]. However, for the other substituted PCn derivatives, the calculated HOMO and LUMO energies and the corresponding gaps complement the experimental data [130] as could be found from table 1. The gas phase calculations on PCn-DA by using B3LYP/6-31g(d) or B3LYP/6-311g(d,p) levels of theory indicate a ground state geometry with C_1 symmetry [84] which corroborate well with the experimental observation as reported from X-ray crystallographic data [82]. The calculated HOMO–LUMO gap of PCn-DA is in the order of 2.1 eV using different levels of theories [84] which also matches well with the available experimental data [82]. Noteworthy, the relative positions of the HOMO (-5.16 eV) and LUMO (-3.08 eV) are very significant for their optoelectronic uses. However, the positions of these frontier orbitals are tunable by introducing different electron withdrawing or donating groups. Thus, one may design novel composite materials for photovoltaic purposes [82,84,130].

2.2 *S,N*-heteroacenes

As already discussed, a series of SN_n molecules ranging from $n = 3–10$ has been synthesized and characterized by using NMR spectroscopy and mass spectrometric techniques [60]. The representative model structures of such species are found in figure 3. On the basis of the structural feature, the molecules can be categorized into two main sub-groups: even heteroacenes, $SN(2m)$ ($m = 2–5$) containing thienothiophene units and having a C_{2h} symmetry, and odd heteroacenes, $SN(2m + 1)$ ($m = 1–4$) containing alternating thiophene and pyrrole rings all of which possess a C_{2v} symmetry. SN_7' is the analogous of SN_7 , but it differs from the latter by the number and sequence of the thiophene and pyrrole rings. All the SN_n molecules exhibit a rigid planar structure which indicates a thorough delocalization along the molecular backbone. However, a slight bond-length alteration (BLA) is observed at the inner parts of the molecules [59,85]. For the lower SN_n , the observed BLA is on the order of 0.014 Å which is slightly lower than that of the corresponding oligothiophenes [69]. However, with increase in conjugation length, the extent of BLA decreases. Functionalizing the molecules with electron withdrawing groups (such as DCV) at the both ends, it increases the extent of delocalization which further reduces the BLA. For example, for DCV- SN_9 and DCV- SN_{10} , the BLA is too small (on the order of 0.005 Å only) indicating ‘nearly complete equalization’ in the inner part of the conjugated backbone [60].

The computed HOMO, LUMO energy levels and the associated gaps of the substituted and unsubstituted SN_n

Figure 2. Structures of some PCn derivatives (**1–12**) with their associated half-lives in minutes (shown in parentheses) [130].

molecules using the HSE06/6-31G** level of theory are displayed in figure 4a. The corresponding experimental results obtained from the CV measurement are also shown in figure 4b for the comparison. Note that for experimental case, the pyrrole rings are functionalized by the hexyl group which, however, affect the energy gap marginally [60,85]. It is interesting to observe that the computed HOMO–LUMO gaps [85] for the unsubstituted SN n match excellently with the (CV) results [60], although, the individual positions of the HOMO and LUMO differ slightly. The figure clearly indicates that the HOMO–LUMO gap decreases with increase in the conjugation lengths of SN n . A similar trend is also observed for the substituted SN n molecules with increasing strengths of electron withdrawing groups [59,93]. This is probably driven by the prominent CT interactions between the rigid molecular backbone of the SN n and the attaching electron withdrawing groups at the two ends [59]. The tunability of such electronic gap as a function of molecular length and the nature of substituent group can be utilized properly for solar energy harvesting processes [85].

3. Transport properties of the molecular nanojunctions

We already introduced that the transport properties of molecular nanojunctions depend on the molecule-lead coupling

pattern. Although the transmission channels are determined from the individual molecular states, their relative positions are guided by the nature of the electrodes that are used. Here, we will show the effect of both types of electrodes, graphene and metal surfaces, mainly Au(111) surfaces. For PCn molecular junctions, people mainly think of PCn–graphene nanojunctions but for the SN n molecules, molecule–Au(111) nanojunctions are considered. The reason is so simple because the PCn molecule can be connected with a variety of modes with graphene, whereas the SN n molecules are more susceptible to make molecular contacts with metal surfaces [11,19,69,76,132].

3.1 Pentacene–graphene nanojunction

Before going to the details of the transport properties of PCn–graphene (mainly GR or GNR) nanojunction, let us recapitulate that the ground state of zGNR is antiferromagnetic with a zero net magnetization and the spin degenerate edge states are separated by a small energy gap around the Fermi level [37,38]. The GGA/PBE calculated band-gap for 4-zGNR is on the order of 0.8 eV [11]. Thus, although PCn is non-magnetic in nature, the overall system consisting of graphene fragments within the scattering region (SR) is treated with antiferromagnetic spin configurations. A model system for computing transport characteristics of such a nanojunction is shown in the top panel of figure 5.

Table 1. Electrochemical and optical properties of PCn derivatives **1–12** [130].

PCn derivatives ($t_{1/2}$)	$E_{1/2}$ [O] ^a (mV)	$E_{1/2}$ [red] ^a (mV)	E_{HOMO}^b (eV)	E_{LUMO}^b (eV)	$E_{g,\text{EChem}}^b$ (eV)	Low-energy λ_{max} (nm)	$E_{g,\text{optical}}^c$ (eV)	$E_{\text{HOMO,LUMO(DFT)}}^d$ (eV)	$E_{g,\text{DFT}}^d$ (eV)
1 (1140)	849, 1093	— 1099	— 5.17	— 3.36	1.81	624, 575, 534	1.86	— 5.20, — 3.03	2.17
2 (750)	755, 936	— 1229, — 1726	— 5.07	— 3.26	1.81	617, 570, 529	1.88	— 5.08 ^e , — 2.89 ^e	2.19 ^e
3 (620)	899	— 1227	— 5.21	— 3.24	1.97	605, 559, 520	1.94	—	—
4 (520)	789	— 1054	— 5.11	— 3.42	1.69	643, 591, 548	1.81	— 5.08, — 3.07	2.01
5 (220)	713	— 1485	— 5.03	— 2.99	2.04	605, 558, 520	1.95	—	—
6 (40)	695	— 1478	— 5.01	— 3.00	2.01	604, 557, 518	1.96	— 4.93, — 2.71	2.22
7 (13)	638, 1372	— 1543	— 4.95	— 2.93	2.02	618, 569, 529	1.90	—	—
8 (9.0)	627, 1224	— 1430	— 4.93	— 3.07	1.86	600, 554, 515	1.93	—	—
9 (8.5)	682	— 1396	— 5.00	— 3.08	1.92	604, 558, 519	1.94	— 4.86, — 2.63	2.23
10 (7.3)	536, 1171	— 1521	— 4.86	— 2.97	1.89	602, 556, 518	1.92	—	—
11 (6.6)	464, 1081	— 1651	— 4.78	— 2.84	1.94	583, 539, 501	2.01	—	—
12 (3.7)	635, 1183	— 1407	— 4.95	— 3.07	1.88	621, 573, 532	1.88	— 4.80, — 2.59	2.21
PCn (7.5) ^f						582, 537, 501	2.08	— 2.67, — 4.96	2.29

