# Photophysical Properties and Orbital Energy Calculation in Diketopyrrolopyrrole Based Conjugated Polyelectrolytes

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**Summary:** Theoretical calculation study of two alternating conjugated polyelectrolytes, named SDPP-PPV and SDPP-PPE, constituted of 1,4-diketo-2,5-bis(4-sulfonylbutyl)-3,6-bis(4-bromophenyl) pyrrolo[3,4-c]pyrrole (SDPP) with 2,5-diethoxy-1,4-phenylenevinylene (DVB) or 2,5-diethoxy-1,4-phenyleneethynylene (DEB) were carried out with Gaussian 09 software. The absorption spectral study shows that SDPP-PPV and SDPP-PPE have broad coverage of visible spectra and considerable red shift compared with water-soluble poly(p-phenylenevinylene)s (PPVs) and poly(p-phenyleneethynylene)s (PPEs). The TD-DFT calculation results show that LUMO of the polymers can be significantly reduced and the HOMO-LUMO gap can be changed by introducing DPP into the backbone. Theoretical study indicates that introduction of electro-deficient unit DPP in the polymer main chain can optimize the band structure of traditional PPV and PPE. The improved optical properties and excellent water solubility of these two novel DPP-based conjugated polyelectrolytes allow them to be promising materials in optoelectronic applications.

Keywords: Conjugated polyelectrolytes; Theoretical calculations; Band gap engineering; Photophysics; diketopyrrolo[3,4-c]pyrrole.

## Introduction

Conjugated polyelectrolytes (CPEs) have been the focus in polymer materials science over the years. The chemical structure of the CPEs provide a unique set of properties, including water solubility and processability, main-chain-controlled exciton and charge transport, variable band gap light absorption and fluorescence, ionic interactions, and aggregation phenomena [1]. With the above-mentioned characteristics, these materials have been actively investigated for a variety of optoelectronic applications, such as polymer light emitting diodes (PLEDs) [2, 3], fluorescent sensors [4-6], and photovoltaic devices [7, 8].

In the field of conjugated polyelectrolytes, classified by main-chain structure, basically three classes [9-11] of π-conjugated polyelectrolytes are mostly used, as illustrated in Scheme-1: (i) polymers made up of alternating aryl and ethylene units, the poly(arylene-vinylene)s (PAVs) [12, 13], (ii) polymers made of alternating aryl and ethynyl units, the poly(arylene-ethynylene)s (PAEs) [14, 15], and polymers consisting of aromatic rings directly linked to each other in a linear manner, the poly(arylene)s (PAs) [16, 17].



poly(arylene)s
**PAs**

poly(arylene-vinylene)s
**PAVs**

poly(arylene-ethynylene)s
**PAEs**
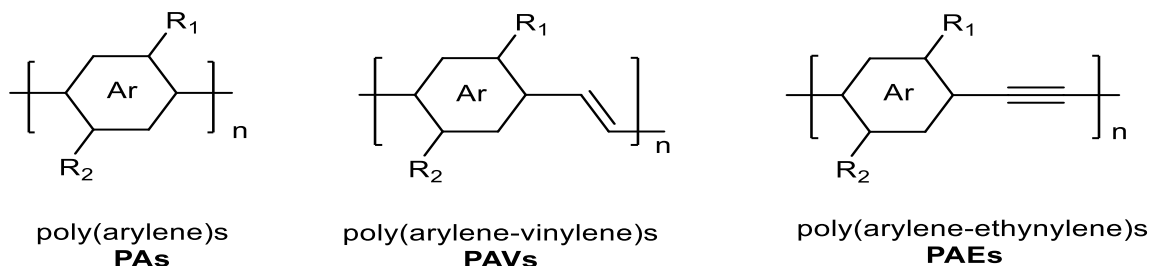
$R_1$=ionic group
$R_2$=ionic group, alkyl or alkyloxyl

Scheme-1: General presentation of three kinds of CPEs.

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In each class of materials, the aromatic moieties may be either benzene derivatives or heteroaromatics such as thiophenes, pyridines, pyrroles and thiazoles. Actually, the water soluble PAVs/PAEs are the most important conjugated polyelectrolytes materials due to their unique advantages of chemical modification in the main chain [18] and convenient functionalization of their side chains [19, 20].

