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A step towards the application of molecular plasmonic-like excitations of PAH derivatives in organic electrochromics

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ABSTRACT

Polycyclic aromatic hydrocarbons (PAHs), are regarded as molecular fragments of graphene and are facilely available through chemical synthesis. Recently, it is found collective charge density oscillations with strong induced electromagnetic field display in PAH derivatives. This phenomenon, analogue to plasmonic excitation in metal, called molecular plasmonics, arise the significant interest of physicists. Instead of discussing its rich physics, this work aims at the application of molecular plasmon-like excitations in electrochromics and optoelectronics. We found that the energy and the intensity of plasmonic-like oscillation could be largely tuned by increasing the conjugation size along both the longitude/transverse axis in PAHs. Besides, the dimeric PAH demonstrates the possibility that molecular plasmonics could be designed using PAHs as building blocks for integration into larger molecular systems. Moreover, this work straightforwardly extends the molecular plasmonic-like property from C–H composed PAHs to much more versatile planar conjugation systems with heteroatoms, achieving transferring between p-type and n-type organic semiconductors. Therefore, with the natural abundance, low cost, easily chemical synthesis of PAH derivatives, we believe this work paves the way for the application of molecular plasmonic-like properties in optoelectronics.

Electrochromism is a phenomenon in which the absorption spectra of the materials shift that response to an electrical field, displaying the color varying in human eyes. Generally, electrochromic materials can either be inorganic or organic. Although the inferior thermal and chemical stability compared with inorganic materials, organic electrochromic materials offer facile chemically modification, versatile colors that span the entire color palette, solution processing, compatibility with large-scale production, *etc.* Those advantages make them significantly attractive for electrochromic industrialization. Therefore, conductive polymers (CPs) have been of interest to the electrochromic community since the last century 90s [1,2].

Many studies have focused on thiophene [3] and aniline [4] based electrochromic polymers, most of which are p-type semiconductors. The band structure of conjugated polymers, which could determine the color of the materials, can be tuned through the donor-acceptor strategy, that is, hybridization of the corresponding frontier orbitals of the different donor and acceptor units [5]. Most of the electrochromic polymers show strong absorption in the visible range at a neutral state (~2 eV bandgap), shifting to the near-infrared after oxidizing (~1 eV). However, small molecules are much more in favor of the industrial application, could display colorless at a neutral state (>3.3 eV HOMO-LUMO energy gap) and exhibit certain colors in a redox state (~2 eV). This native colorless property gives small molecular electrochromics an enormous advantage for their application in smart windows or displays. Besides, the small molecular system leads the bandgaps are extremely sensitive and feasible to be tuned through the molecular structure. For example, electrochromic small molecules based on thiophene [6] and carbazole [7,8] have been successfully designed and applied.

Polycyclic aromatic hydrocarbon (PAH), regarded as a molecular fragment of graphene and readily available through chemical synthesis, has been extensively investigated in a variety of optoelectronic device applications. Recently, it was found that PAH molecules, or with the addition/removal of a single electron, can support molecular plasmon (collective) resonances in the visible region [9,10]. The collective motion of electrons is driven by their mutual Coulomb interaction, similar to the plasmonic excitation

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counterparts sustained by graphene or metallic nanoparticles. This phenomenon largely expands the application from mid-infrared of grapheme [11–15] to a much higher frequency–visible range [16] of organic small molecules.

So far, most studies focus on the rich physics of molecular plasmonics in PAH systems. Chapkin *et al.* experimentally proved the charged PAHs exhibit more rapid decay dynamics than the neutral state due to molecular plasmonics, which is collective charge density oscillations with a strong induced electromagnetic field in a planar π-electron molecular system [17]. Although the arguments regarding their classification as plasmonics persist, because of the blurred boundaries between conventional plasmonic resonance and electron-hole (e-h) pair transitions, which both display as optical resonances [18]. It offers a platform for material scientists to understand how the optical absorption property of the PAH molecules is tuned by the molecular plasmonic-like excitation, besides the conventional optical tune strategy through molecular structure design such as cross-conjugation [6] or intramolecular charge transfer [8]. Meanwhile, it is significantly meaningful for molecular plasmonics to be pushed forward to the application in optical-electrical devices, such as organic electrochromic devices.