^aRecorded $E_{1/2}$ values vs. Ag/Ag⁺ in CH₂Cl₂ with TBAPF₆ as the supporting electrolyte.^bHOMO and LUMO energies and electrochemical HOMO–LUMO gaps determined from the onset of the first oxidation and the first reduction waves in cyclic voltammograms.^cOptical HOMO–LUMO gaps determined from the onset of lowest-energy visible absorption band. The onset is defined as the intersection between the baseline and a tangent line that touches the point of inflection.^dCalculations are performed using the B3LYP/6-311+G**/PM3 level of theory.^eCalculation for analogous 6,13-bis-(methylthiophenyl)pentacene rather than **2**.^fSaturated PCn in *o*-dichlorobenzene (1.67×10^{-7} M); all other compounds (**1–12**) in CH₂Cl₂ at 2.0×10^{-4} M.

Figure 3. Optimized geometries of the SN_n ($n = 5$ – 10) molecules showing the sequence of fusion of thiophene and pyrrole rings [85].

Figure 4. HOMO–LUMO energies and their corresponding gaps for SN_n and DCV- SN_n molecules of different conjugation lengths obtained from (a) computations using the HSE06/6-31G** level of theory [85] and (b) CV measurements [60].

It is basically a two probe model where the two edges of PCn or substituted PCn are connected with two semi-infinite electrodes (LHE/RHE, i.e., 4-zGNR in this case) *via* H-terminated graphene fragments. However, in some

Figure 5. Optimized supercell structure (LHE-SR-RHE) of the PCn-zGNR nanojunction (top panel), band structure of 4-zGNR (bottom left panel), and energy levels of PCn molecule (bottom right panel). Grey and white coloured balls represent C and H atoms, respectively. The encircled H atoms in PCn indicate the places of substitutions. For energetic representation, the Fermi energy of individual system has been set to zero [11].

cases, the molecules are connected through amide linkages or *via* oxygen atoms [19]. The region in between the two electrodes, as a whole is known as SR. The coherent electron transport as a result of voltage difference between two electrodes is measured in terms of transmittance by using Landauer–Buttiker formula which utilizes nonequilibrium Green’s function method [55,133,134]. The total integrated current can be expressed as

$$I(V_b) = \frac{e}{h} \int_{-\infty}^{\infty} T(E, V_b) [f_L(E, \mu_L) - f_R(E, \mu_R)] dE, \quad (1)$$

where $f_{L(R)}$ is the equilibrium Fermi–Dirac distribution function for left (right) electrode, $\mu_{L(R)}$ is the electrochemical potential of the left (right) electrode such that energy bias $eV_b = \mu_L - \mu_R$, and $T(E, V_b)$ is the transmittance of an incident electron with energy E which can be obtained using the below equation:

$$T(E, V_b) = \text{Tr}[\Gamma_L G^R \Gamma_R G^A], \quad (2)$$

where $G^{R(A)}$ is the retarded (advanced) Green’s function of the SR, and $\Gamma_{L(R)}$ is the coupling strength of the left (right) electrode.

Figure 6. Transmission plots for weakly coupled PCn-GR nanojunctions (shown in ball and stick model); the top panel shows the unsubstituted PCn and the bottom panel demonstrates the effect of CN functionalization to that. The dashed-dotted lines in the top panel represent the corresponding eigenenergies. The differences between the zigzag and armchair nanocontacts are also shown by different colours. The inset highlights the edge-induced peak with and without CN substitution [19].

Figure 6 (top panel) shows the spin independent transmission function of the amide-linked PCn-GR nanojunction [19]. It exhibits a series of transmission peaks which can be classified into two groups. The high intensity (with a maximum value of unity) isolated transmission peaks which are referred as the molecular resonance transmissions and the low intensity double peak transmission which appears close to the Fermi energy. Each of the molecular resonance transmissions is always associated with some discrete energy level of the molecular bridge and hence appears close to that particular state. The widths of these peaks depend on the molecule-coupled coupling. On the other hand, the low-intensity peak close to the Fermi energy cannot be related directly to molecular eigenstates and this does not correspond to direct tunnelling between the GR electrodes, rather this is assigned as an additional transport channel induced by the edge states of the GR leads or simply edge-induced transport channel. Noticeably, similar edge-induced transport channels have also been reported in different molecular nanojunctions made of CNTs and other metal surfaces [69,74,135–137]. Low-bias conductance of the molecular junction is mainly guided by those transport channels due to their close proximity to the Fermi energy.

The intensity of the edge-induced transmission channels may however be enhanced if the molecular levels appear closer to the Fermi energy. For example, if the PCn is functionalized with CN, it causes an overall shifting of the molecular eigenstates to a relatively lower energy levels. Consequently, the LUMO of PCn comes closer to the Fermi level

Figure 7. Energy spectrum of CN-functionalized PCn-GR nanojunction formed by the weakly coupled scheme through amide-binding groups. The highlighted area demonstrates the appearance of eight edge states (including HOMO-3 and HOMO-4) and one molecular state (LUMO+4, which has been embedded into the family of edge states through CN-functionalization to the PCn). The energies of the states indicated by arrow correspond to the peaks at $E = -0.2$ and $+0.2$ eV, respectively [19].

of the electrode, thereby causing a better overlap between the molecular states and the edge-states of GR. This results in an additional intensity of the edge-induced transmission peaks as could be found in the bottom panel of figure 6 [19]. Figure 7 further analyses the nature of edge-induced transmission channels for the CN-functionalized PCn-GR nanojunction. It shows the isosurface plots of the MOs of the overall nanojunction close to the Fermi energy. As found, these states can be classified into two groups: first, the states localized preferentially in the GR contacts (HOMO-3 and HOMO-2) are nothing but the well-known edge states of zGNR [38,138,139], and second, the molecular states mostly localized on the bridge (LUMO+4). It has been demonstrated that the edge-states, due to their localization at the molecule-GR interface, strongly interact with the molecular states and thus, induce the additional transport channels. For example, the transmission spectrum shown in figure 7 (bottom panel) demonstrates that for the CN-functionalized PCn, the edge-induced transmission peak at $E = -0.2$ eV corresponds to the near-degenerate pair of states, HOMO-2 and HOMO-3. On the other hand, the transmission peak at $E = +0.2$ eV corresponds to the regular transmission channel caused by the state LUMO+4. To unambiguously prove that the appearance of edge-induced transmission channel is due to the edge states of zGNR nanocontacts, one can reproduce similar transport characteristics with aGNR nanojunctions. As aGNRs do not possess edge states [37,51,53], the transmission functions for such nanojunctions should differ. More precisely, the edge-induced transmission channels are not expected to appear for those systems [19].