Although water-soluble poly(p-phenylenevinylene)s (PPVs) and poly(p-phenyleneethynylene)s (PPEs) are studied thoroughly as the fluorescent chemosensor materials, their potential in photovoltaic applications is not explored enough due to the drawback of traditional PPVs and PPEs. These traditional conjugated polyelectrolytes have relatively large band gap and improper energy level position, thus limiting their applications in optoelectronic devices. PPV-type materials are predominantly hole-conducting materials with high-lying LUMO levels [21]. Although PPE-type materials have comparatively lower-lying LUMO due to enhanced electron affinity [22], the band gap of this kind of polymers is larger than PPVs because of the poor conjugation of triple bond compared to the double bond. Hence there is an urgent and important mission to find an effective method to modify the electronic structures of these conjugated polyelectrolytes.

Recently an important approach which usually employed in optimizing the band structure of PPVs and PPEs for optoelectronic devices is the analogous approach as donor-acceptor (D-A) strategy [23, 24] to covalently link a phenylene unit and an electron-accepting moiety as the repeating unit with the bridge of C=C/C≡C bond in the main chain. As reported from previous studies [25, 26], copolymerization by using different monomer units is the most frequently-used, simple and convenient method to obtain new conjugated polyelectrolytes. Various conjugated polyelectrolytes with poly(aryleneethynylene) (PAE) backbones containing a variety of different aryl units in the π-conjugated backbone have been synthesized and different aryl units give rise to materials with a wide range of HOMO-LUMO gaps [14]. Moreover, it is verified that the band gap in the conjugated polyelectrolytes could be controlled by combining the various monomer units with an electron deficient unit along the chain.

1,4-diketopyrrolo[3,4-c]pyrrole (DPP) which invented by Ciba and some of its derivatives are commercialized as high performance pigments with exceptional light, weather, and heat stability [27]. It has a well-conjugated structure which leads to strong $\pi$-$\pi^*$ interaction and the lactam ring makes the molecular exhibit a strong electron-withdrawing effect, offering a high electron affinity. Furthermore, DPP and their derivatives are important chromophores with high absorption in visible and near-infrared regions. Thus DPPs are considered as unique copolymerization units for the synthesis of conjugated polymers with excellent optoelectronic properties [28, 29] such as low band gap, broad absorption range, high mobility, and appropriate molecular energy levels. So, introduction of DPPs can achieve the goal of the ideal properties of polymer photovoltaic materials including not only good harvesting of sunlight but also ideal charge separation and transportation [28]. It is worth pointing out that the DPPs can effectively lower the LUMO of the polymers [30], produce efficient charge transport [31] and make these polymers a kind of low-band gap photovoltaic materials [32].

As mentioned above, although DPP and its derivatives were commendably used as a copolymerization unit to modulate the energy-level structure of the oil-soluble conjugated polymer materials [33-38], few publications concerning water-soluble DPP-containing polymers were published [39, 40]. Two novel alternating π-conjugated anionic copolyelectrolytes constituted by sulfonate functionalized DPP unit with short alkoxy modified 1,4-phenylenevinylene (DVB)/1,4-phenyleneethynylene (DEB) structure units respectively, have been reported [41], as illustrated in Scheme-2.