Besides, as is well known for the application of PAH molecules in organic electronics [19–21], they mainly apply as the p-type carrier transport materials. From the industrial application point of view, the versatility of carrier transport property is necessary for different devices with different functions. Therefore, both n-type and p-type materials are essential for organic electronics [22]. Molecular structure engineering of PAH derivatives would be the most efficient way to tailor their carrier transport property.

Here, instead of focusing on the detailed discussion about the definition of “molecular plasmonics”, or its physics source; we stand from the application point of view, pacifically but not limited to the organic electrochromics, discuss how the molecular plasmon-like excitations are tuned in PAHs and the hetero-modified PAH derivatives at the visible range. In this work, we perform fully quantum theoretical calculations on tunable plasmonic behavior in PAH derivatives. It is found that excitation energy and intensity could be largely tuned by increasing the benzene ring along both the longitude and transverse axis of PAH molecules. By employing heteroatoms such as O or N in the planar π-electron molecular system of PAH derivatives, the carrier transport property could be tuned from p-type to n-type with a very minimal redshift of the optical absorption property. Therefore, this work straightforwardly extends the molecular plasmonic-like property from PAHs, which is quite a small number of molecules, to a diverse planar π-electron molecular system with multi-elements, in which the optical property and the carrier transport property (e- or h-transport) could be facilely tuned through hetero-modification. This insight paves the way for applying molecular plasmonics in the organic optoelectrical device.

Firstly, since the molecular plasnomics were discovered based on PAHs [9], the study of how the collective oscillation is tuned by the size of the PAHs and PAH derivatives is necessary for the application of plasmonic-like transitions. In the linear PAH molecules (Fig. 1a), the longitudinal excitations perform the plasmonic characteristic where the linear planar electron gas is sensitive to the length (from naphthalene to tetracene). As shown in Fig. 1b, the principal absorption energy exhibits redshift (from 6.2 eV to 4.8 eV) with the increasing molecule length from two to four fused rings. Meanwhile, it shows that the larger the conjugation size, the stronger its principal absorption, which is analogous to the situation in metallic nanorods [23,24]. Besides, the larger conjugation size leads to the satellite absorption peaks from the UV range bathochromic shift to the visible range (from 4.6 eV to 2.6 eV), indicating the strong tune of the HOMO-LUMO gap of the molecules. Moreover, the plasmonic-like excitations could be tuned when PAH molecular system is enlarged along the transverse direction. It shows the obvious distinction in the excitation energy and intensity of anthracene and pyrene by comparing their absorption spectra (Fig. 1).

Furthermore, after one-electron injection, the molecular plasmonic can be detected both for anthracene and pyrene, with the induced charge densities polarized along the long axis as shown in Fig. 1c. The highest peaks in visible region for the −1 charged anthracene (2.1 eV) and pyrene (2.7 eV) both belong to longitudinal molecular plasmonic (LP) [16]. Besides, there are smaller peaks shouldering the LP oscillation, induced by transverse molecular plasmons (TP), which are perpendicular to the long axis (Fig. S1 in Supporting information). The oscillation strength of TP at −1 charged state is much weaker than LP, which performs similar to the noble metal nanorods [25]. It also displays that the oscillation energy of both LP and TP tends to be red-shift when the molecules are doped, comparing Figs. 1b and c. Therefore, the tunable longitudinal and transverse plasmonic-like oscillation in PAHs is achieved through manipulating the molecular size of both directions of the molecules, and the doping state of the molecules.

Apart from the fused-expansion of PAHs, connected with a covalent bond between molecular fragments is a direct way for molecular structure design and synthesis. As shown in Fig. 2, we introduce one prototypical example of a dimeric PAH dye −2,2′-bianthracene (**2A**), taking anthracene as building blocks. It displays a substantial intramolecular interaction of the plasmonic oscillations between the two anthracenes. It is similar to the traditional metal-based plasmonics, the interaction between neighboring plasmons results in energy shifts and new splitting in the visible range [26].