As already introduced, another important aspect of PCn-GR nanojunctions is their spin-induced transport characteristics. Because zGNRs possess spin-degenerate edge states, external or internal influence of charge or magnetic dipole will surely lift that degeneracy and that would be reflected in the transport characteristics of the nanojunction. The

Figure 8. Spin resolved I – V characteristics of (a) pristine PCn–zGNR nanojunction, (b) nitro-amine-bifunctionalized PCn–zGNR nanojunction. Black and red lines represent the spin currents for spin-up and spin-down channels, respectively. For the pristine one, the two spin currents are inseparable. (c) Spin resolved transmission spectra of nitro-amine-bifunctionalized PCn–zGNR nanojunction. Vertical dotted red lines indicate bias window [11].

computed spin-induced transmission characteristics of such nanojunctions consisting pristine and dipolar group-functionalized PCn are shown in figure 8. The small transport gap of zGNR close to the Fermi level, in each case, is attributed to the band opening of the zGNR leads [11]. For pristine PCn molecule, the spin channels are almost indistinguishable, however, in the case of the substituted PCn, two spin components are resolved as found in figure 8c.

For the unsubstituted PCn, the observed I – V curve (figure 8a) is antisymmetric in nature since the overall SR has a mirror symmetry. As already discussed, the low-bias conductance is mediated by edge-induced transmission channels producing a very low current (I). After the threshold voltage (half of the band-gap energy), the current increases by the influence of HOMO or LUMO resonating channels. With increasing the applied bias, the current increases up to 2.2 V and thereafter, it falls within the bias ranging from 2.2 to 2.6 V. This indicates a NDR behaviour of the PCn–GNR nanojunction as also commonly observed for many GNR contacts [51,139–141]. The observed NDR phenomenon is attributed to the localized states of PCn molecule (figure 5) [11,142]. For a large applied bias, there occurs asymmetric coupling between the molecular states and the electrodes and this causes the appearance of asymmetric potential near the source electrode. As a consequence, there occurs strong

localization of molecular states along the different parts of the SR which ultimately reduces the transmission coefficient and hence, the current [142]. Such kind of NDR phenomena may also originate from the poor coupling between the doped leads and the discrete molecular states where the doped leads produce narrow density of states (DOS) [140].

Figure 8b displays the I – V characteristics of PCn–zGNR nanojunction where PCn is functionalized by both nitro and amine groups at R and R', positions, respectively, as shown in figure 5. Figure 8c depicts the transmission spectra of the corresponding nanojunction at different applied biases. At some finite bias (0.8 V), the stronger transmission peak at the Fermi level is expected due to the contribution from the edge states. However, with increasing the bias, this peak disappears, instead, two peaks of similar intensity appear. Interestingly, the up and down spin components are resolved beyond the threshold voltage, resulting in different spin currents. However, both the spin currents show NDR behaviour, but with different peak positions and different peak-to-valley ratios [11].

The origin of the spin resolved transport characteristics of the PCn–zGNR nanojunction may be understood on the basis that under transverse electric field, zGNRs exhibit half metallic property [36,143] which stems from a unique interplay of the edge magnetizations, their antiferromagnetic coupling and

as a consequence, relative potential shifting between the two edges of the zGNRs. Apart from external electric fields, this may also happen due to other causes such as, introduction of quantum dots at the zigzag edges, substitution of the edge carbons by boron, nitrogen, etc., functionalization of the zGNR edges or by deposition of ferroelectric materials on the zGNR surface [38,144–146]. So, it is unambiguous that proper functionalization of PCn with dipolar groups will affect the edge magnetizations of zGNR. As a consequence, the edge induced spin states are resolved upon the application of external bias voltage. This argument can easily be proved by proper choice of functional groups and also by varying the positions of functionalization. When PCn is functionalized with a relatively weak electron withdrawing or donating group, which obviously have low dipolar effect, the spin resolution is found to be weak [11]. Even, when the two same groups are attached at the opposite sites of PCn (substituted at R and R' positions as shown in figure 5), the dipolar effect is nullified and thus, unpolarized transport properties are observed [11,19]. In contrast, a more prominent spin resolved transport properties are observed when the PCn molecule is functionalized simultaneously with nitro and amine groups at two opposite sides [11]. In that case, a pronounced dipolar effect as a result of opposing electronic effects of the nitro and amine groups produces severe spin resolution in the transmission channels [11,145]. The consequence of spin resolution in the transport properties is the spin filtering ability by the properly functionalized PCn–GR nanojunctions, which can be quantified in terms of spin resolved current at finite bias (I_s) and is defined as $I_s = (I_{dn} - I_{up}) / (I_{dn} + I_{up})$. The highest value of $I_s = 0.41$ is reported at an applied bias $V_b = 2.6$ V for nitro-amine bifunctionalized PCn [11].

3.2 *S,N*-heteroacene–Au(111) nanojunction

SNn molecules could be anchored to Au-surface through various modes. The transport properties of molecular nanojunction strongly depend on the anchoring groups through which the molecules are connected with the electrodes [147]. For anchoring a molecule with metal surfaces, in general, thiols/thio-ethers, amines, carboxylic acids, sulphides, phosphides, etc. are used. The overall transport properties of a molecular nanojunction thus must be influenced by the electronic coupling between the molecule and the electrodes. The stronger the coupling between the discrete energy levels of the molecule and the continuum of metal sub-bands, the larger the broadening of transmission resonances close to the Fermi surface and consequently, the nanojunction would be more conducting. The use of thiols or thio-ethers as anchoring groups is advantageous because of their flexibility as required in STM–BJ experiments. In these instances, the optimized Au–S bond lengths are reported in the range of 2.29–2.39 Å [148–151]. However, direct Au–C covalent linkages are also reported in the literature showing highly conducting molecular nanojunctions [152–154]. On the other hand, Au–N contacts have recently been reported for the amine

Figure 9. Optimized geometries of the metal–molecule contacts for the pristine (a) SNn, (b) DCV-SNn and (c) SME-SNn (SN5 as a representative) molecules [157].

or cyano-terminated molecules with an appreciable amount of resonance transmission [151]. In case of amines, an $\text{Au} \leftarrow \text{N}$ dative bond (average bond distance 2.35 Å) is formed by the donation of lone pair of electrons over the N atom to the vacant d-orbital of a suitable Au atom of the Au(111) surface [155], while for the latter case, an Au–N covalent bond is formed with an average bond distance of 2.15 Å [151,156]. Some model nanojunctions (Au–molecule–Au) consisting of pristine and substituted SNn with Au(111) surfaces are shown in figure 9 [157].