In this article, according to the calculated results, it is found that introduction of the DPP unit leads to a lowering of LUMO level and an arising of HOMO level. Thus the band gaps of the two CPEs were strongly decreased with respect to the traditional PPVs or PPEs. These properties render these CPEs great potentials in optical and electronic applications, especially in self-assembly photovoltaic devices.
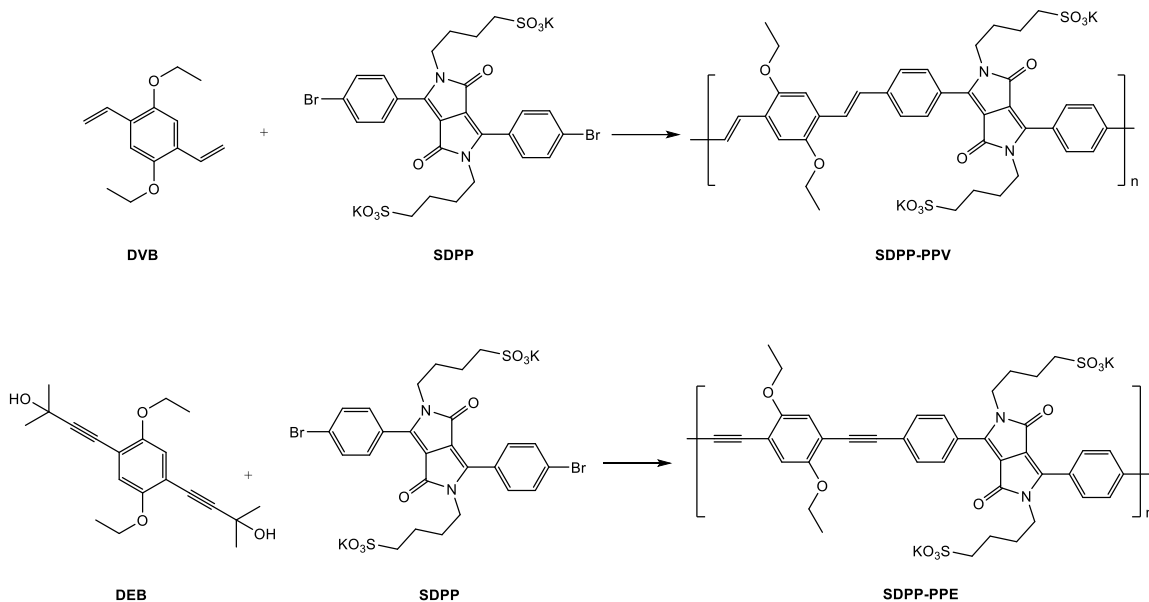
Scheme-2: Structures of monomers and polymers.

## Experimental

Density functional theory (DFT) calculations were performed to study the effect of copolymerization on the electronic structures and optical properties of conjugated polyelectrolytes. Full geometry optimization were carried out for all the monomers (DVB, DEB, and SDPP) and polymers (SDPP-PPV and SDPP-PPE) using Becke's three-parameter Lee-Yang-Parr hybrid functional (B3LYP) [42, 43] and triple-zeta 6-311+G(d,P) [44, 45] basis sets by Gaussian 09 program [46]. A frequency calculation was performed on the optimized geometries to ensure a local minimum was found. The optical properties of model monomers and polymers were studied by time-dependent a DFT (TD-DFT) calculation, which offers orbital picture for a physical understanding of the excitation processes [47]. The 2-propanol protection unit of DEB was replaced by hydrogen unit in the calculation to avoid excessive computation demand, since it does not significantly affect the equilibrium geometry and thus the electronic properties.

## Results and Discussion

*Electronic structures of the monomers and the polymers*

As shown in Fig. 1, the HOMO-LUMO gaps for the copolymerization monomers are relative large, which are 3.82 eV for DVB and 4.09 eV for DEB, respectively. The SDPP monomer, with a diketopyrrolopyrrole group, is a typical electron acceptor unit. The HOMO level of SDPP is close to that of DVB and DEB and its LUMO level is much lower than DVB and DEB. After formation of copolymer SDPP-PPV and SDPP-PPE, one can find that both the energy levels of frontier orbitals and the HOMO-LUMO gap are changed dramatically via orbital interactions. In SDPP-PPV and SDPP-PPE, the DVB and DEB units act as an electron donor and the SDPP acts as an electron acceptor. Because the HOMO level of DVB (DEB) is close to that of SDPP, the orbital interactions give rise to two new orbital in the copolymers.
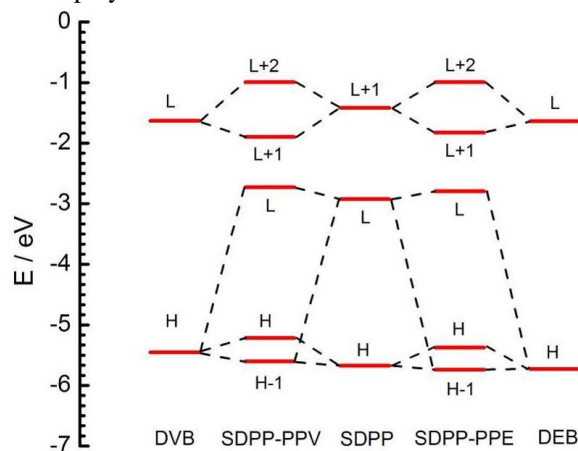


Fig. 1:   Orbital mixing diagrams for the frontier orbitals of the model polymers SDPP-PPV and SDPP-PPE.