As shown in Fig. 2a, the principal peak from 5.4 eV of anthracene redshifts to 4.2 eV of **2A** at a neutral state. The new splitting appearing at 2.8 eV for **2A** is due to the relative dipole moment of the two anthracene groups, which is the main factor that plays in the intramolecular interaction. Compared with the study of Li *et al.* [27], they accommodate two closely oriented plasmon-supporting p-moieties through a linker, shifting the principal absorption peak (plasmon-like) toward larger, rather than lower energies. This is not necessary to happen all the time [28], when the two PAH groups are face to face arranged in one plane.

Besides, when **2A** is at +1 charge state, it exhibits very close plasmonic excitons (Fig. 2a) and almost the same photoinduced charge density (Fig. 2b) as at −1 charge state at a similar excitation energy (around 3.16 eV and 3.17 eV, respectively), which is due to the similar constructive compositions of molecular orbitals transition. Therefore, it could prove that employing multi-PAH groups in one molecular system by promoting a strong interaction between the plasmon-supporting conjugated systems, is an effective way to maintain the plasmon-like oscillation, and generate a multi-peaked absorption, thus can broaden the absorption of a dye, especially at their charged state.

It is demonstrated above that in typical PAH small molecular systems, how the optical property evolutes during the enlarging of the molecular size. It proves that the absorption could be broadened and the excitation energy could be tuned through taking small molecular plasmonic units as building blocks for large molecular plasmonic systems.

As is well known, in organic electronics, the versatile optical, and electrical property is one of the most advantages of organic semiconductors. Therefore, based on the aimed function, besides the optical property, modifying the PAH molecular structure to tune their carrier transport property would provide the molecular plasmonic large space in device applications [27]. As shown in Fig. 3, by functionalizing with electron-withdrawing groups of pyrene, such as nitrogen atom, oxygen atom and carbonyl (C=O), new materials are obtained NDI-N, NDA and NDI, respectively.

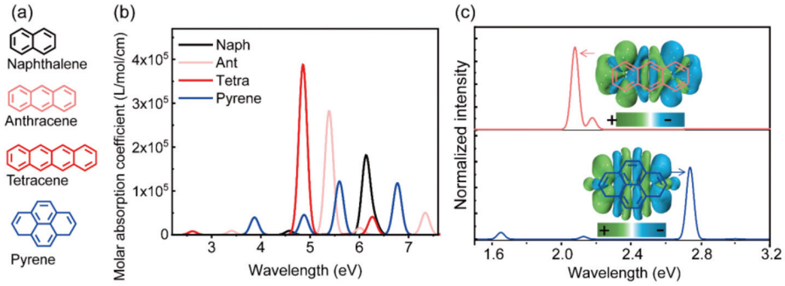

Fig. 1. (a) Chemical structures of PAH molecules. (b) The absorption spectra of the PAH molecules. (c) Photoinduced charge density plots (longitude) and absorption spectra of anthracene and pyrene at their neutral state (gray line) and −1 charged states (red/blue) in the visible range.

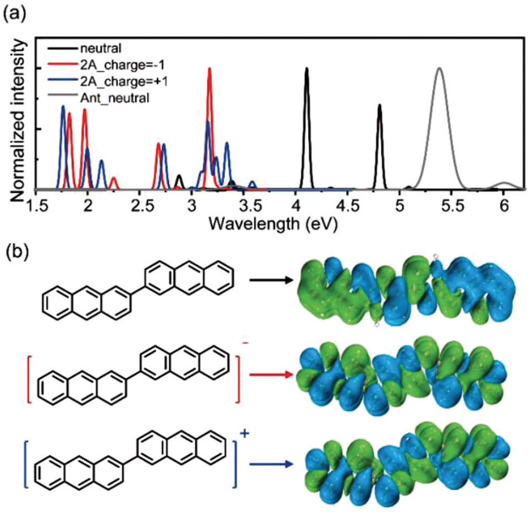

Fig. 2. (a) The photoinduced spectrum of **2A** at neutral, charge −1 and +1 states with a black, red and blue line, respectively. The absorption spectrum of anthracene is gray for comparison. (b) The transition density of the molecular plasmon-like principal peaks of **2A** at neutral (at 4.26 eV) and charged states (at 3.17 eV for charge −1 and 3.16 eV for charge +1).