The Au–molecule–Au nanojunctions constituted of pristine SNn and their different derivatives, especially DCV-SNn show quite interesting transport phenomena. The DCV-SNn molecules, where two DCV groups are attached at the two ends of the SNn molecules, have recently been synthesized with a narrower band gap and high thermal stability [59,60,85]. DCV being strong electron withdrawing in nature, imparts a lower HOMO–LUMO gap and as a consequence, a red-shifting is occurred in the intramolecular CT band which in turn helps to improve the photocurrent of the devices [95]. Besides, other derivatives of SN5 also show promise as prominent hole transporters and absorbers in perovskite-based solar cells with moderate and high PCE [58,158,159]. Another member of this series, DCV-SN6 has also very intense optical transition. DCV-SN6 is reported to exhibit good p-channel charge-carrier mobility, up to $0.02 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ as a consequence of an extended band-like π -conjugated backbone [59]. Noteworthy, while comparing the conducting properties of the SNn molecules as a function of conjugation length, it has to be kept in mind that the SNn molecules show a difference in their heteroatomic orientation and ordering for the even and odd number of fused rings (figure 3). This orientation difference leads to a different extent of

Figure 10. Low-lying MPSH eigenvalues of the SN n and DCV-SN n molecular junctions at zero applied bias [157].

intramolecular charge separation [85]. However, in both the cases, the molecular conductance (G) decreases exponentially with increase in conjugation length (l). Obviously, one gets a linear plot of $\ln G$ vs. l and the negative slope of the straight line gives the conductance decay constant (β) [74,132,160]. For the odd SN n molecules, $\beta = 0.06 \text{ \AA}^{-1}$, while for the even ones, it is $0.04 \text{ \AA}^{-1}$. The β values for the odd and even DCV-SN n molecules are reported to be 0.29 and $0.10 \text{ \AA}^{-1}$, respectively, and those for the odd and even SMe-SN n molecules are 0.23 and $0.12 \text{ \AA}^{-1}$, respectively [157]. In each case, the odd ones show relatively higher β values in comparison with that of the even ones. However, the computed β values for the SN n and DCV-SN n molecules are to some extent lower in comparison with that of the oligothiophene or oxidized oligothiophene chains [74,132].

Now, the conductance characteristics of the molecular junctions could be known from the relative positions of the highest occupied and lowest unoccupied Kohn–Sham states projected over the molecules with respect to the Fermi energy of the metal electrode. These are nothing but the eigenstates of the molecular-projected self-consistent Hamiltonian (MPSH states). Figure 10 shows the zero bias eigenvalues of those frontier eigenstates projected over the SN n and DCV-SN n molecules with respect to the Fermi energy of Au(111) surfaces as electrodes. These are the possible eigenchannels through which electron transport may occur. As could be found from figure 10, for the SN5–Au molecular contact, the projected HOMO and LUMO energy positions are -0.34 and 2.51 eV, respectively. The corresponding values for DCV-SN5 are -1.55 and -0.05 eV, respectively. Clearly, HOMO of SN5 and LUMO of DCV-SN5 are closer to electrode Fermi energy and thus, they serve as the main transporting channels for the corresponding molecular nanojunctions. Similar situations are arrived for the other pairs of SN n and DCV-SN n molecular junctions with similar molecular lengths. Now, for SMe-SN n molecular junctions, the relative energy positions of the eigenstates are changed but still, the HOMO levels are closer to the Fermi level, at least for the longer chains.

Figure 11. Zero and finite-bias transmittance of the SN n (left panel) and DCV-SN n (right panel) molecular junctions as a function of relative Fermi energy. One of each isosurface plots of the MPSH eigenchannels of the SN n and DCV-SN n molecular junctions at zero applied bias are shown to indicate their distinct characteristics as molecular HOMO and LUMO levels, respectively [157].

Figure 11 shows the transmittance plots of the unsubstituted and DCV-substituted SN n molecular junctions (left and right panels, respectively). It is clear from the figure that at a particular applied bias, the major transmission peaks at both sides of the Fermi level (set to zero energy) correspond to the molecular HOMO and LUMO levels. The figure clearly indicates that the closest transmission peaks to the Fermi energy, in the case of SN n nanojunctions, correspond to the HOMO resonating channels, while those for the DCV-SN n nanojunctions, correspond to the LUMO resonating channels. For the SMe-SN n nanojunctions, there is a transmission gap around the Fermi level, however, some low intensity peaks are appeared in between the two major peaks. These are referred to the metal-induced transmission channels [11,74,75] which are mainly responsible for their low-bias transport properties. To demonstrate the fact, one can obtain the isosurface plots of the transmission eigenchannels (MPSH states) at different applied biases. It has been revealed that for the pristine SN n molecules, the lowest transmission eigenchannels in the low bias region correspond to the molecular HOMO states. Although there are slight differences between the MPSH eigenchannels and the corresponding HOMOs in the case of SMe-SN n nanojunctions, they mostly resemble HOMO, not the LUMO nor even the HOMO–1. So, the SN n and SMe-SN n molecules are mainly hole transporting materials. In contrast, the lowest MPSH states corresponding to the DCV-SN n molecules corroborate with the LUMO levels of the respective free molecules, clearly indicating the n-type of conductance. What happens is that, the strong electron withdrawing DCV group pulls down the LUMO energies

of the DCV-SN n molecules as compared to those of the corresponding unsubstituted ones. Thus, the LUMOs become closer to the Fermi-level of the electrode and this facilitates electron transport from the metal electrode to the vacant orbitals of the molecules. These clearly reveal that the SN n or SMe-SN n molecules are hole conducting, while the DCV terminations at both ends of the molecules turn them into electron conducting [157]. Such kind of substitution-induced carrier switching deserves much attention for possible use in electronic devices such as organic FETs [66].