DFT calculations on the model compounds of the two polymers show that they are basically planar molecules, which enables the electrons to be delocalized within the molecule by conjugation (Fig. 2). The new HOMO in copolymer is a delocalized orbital, in which the electron density populates on both donor unit and acceptor. Note that the energy level of the new HOMO in copolymer is slightly higher than the parent DVB and DEB. The LUMO of SDPP-PPV (SDPP-PPE) is a localized orbital, in which the electron density mainly distributes in the electron acceptor SDPP unit. The charge transfer from the HOMO of DVB (DEB) to the LUMO of SDPP through orbital interaction leads to an increase of the new LUMO in copolymer. Also note that the LUMO level of DVB (DEB) is close to the LUMO +1 level of SDPP, the interaction between these two orbitals produce two new orbitals in the copolymer, which is LUMO + 1 and LUMO +2.
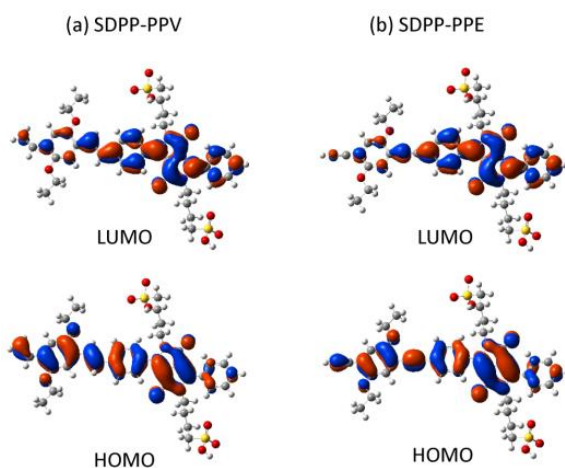


Fig. 2:     Electron density distributions of HOMO and LUMO of SDPP-PPV (a) and SDPP-PPE (b)

Comparing with the parent DVB (DEB) monomer, the HOMO level of SDPP-DVB increase from -5.46 (-5.73) eV to -5.22 (-5.37) eV, the LUMO levels decreases from -1.63 (-1.83) eV to -2.73 (-2.80) eV, and thus the HOMO-LUMO gap is significantly decreased.

*Optical properties of the monomers and the polymers*

SDPP-PPV and SDPP-PPE are readily soluble in water and DMSO. The aqueous solution of SDPP-PPV exhibits no luminescence, only slight luminescence can be observed in aqueous solution of SDPP-PPE. Both the two polymers exhibit luminescence in DMSO. Thus the photophysics properties of the polymers were characterized in DMSO.

Fig. 3 shows the UV-vis and PL spectra of the polymer SDPP-PPV, DVB, and SDPP. Compared with monomer DVB, the absorption band of SDPP-PPV exhibits a large red shift from 344 to 524 nm. The red-shift of the absorption band is due to the extended π-conjugation framework of SDPP-PPV vs. the two monomers, which can be understood from the TD-DFT calculations.
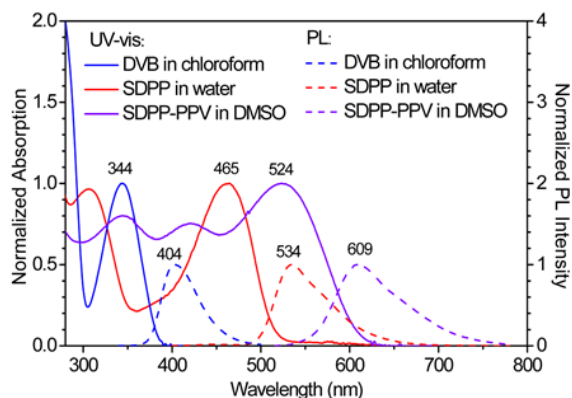


Fig. 3:     UV-vis and PL spectra of DVB, SDPP and SDPP-PPV.