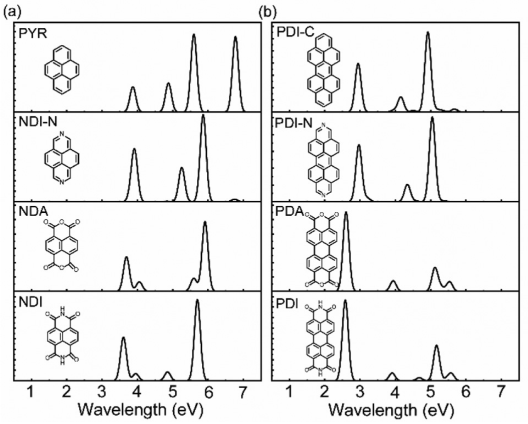

Fig. 3. Plasmonic-like oscillations at visible and UV range for (a) PYR, NDI-N, NDA and NDI in the left column; (b) PDI-C, PDI-N, PDA and PDI in the right column, respectively.

Hence, it gradually transits a typical p-type material (pyrene, PYR) [29,30] to a typical n-type material (NDI) [31–34].

By employing heteroatoms in PAH derivatives, the carrier transport property could be largely tuned. However, the plasmonic-like oscillation induced optical properties are largely reserved as shown in Fig. 3 [22]. The absorption in the visible range is almost kept at around 3.5~4 eV for pyrene, NDI-N, NDA and NDI. The absorption in deep UV range from 6.8 eV in pyrene gradually bathochromic shift to 5.8 eV in NDI. Besides, comparing Figs. 3a and b, when enlarging the hetero-PAH molecular system in the longitude axis direction, their optical property could be tuned in a similar way to the linear PAH molecules. It displays a bathochromic shift in the visible range as the longitude axis length of the molecules increases. From Figs. 3a and b, it can be noticed that the slight difference caused by heteroatoms is weakened during the size increasing in the molecules (Figs. S2 and S3 in Supporting information). Meanwhile, the absorption in the UV range becomes weaker without much shift of the energy of the peak location when prolonging the molecular system.

Therefore, on one hand, it proves that tailoring the molecular structure of the PAH derivatives by employing the electron-deficient groups could realize the tuning of the carrier transportability, the p-type materials transit into n-type material. On the other hand, in those planar π-electron molecular systems, the aromatic-diimide system material largely reserves the molecular plasmonic-like optical property.

High-performance n-type semiconductors are critical components for various organic optoelectronic devices, especially for complementary circuits. Compared with the excellent performance and large option for p-type materials, it is still a long way for n-type materials to catch up with [35]. Recently, NDI has demonstrated good air stability with an adequate electron transport mobility [36] in organic electronic devices. More studies and chemical modifications on its core of it have been conducted to derive the development of n-type semiconductors [37].

It proves in Fig. 3 that NDI and PDI, could support molecular plasmonic-like oscillation in their planar π-electron molecular system (Table S1 and Fig. S4 in Supporting information), like the molecular plasmonics of anthracene (Table S2 in Supporting information). To detect their application potentials in electrochromics, we further calculate the absorption spectra of singly charged linear hetero-modified PAHs with increasing molecular length (from two- to four-unit aromatic rings), as shown in Fig. 4a. The optical property is consistent with the linear PAHs, at neutral states (Fig. 4b). With the increasing size of longitude from NDI to QDI, the photoinduced peaks show a decent and redshift trend, similar to the plasmons in metal nano-rods.