4. Photovoltaic activities of the acenes and heteroacenes

Recently, a significant effort has been devoted to the rational design and synthesis of π -conjugated small organic molecules with the aim of their successful implementation in solar cell devices. These include different kinds of acenes, heteroacenes, etc. with a common molecular architecture D- π -A [20,57,58,85,95,96,161–164]. However, the reported power conversion efficiencies of the devices are relatively poor. This is because of the fact that in spite of suitable optical gap of the molecular dyes, the absorption coefficients for the low energy transitions are low. Secondly, those acene- and heteroacene-based dyes are relatively less soluble in water as well as in other common organic solvents. Furthermore, most of the acene-based dyes tend to aggregate which substantially reduces their power conversion efficiency [82,165]. Nevertheless, people have also found the ways to get rid of these problems, e.g., by functionalizing the acenes by various functional groups. Anthracene-based tetrathiafulvalene derivative (ext-TTF), in particular is very promising in this regard [165–168]. However, in the following sections, we will point out some interesting features of PCn and SN n molecules as potential donors in small molecule-based BHJ solar cells.

Before going to the details of such discussion, let us have a look on the controlling parameters of a photovoltaic cell. The efficiency of a BHJ solar cell can be expressed as

$$\eta = \frac{FF \cdot J_{SC} \cdot V_{OC}}{P_{inc}}, \quad (3)$$

where FF is the fill factor at which the device operates with the maximum power. This is mainly related to the total series resistance of the cell. P_{inc} is the input power of incident solar radiation and J_{SC} is the short circuit current density of photovoltaic cell which can be expressed as [169]

$$J_{SC} = \int \text{LHE}(\lambda) \Phi_{\text{inject}} \eta_{\text{collect}} d\lambda, \quad (4)$$

where $\text{LHE}(\lambda)$, the light harvesting efficiency is a function of absorption wavelength (λ), which can be evaluated from the

intensity of absorption (oscillator strength, f) as given below:

$$\text{LHE}(\lambda) = 1 - 10^{-f}, \quad (5)$$

and Φ_{inject} and η_{collect} are the electron injection efficiency to conduction band of the A and the electron collection efficiency at the transparent conductive electrode, respectively. Note that Φ_{inject} is related to the driving force (ΔG_{inject}) of electrons injection from the photoexcited D to the A counterpart which can be approximated as [124,126]

$$\Delta G_{\text{inject}} = E_{\text{LUMO}}^{\text{D}} - E_{\text{LUMO}}^{\text{A}}. \quad (6)$$

Apart from these, the open-circuit voltage (V_{OC}) of a BHJ solar cell can be estimated as [170]

$$V_{OC} = \frac{1}{e} (|E_{\text{HOMO}}^{\text{D}}| - |E_{\text{LUMO}}^{\text{A}}|) - 0.3V, \quad (7)$$

assuming that an energy difference of 0.3 eV between the LUMOs of D and A is sufficient for efficient charge separation from the initially produced exciton.

4.1 Pentacene and its derivatives

The major characteristic of a donor molecule in photovoltaic cell is to produce suitable energy band alignment with a suitable acceptor counterpart. PCn-C₆₀ nanocomposites are well studied for this purpose [83,84,121]. Here, we explore the possibility of tuning frontier energy levels of PCn by substituting various functional groups. Noteworthy, the electron donating group in general pushes up both the energy levels of HOMO and LUMO, while the electron withdrawing group pulls down both of them. However, the extent of raising or lowering of the individual frontier orbitals may differ, resulting in slight change in the HOMO–LUMO gap. Table 2 depicts the relative energy positions of the HOMOs and LUMOs and their respective gaps for differently substituted PCn molecules. Figure 12 shows a more clear pictograph of their relative positions with respect to those of an acceptor, C₆₀. From the relative energy positions, one may expect that all the donor molecules are capable of donating photoexcited electron from their respective LUMOs to the LUMO of C₆₀. As a matter of fact, this energy difference between the LUMOs of D and A measures the driving force for electron injection (ΔG_{inject}) [126,171,172]. Thus, one may choose suitable functionalized PCn molecules for modelling photovoltaic devices with better performances. Very strong electron donating group may increase the rate of electron injection, but this subsequently increases the position of the HOMO too which in turn increases the chance of electron–hole recombination, causing negative effect on photovoltaic performance. So, a balance is required between the charge injection and recombination rates [84].

To have a more realistic picture, one needs to study the D–A composite system which can mimic the fabricated device. The

Table 2. Computed HOMO/LUMO energy levels ($E_{\text{HOMO/LUMO}}$), their respective gaps (Δ), open circuit voltage (V_{OC}), free energy change for electron injection (ΔG_{inject}) and dipole moment (μ) for the PCn derivatives.

Sl. no.	Species	E_{HOMO} (eV)	E_{LUMO} (eV)	Δ (eV)	V_{OC} (eV)	ΔG_{inject} (eV)	μ (D)
I	PCn	−4.60	−2.39	2.21	1.07	0.84	0.00
II	PCn-DA	−4.82	−2.73	2.09	1.29	0.50	0.00
III	NO ₂ -PCnA	−5.09	−3.04	2.05	1.56	0.19	3.10
IV	CN-PCnA	−5.07	−3.05	2.03	1.54	0.18	3.36
V	NH ₂ -PCnA	−4.44	−2.39	2.04	0.91	0.84	4.06
VI	OMe-PCnA	−4.66	−2.54	2.12	1.13	0.69	2.19
VII	CO ₂ -PCnA	−4.86	−2.77	2.09	1.33	0.46	0.58
VIII	CF ₃ -PCnA	−4.94	−2.85	2.09	1.41	0.38	1.29
IX	CH ₃ -PCnA	−4.66	−2.53	2.12	1.13	0.70	2.45
	C ₆₀	−5.98	−3.23	2.76	—	—	—

R-PCnA indicates the replacement of terminal carboxylic acid group of PCn-DA by the R group. The corresponding values of C₆₀ are also given for comparison [84].

Figure 12. Relative energy positions of the HOMO (blue) and LUMO (red) states for the individual molecules (narrow line) and the corresponding composites with C₆₀ (bold line) obtained at the B3LYP/6-31G(d) level of theory. The Roman numbers correspond to the molecules as those in table 2. Similar HOMO and LUMO energy levels of C₆₀ are presented by dotted blue and red lines, respectively. HOMO/LUMO isosurface plots of the PCn-DA-C₆₀ composite are shown to indicate the spatial separation of electron and hole densities [84].

photovoltaic properties of such a model structure can actually predict the performance of such device. Even a computational analysis of such composite structure can provide intuitive ideas to further improve the power conversion efficiency. As found from table 2 and figure 12, the individual energy positions of the PCn derivatives and the C₆₀ counterparts have been changed to some extent in the composite system due to D–A CT interactions. However, the relative energy ordering is retained, thereby giving rise to a type-II band alignment, which still indicates the possibility of charge injection from D to A counterpart. Molecular orbital analysis of the composite materials clearly reveals that the HOMO of the composite system always resides on the donor PCn derivative whereas the LUMO stays on the acceptor, C₆₀. This special charge

separation substantially reduces the chance of charge recombination [84,111,112,171]. A more clear picture could be figured out from the analysis of the corresponding electronically excited state of the composite system, namely the CT state which originates as a result of CT from the HOMO of the D to the LUMO of the A counterpart [84,119,120,124].