Fig. 4 (a) shows the frontier molecular orbitals involved in the vertical transitions of model monomers (DVB and SDPP) and copolymer SDPP-PPV. For SDPP-PPV, the first absorption band at 524 nm is assigned to arise from the transition from the delocalized HOMO to the localized LUMO. The second peak at around 344 nm was associated with the absorption of 1,4-phenylenevinylene segments [18]. According to our calculation, this peak should be assigned to charge-transfer transition from the electron donor unit DVB (HOMO-2) to the electron acceptor SDPP (LUMO). Furthermore, SDPP-PPV exhibits a red shift of 88 nm in absorption maxima compared with a common water soluble PPV (436 nm) [25]. Hence, when DPP unit was incorporated into the polymer backbone, the absorption range was controlled as expected.

As shown in Fig. 2, the frontier orbitals of SDPP-PPV and SDPP-PPE are all delocalized π orbitals. TD-DFT calculations reveal that the first adsorption peak could be attributed to the HOMO to LUMO transition (Table-1). The calculated absorption wavelength matches well with the experimental observation.
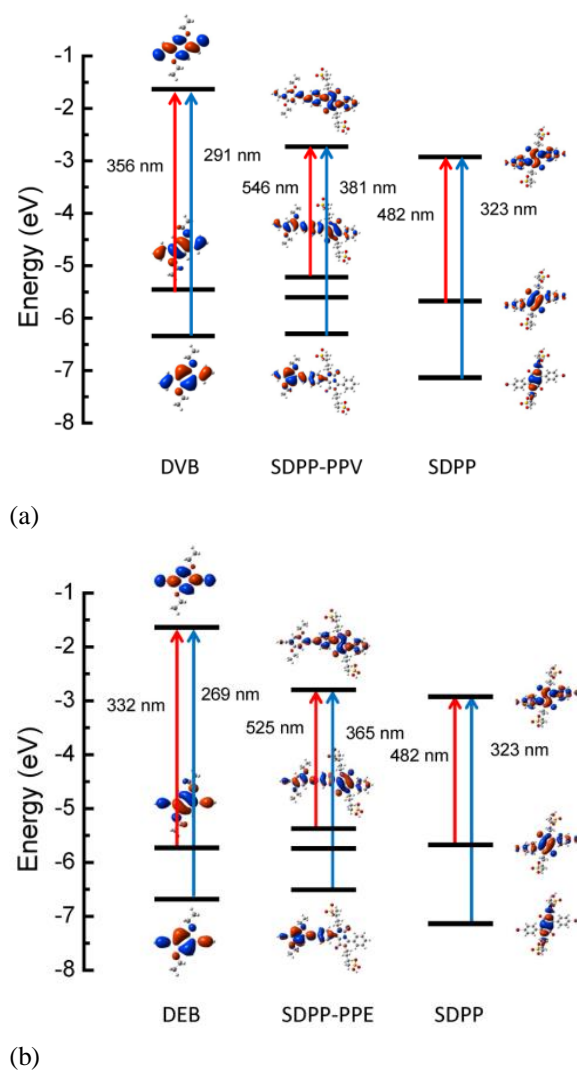
(a)



(b)

Fig. 4: (a) Frontier molecular orbitals involved in the vertical excitation (UV-vis absorption) of DVB, SDPP, and SDPP-PPV; (b) Frontier molecular orbitals involved in the vertical excitation (UV-vis absorption) of DEB, SDPP, and SDPP-PPE. Only selected MOs are present; for details, (Table-1).