At their −1 charged states (Fig. 4c), the LP and TP decomposition of molecular plasmon-like excitations of NDI, PDI, TDI and QDI indicate the consistent behavior with PAHs plasmonics. The radical anions exhibit a dramatic bathochromic shift compared with their neutral states. In which the principal oscillation energy redshift from 5.8 eV to 2.8 eV (NDI and NDI^{-1}), from 2.8 eV to 2.1 eV (PDI and PDI^{-1}), from 1.7 eV to 1.5 eV (TDI and TDI^{-1}), from 2.1 eV to 1.8 eV (QDI and QDI^{-1}), respectively. Therefore, as n-type semiconductors, the optical property controlled by the plasmonic-like oscillations of the NDI derivatives could be facilely manipulated

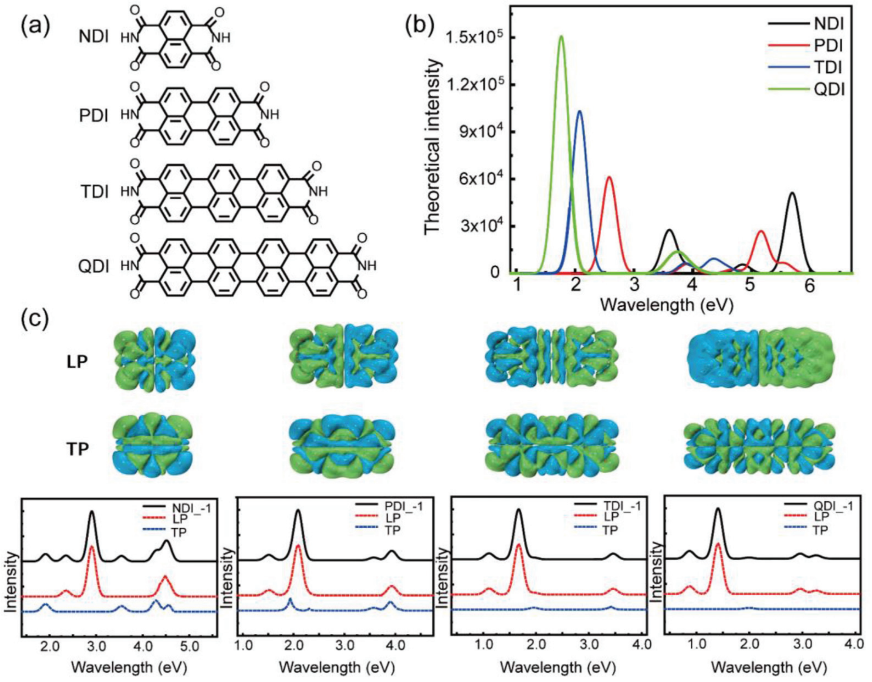

Fig. 4. (a) Chemical structures and (b) computed absorption spectra of NDI, PDI, TDI and QDI. (c) The LP and TP decomposition of molecular plasmon-like excitations at neutral and −1 charged state of NDI, PDI, TDI and QDI. All the results were calculated at TDDFT PBE38/cc-pvtz level and performed with Gaussian 09 package.

through the size of the molecules. This demonstrates a significant space of the molecular plasmonics application in electrochoromic devices and other optoelectronic devices.

In this work, aiming at the application of molecular plasmon-like excitations in electrochromics and optoelectronics, we discuss how the molecular plasmon-like excitations in PAH derivatives are tuned through molecular size and heteroatom-modification from a theoretical perspective. We found that the energy and the intensity of plasmonic-like oscillation could be largely tuned by increasing the conjugation size along both the longitude/transverse axis in PAHs. Besides, the dimeric PAH molecules (**2A**) demonstrates the possibility that molecular plasmonics could be designed using PAHs as building blocks for integration into larger molecular systems. Moreover, this work straightforwardly extends the molecular plasmonic-like property from C–H composed PAHs to much more versatile planar conjugation systems with multi-elements. Thus, typical p-type organic semiconductors could be tuned into n-type organic semiconductors through heteroatom modification. Meanwhile, their molecular plasmonic-like oscillation property is largely preserved, which greatly expands the application prospect of molecular plasmonics in organic optoelectronics. Therefore, with the natural abundance, low cost, easily chemical synthesis of PAH derivatives, we believe this work paves the way for the application of molecular plasmonic-like properties in optical-electrical devices.

Declaration of competing interest

All the authors declare that they have no financial and personal relationships with other people or organizations that can inappropriately influence our work reported in this paper.

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Supplementary materials

Supplementary material associated with this article can be found, in the online version, at doi:10.1016/j.cclet.2022.05.064.

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