In organic PVCs, the process of charge generation involves photoinduced electron transfer from D to A counterpart as already discussed. This leads to either a direct charge-separated state or in most cases, an intermediate CT state is produced, which then evolves into a charge-separated state [173,174]. The CT state is thus a key intermediate electronic state in the operational process of organic photovoltaic devices because it plays the deterministic role in the exciton-dissociation as well as in the charge recombination processes [121,175]. Combined time-resolved femto-second spectroscopy and first-principles quantum dynamics simulation studies demonstrate how the coherent motion of atoms governs the photo-induced charge generation and thereafter interfacial charge separation, which generally occur at the femto-second (fs) time scale [176]. These studies also point out the precise role of vibronic coupling in the evolution of the CT state.

Combined *ab initio* molecular dynamics (AIMD) simulations and DFT calculations have been performed to probe the dynamics of the lowest CT state of the PCn-C₆₀ composite at the fs time scale that furnishes better insights into the charge-separation and recombination dynamics at the D–A interface [121]. As could be visualized from the top panel of figure 13, the two lowest excited states of the PCn-C₆₀ composite are identified as the CT states, while the third and fourth excited states are admixture of local excitations (LE) on PCn and a CT excitation [121]. The excess (negative) charges on C₆₀ for the lowest four excited states are also displayed in the same figure. Importantly, the total energy difference between the first and fourth excited states is only in the order

Figure 13. Top panel: the lowest four excited states of the PCn–C₆₀ composite. λ indicates the contributory fraction of the hole–electron pair in the given electronic transition. The amount of Mulliken charge on C₆₀ is also presented to indicate the extent of charge separation. Bottom panel: time-dependent variation of Mulliken charge population on C₆₀ in the PCn–C₆₀ complex for a representative trajectory (Traj-3). Calculations are done at the tuned TD- ω B97XD/6-31G(d) ($\omega = 0.137 \text{ bohr}^{-1}$) level of theory [121].

of 150 meV. This actually makes the composite particularly interesting because it can be taken as a representative of D–A composite systems having a small energy gap between the LE and CT states which is highly desired to minimize the energy (and voltage) loss during the energy conversion processes.

The dynamics of the lowest excited state could be followed to see the electron–phonon coupling involving some high-frequency modes within the PCn molecule. Usually, the C–C bond-stretching and ring-breathing vibrational modes strongly couple with the electronic excitations in such π -conjugated molecules. This typically happens within the 100 fs time scale [121]. Here, a useful descriptor of the dynamics in the first excited state (S_1) is the amount of excess negative charge on the A counterpart (C₆₀). The time evolution of such state is shown in the bottom panel of figure 13. Noteworthy, during the course of the CT processes, the hole wave function in the S_1 state remains localized on A, while the electron wave function strongly fluctuates between the D (PCn) and A. The electron starts on C₆₀, jumps onto the PCn molecule after some 18–20 fs of time before going back to C₆₀. In the meantime, it takes 2–3 fs of time to complete a jump, in the middle of which the S_1 state has a hybrid LE–CT character. However, as a whole, it can be argued that the electron transfer between PCn and C₆₀ occurs within a fs time scale [121,177,178].

Figure 14. Time-dependent evolution of the LUMO, LUMO+1, LUMO+2 and LUMO+3 energy levels of the PCn–C₆₀ complex for the Traj-3 trajectory, computed by using the ω B97XD/6-31G(d) ($\omega = 0.137 \text{ bohr}^{-1}$) level of theory [121].

For better understanding the oscillations in the electron transfer processes between PCn and C₆₀, one may analyse the fluctuations in the MO energies of the PCn–C₆₀ composite. The HOMO and LUMO+3 levels of the composite are shown to reside on PCn, while the LUMO, LUMO+1 and LUMO+2 levels (localized on the C₆₀) are nearly degenerate and correspond to the triply degenerate LUMO states of C₆₀ [121]. From figure 14, it is clearly revealed that when S_1 state of the composite gains a LE character, the (PCn-based) LUMO+3 energy comes close to the (C₆₀-based) LUMO+2 energy. Interestingly, the transition between the LE and CT characters of the S_1 state passes through a mixed LE–CT state as already discussed. Such a transient hybrid state has recently been observed in a polymer–C₆₀-based thin film solar cells [179]. Noteworthy, in that case also, the energy difference between the S_1 state (polymer-based) and the interfacial CT state is reported to be very small.

4.2 *S,N*-heteroacenes

We already introduced that even SN n molecules experience poorer charge separation in their first excited state in comparison with that of the odd ones which should be reflected in their photovoltaic activities in D–A type of composites [85,93]. Before going to such details, let us have a look on the absorption and excited state properties of DCV substituted SN5 and SN6. On the basis of first principle calculations, it has been reported that the first excitation energy, which is designated as the band-gap absorption, decreases by 0.07 eV, while going from SN5 to SN6 [85]. Although for both the molecules, the excited-state CT amount (q^{CT}) is almost same, the associated CT lengths (l^{CT}) show a remarkable difference. For the first excited state, the computed l^{CT} values are reported to be 0.068 and 0.0001 Å for SN5 and SN6, respectively. This affects the charge transport and carrier dynamic seriously. Additionally, because of their rigid coplanar backbone, the SN n molecules show intense photoluminescence and high carrier

Figure 15. Left panel: (a–c) CDD plots for S_1 (LE), S_5 (LE) and S_{14} (CT) excited states of the SN5–PC₆₁BM composite system, and (d–f) S_1 (LE), S_5 (LE) and S_{18} (CT) excited states of the SN6–PC₆₁BM composite system. Right panel: (a–c) CDD plots for S_1 (LE), S_3 (LE) and S_5 (CT) excited states of the SN9–PC₆₁BM composite system, and (d–f) S_1 (LE), S_3 (LE) and S_6 (CT) excited states of the SN10–PC₆₁BM composite system. LE and CT stand for local excitations (involving either SN n or PC₆₁BM) and CT states, respectively. Blue (red) stands for depletion (accumulation) of negative charges [85].

mobilities [93,180]. The coplanar architecture of the molecules also suppresses the conformational disorder, resulting in a decrease in reorganization energy which in turn increases their intrinsic charge mobility and hence photocurrent efficiency (PCE) [91]. The planar mixed active layer of DCV-SN5 blended with C₇₀ is reported to show an excellent PCE of 5.64%, while under similar conditions, SN6 derivative shows only 3.02% PCE [93]. In sharp contrast, the absorption intensity of the first intense transition for SN6 is higher than that of SN5. Furthermore, some sub-transition dipoles are eliminated due to C_{2v} symmetry of the SN5. So, in spite of better absorption characteristics, the improper charge separation leads to faster charge recombination and thus, the PCE is lower for SN6 [85,93]. For its better justification and to generalize such phenomena, a recent computational work has been performed on an additional pair of SN9 and SN10 which also reports similar observation [85].