Table-1: TD-DFT Calculated Vertical Excitations (UV-Vis Absorption) of Model Compounds DVB, DEB, SDPP, SDPP-PPV, and SDPP-PPE

| | transitions | excitation energy(nm) (oscillator strength) | transitions | excitation energy(nm) (oscillator strength) |
|---|---|---|---|---|
| DVB | H→L(+90%) | 356(0.30) | H-1→L(+89%) | 291(0.33) |
| DEB | H→L(+91%) | 332(0.24) | H-1→L(+79%) | 269(0.34) |
| SDPP | H→L(+100%) | 482(0.54) | H-1→L(+84%) | 323(0.33) |
| SDPP-PPV | H→L(+100%) | 546(1.19) | H-1→L(+81%) | 381(0.40) |
| SDPP-PPE | H→L(+99%) | 525(1.06) | H-1→L(+70%) | 365(0.33) |

H = HOMO, L = LUMO

Fig. 5 shows the UV-vis and PL spectra of the polymer SDPP-PPE, DEB, and SDPP. Compared with DEB the absorption band of SDPP-PPE exhibits a large red shift from 335 to 507 nm. SDPP-PPE has a shorter absorption wavelength compared with SDPP-PPV because of the poor conjugation of triple bond compared with double bond. Fig. 4 (b) shows the frontier molecular orbitals involved in the vertical transitions of model monomers (DEB and SDPP) and copolymer SDPP-PPE. The first absorption band at 507 nm is assigned to arise from the transition from the delocalized HOMO to the localized LUMO. The second peak at around 378 nm was associated with the absorption of 1,4-phenyleneethynylene segments. According to our calculation, this peak should be assigned to charge-transfer transition from the electron donor unit DEB (HOMO-2) to the electron acceptor SDPP (LUMO). Furthermore, SDPP-PPV exhibits a red shift of 82 nm in absorption maxima compared with a common water soluble PPE (425 nm). Here absorption property of PPE can be changed via introduction of DPP unit.
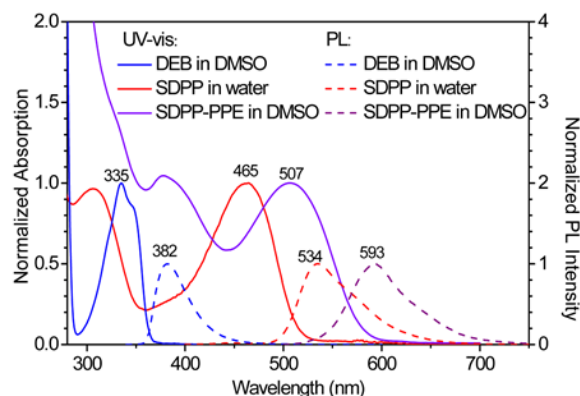


Fig. 5: UV-vis and PL spectra of DEB, SDPP and SDPP-PPE.

The absorption band of SDPP-PPV and SDPP-PPE also exhibit a red shift with respect to the SDPP. In Fig. 3 and 5, the absorption band locates at 465 nm, which is assigned to a HOMO-to-LUMO transition of diketopyrrolopyrrole. After formation of copolymer SDPP-PPV and SDPP-PPE, the HOMO level increases a lot through orbital interactions and the LUMO level increase slightly through ground-state charge transfer. The change in frontier orbital levels of SDPP-PPV and SDPP-PPE leads to the red shift of the absorption band. Note that the absorption energies of the copolymer SDPP-PPV and SDPP-PPE are lower than all the monomer DVB,

DEB, and SDPP. Their optical properties are effectively improved by copolymerization.

These results indicate that the decrease in the band gaps of the two polymers is due to the introduction of the DPP segment, in accordance with the change in the absorption spectra.

**Conclusion**

Two novel DPP-based conjugated polyelectrolytes SDPP-PPV and SDPP-PPE, which contain diketopyrrolo[3,4-c]pyrrole (DPP) as the energy band gap tuning unit, have been investigated with orbital energy calculation. Computational study shows that energy-level tuning of common PPV and PPE can be achieved by copolymerization with an electron acceptor unit DPP. By introducing the DPP in the backbone, it is possible to lower the LUMO drastically and change the HOMO-LUMO gap of PPV/PPE, resulting in the two polymers (SDPP-PPV and SDPP-PPE) that display absorption maximum at wavelengths of 524 nm and 507 nm and fluorescence maximum at 609 nm and 593 nm in DMSO, respectively. Compared with traditional PPVs and PPEs, the two polymers exhibit large red shift with both the absorption and emission. These results indicate that DPP is a promising material used to adjust the energy structure of the regular conjugated polyelectrolytes. And the two polymers are potential materials for optoelectronic applications, especially in self-assembling photovoltaic devices due to their ionic side chains.

**Acknowledgement**

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