In view of their practical implementation, a more realistic model, D–A type of composites have been studied with different SN n molecules as D and PC₆₁BM as an A. In the optimized structure, the PC₆₁BM occupies a vertical orientation over the SN n molecular surface. The computed optical properties reveal that all the low-energy transitions are of LE type involving either the D or the A counterpart. The first CT state for SN5–PC₆₁BM is characterized to be S_{14} (appearing at 403 nm), while for the SN6-composite is S_{18} . Although the absorption intensities of the transitions relating to those states are poor, those states are mainly responsible for photovoltaic activities as already discussed [121]. The CT characteristics in those excited states could be visualized from the charge density difference (CDD) [181] plots as depicted in figure 15. Note that the CDD between the excited state and the corresponding ground state has been expressed in terms of $\Delta\rho(r) = \rho^{\text{elec}}(r) - \rho^{\text{hole}}(r)$, where the electron and

hole densities are expressed in terms of the coefficients of configuration state function (c_i) as [182]

$$\rho^{\text{elec}}(r) = \sum_{i \rightarrow l} (c_i^l)^2 \phi_i(r) \phi_l(r) + \sum_{i \rightarrow l} \sum_{j \neq i \rightarrow l} c_i^l c_j^l \phi_i(r) \phi_j(r), \quad (8)$$

and

$$\rho^{\text{hole}}(r) = \sum_{i \rightarrow l} (c_i^l)^2 \phi_l(r) \phi_l(r) + \sum_{i \rightarrow l} \sum_{i \rightarrow m \neq l} c_i^l c_j^l \phi_l(r) \phi_m(r). \quad (9)$$

Obviously, the CT states experience a huge CT length (l^{CT}) which also follows a similar trend as that for single SN n molecules. Similar is the situation for the SN9 and SN10 composites, for which the lowest CT states are S_5 and S_6 , respectively (see figure 15). Note that much lower excitons are now responsible for generating the CT states.

The photovoltaic performance of a material is crucially determined by the carrier transfer dynamics within the system. In a simplified form, the corresponding rates of CT and recombination can be followed by using Marcus theory [127] as given below:

$$k = \sqrt{\frac{4\pi^3}{h^2 \lambda k_B T}} |V_{\text{DA}}|^2 \exp\left(-\frac{(\Delta G + \lambda)^2}{4\lambda k_B T}\right), \quad (10)$$

where λ is the reorganization energy, V_{DA} is the CT integral between the D and A states, and ΔG is the free energy change for the corresponding process (ΔG_{CT} for CT and

Table 3. Computed charge transfer/recombination rate constants and associated dynamical parameters for the SN*n*-PC₆₁BM/PDI composite systems.

System	E_b (eV)	$\Delta\mu$ (a.u.)	μ_{tr} (a.u.)	V_{DA} (eV)	V_{OC} (V)	ΔG_{CR} in eV (k_{CR} in s^{-1})	ΔG_{CT} in eV (k_{CT} in s^{-1})
SN5-PC ₆₁ BM	0.35	3.06	0.0355	0.0357	1.88	-2.18 (4.11×10^{-11})	-0.58 (2.67×10^{13})
SN6-PC ₆₁ BM	0.31	6.92	0.0079	0.0036	1.81	-2.11 (4.60×10^{-11})	-0.53 (3.10×10^{11})
SN9-PC ₆₁ BM	0.26	4.17	0.4726	0.2745	1.29	-1.59 (1.68×10^5)	-0.72 (6.97×10^{14})
SN10-PC ₆₁ BM	0.23	7.98	0.1359	0.0451	1.28	-1.58 (7.56×10^3)	-0.67 (2.70×10^{13})
SN5-PDI	0.35	5.47	0.1518	0.0686	1.29	-1.59 (1.01×10^4)	-1.17 (1.85×10^{10})
SN9-PDI	0.26	6.60	0.0250	0.0089	0.70	-1.00 (1.40×10^{10})	-1.31 (5.92×10^6)

Calculations are performed in the gas phase. E_b , $\Delta\mu$, μ_{tr} and V_{OC} stand for exciton binding energy, dipole moment difference between ground and excited states, transition dipole between ground and excited states, and open-circuit voltage, respectively [85].

ΔG_{CR} for charge recombination) at a particular temperature T . In principle, $\Delta G_{CR} = E_{IP}(D) - E_{EA}(A)$, where $E_{IP}(D)$ and $E_{EA}(A)$ are the ionization potential of D and electron affinity of A, respectively. However, $E_{IP}(D)$ and $E_{EA}(A)$ could approximately be estimated as the HOMO and LUMO energies of the D and A counterparts, respectively [183]. Now, with the help of ΔG_{CR} , one can estimate the value of ΔG_{CT} using the Rehm-Weller equation [184], $\Delta G_{CT} = -\Delta G_{CR} - \Delta E_{0-0} - E_b$; where ΔE_{0-0} and E_b are the first excitation energy of the free-base donor and the corresponding exciton binding energy [185], respectively.

Equation (10) involves another important parameter i.e., reorganization energy (λ) which basically consists of two parts, inner reorganization energy (λ_i) and outer reorganization energy (λ_s) [120]. λ_i is originated from the geometric change in the D and A counterparts of the composite at the time of charge separation phenomena and thus, it is the sum of two terms, electron and hole reorganization energies (λ_e and λ_h , respectively). On the other hand, the λ_s comes from the electronic and nuclear polarizations/relaxations of the surrounding medium. Now, λ_e and λ_h could be estimated as $\lambda_e = E(A^-) - E(A)$ and $\lambda_h = E(D) - E(D^+)$, where $E(A^-)$ and $E(A)$ are the energies of the neutral acceptor at the anionic geometry and optimal ground-state geometry, respectively; and $E(D)$ and $E(D^+)$ are the energies of the radical cation donor at the neutral geometry and optimal cation geometry, respectively. In an alternative way, λ_i can be calculated by taking the average of λ_{i1} and λ_{i2} , where the two terms come from the reorganization of intramolecular excited state to charge separated state and vice versa, respectively [119,186]. However, the theoretically calculated λ_i values of the dye-PC₆₁BM composites run in the range of 0.20–0.25 eV [85,124,187]. The estimated values of λ_s also lie in that region such that the overall λ values appear around 0.50 eV which corroborate well with the experimental values [124,188].

Now, the D-A CT integral (V_{DA}) for the CT state involving the transition from the ground state (S_0) to the excited state (S_n) can be expressed in terms of generalized Mulliken-Hush (GMH) model [189]

$$V_{DA} = \frac{\mu_{tr} \Delta E}{\sqrt{(\Delta\mu)^2 + 4(\mu_{tr})^2}}, \quad (11)$$

where μ_{tr} is the component of the transition dipole moment along the major axis, $\Delta\mu$ the dipole moment difference between the S_0 and S_n states, and ΔE the vertical excitation energy. Now, $\Delta\mu$ can be computed by using the finite field method on the excitation energy [190,191]. The calculated $\Delta\mu$, μ_{tr} and thereafter, the corresponding V_{DA} values for some SN*n*-based composite systems are shown in table 3.

As table 3 shows, for the SN5-PC₆₁BM composite, the estimated value of ΔG_{CR} is -2.18 eV and hence $\Delta G_{CT} = -0.58$ eV. The negative value of ΔG_{CT} indicates the thermodynamic feasibility of the electron transfer process. However, comparing the calculated rate constants of the concerned processes one may argue that SN5 involves a slower charge recombination and faster CT rate in comparison with those of SN6. Similarly, SN9 composite also experiences a faster CT rate than that of SN10. Therefore, it rationalizes the fact why the odd SN*n* molecules (SN5/SN9) provide better photovoltaic performances than the even ones [85,93]. A similar conclusion could also be drawn based on the composites comprising SN*n* and helical perylene diimide dimer (PDI) [192] as a non-fullerene acceptor [85].

5. Conclusions and future outlook

In summary, we present here, the very recent developments on the charge transport and CT properties of different nanojunctions based on PC*n* and SN*n* molecules of different conjugation lengths. In case of PC*n*-graphene nanojunctions, the low bias conductance is mainly mediated by edge-induced transmission channels originating from zigzag edges of GNR. Attachment of strong electron withdrawing groups like CN to the PC*n* molecule will pull down the transmission eigenchannels closer to the Fermi level which increases the intensity of edge-induced transmittance, thereby increasing the conductivity. Proper functionalization of PC*n* with electron donating and withdrawing groups imparts an internal field across the molecule which subsequently lifts the degeneracy of the zGNR edge states and this is responsible for generating spin currents in the PC*n*-zGNR nanojunctions. Spin-dependent I - V characteristics of these devices show NDR behaviour which is attributed to the poor coupling between the discrete

molecular states of PC_n and the zGNR leads at some specific bias region. Although the nanojunctions are predicted to show low spin filtering ability, the exhibited spin transport properties are quite useful for fabricating bias dependent spintronic devices.

The transport properties of different edge-terminated SN_n molecule–gold-surface nanojunctions also deserve much attention. Although such nanojunctions constituting bare or SMe-terminated SN_n are hole conducting, termination with very strong electron withdrawing DCV groups led them to electron conducting. Such kind of SN_n molecule-based n-type materials are predicted to be thermodynamically stable and thus expected to be realized in near future. Very strong electron withdrawing effect of DCV pull down the molecular LUMO level, thereby promoting easier way of electron conduction through that state. Such kind of carrier switching through simple chemical modification on SN_n would be very beneficial in OFET or diode industry.

On the other hand, by structural modification of PC_n molecule through proper substitution, one can optimize the photovoltaic performance of a BHJ solar cell with C₆₀ as an acceptor. It has been proposed that PC_n molecules functionalized by strong electron donating substituents may offer a faster interfacial electron transfer rate, however, strong electron withdrawing groups like CN provide a better light harvesting efficiency. The electronic structure calculations reveal that PC_n–C₆₀ nanocomposites show type-II band alignment which substantially reduces the charge recombination rates, thereby increasing photovoltaic performances. A combined DFT and AIMD simulations of the lowest excited state in the PC_n–C₆₀ composite underline that some specific high frequency vibrational modes, namely the C–C bond-stretching and ring-breathing in PC_n are mainly responsible for the major oscillations in the energy levels of the composite. Thus, such vibronic couplings have an influence on the evolution of the lowest excited state of the composite which in fact activate transition between a CT and LE-type of states, *via* a transient hybrid LE–CT state. The dynamics in the composite system results in a distribution of the lowest excited-state energy over several tenths of eV. Such kind of phenomena has important implications regarding small molecule-based organic solar cells.

Recent experimental and quantum chemical investigations highlight the potential applicability of SN_n molecules in photovoltaic devices. The rigid architecture of the SN_n suppresses the conformation disorder and thus reduces the reorganization energy, thereby enhancing the intrinsic charge mobility. The first optical absorption energy gradually decreases with increasing the conjugation length of the SN_n backbone. Additionally, strong electron withdrawing groups attached to the both ends of the SN_n impart extended delocalization which results in further red-shifting in the absorption maxima. An even–odd relationship is observed for the intramolecular charge separation process of the SN_n, the odd ones providing longer CT length than the even ones. Similar event also happens at the D–A interface with PC₆₁BM as a global acceptor.

Thus, it has been predicted that the odd SN_n molecules would provide a faster interfacial CT rate, indicating their better photovoltaic performances.

Acenes and heteroacenes are therefore very promising for the next generation optoelectronic devices. Their intrinsic molecular properties are very suitable for their extraordinary performances in charge transporting or energy conversion processes. The major drawback is their poor solubility in common solvents. Further studies are therefore necessary with the aim to increase their solubility through proper substitution, specially by polar electron withdrawing groups. However, this should not affect the carrier mobility too much, and secondly, the planar backbone architecture should also be retained. Finally, carrier transport dynamics is an essential tool for predicting the actual device performances of those materials. For that, one needs to study a large scale non-adiabatic molecular dynamics simulations over the D–A interface [193,194]. Although some efforts have already been given [193], we do hope that more sophisticated experimental and theoretical researches will bring further insights into the carrier transport dynamics of acenes and heteroacenes systems.

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