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Conjugated Dimeric and Trimeric Perylenediimide Oligomers

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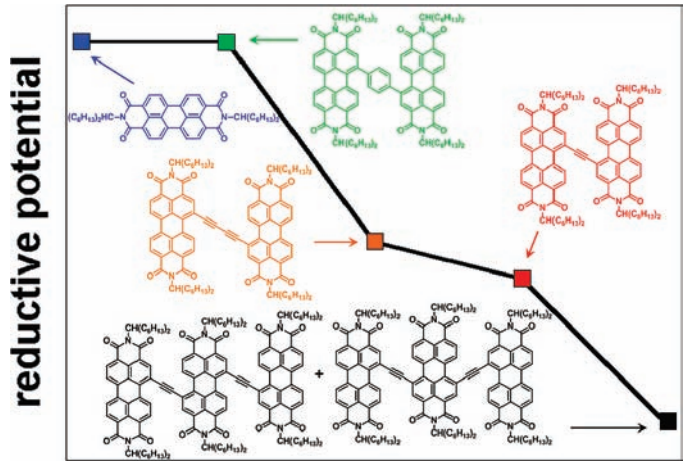
ABSTRACT



Dimeric and trimeric molecules comprising perylenediimide units conjugatively linked by phenylene, ethynylene, or a butadiynylene spacer via the bay positions were prepared. Electrochemical and photophysical characterizations showed that oligomers connected by C−C triple bond(s) exhibited effectively lowered LUMO compared to the monomer. Molecular modeling confirmed that the C−C triple bond realized efficient delocalization of frontier orbitals, while phenylene was less competent in extending the conjugation, partially due to steric interactions.

Perylenediimide (PDI) and derivatives have attracted great attention for their unique optical and electronic properties.[1−3] In particular, they emerged as potent organic electron-transport materials due to the optimal capability in stabilizing and transporting negative charges.[2] The self-assembly of PDI and derivatives into ordered supramolecular structures has also been intensely studied, as the association motif and material morphology strongly influence the optical and electronic properties.[3] Compared with hole-transport materials, developing organic electron-transport semiconductors looms more challenging.[4] To achieve air-stable, organic electron transport materials, lowering the LUMO level of the system is a critical issue. Hence, PDIs with various electron-withdrawing substituents were investigated and exhibited promising electron-transport capacities with the vapor deposition technique.[2c,i−1]

Conceivably, making conjugative polymers of PDI offers a viable approach to solution-processable electron-transport materials. However, as the imide nitrogen atoms of PDI are the nodal points of frontier orbitals,[1a] connecting PDI units through these nitrogen atoms would not disturb the PDI frontier orbitals.[5] On the other hand, attaching various substituents at the bay positions of PDI has proven effective in modifying the frontier orbital levels.[2,6,7]

Herein we carried out an investigation at identifying suitable nonelectron-donating linkers that couple PDI units

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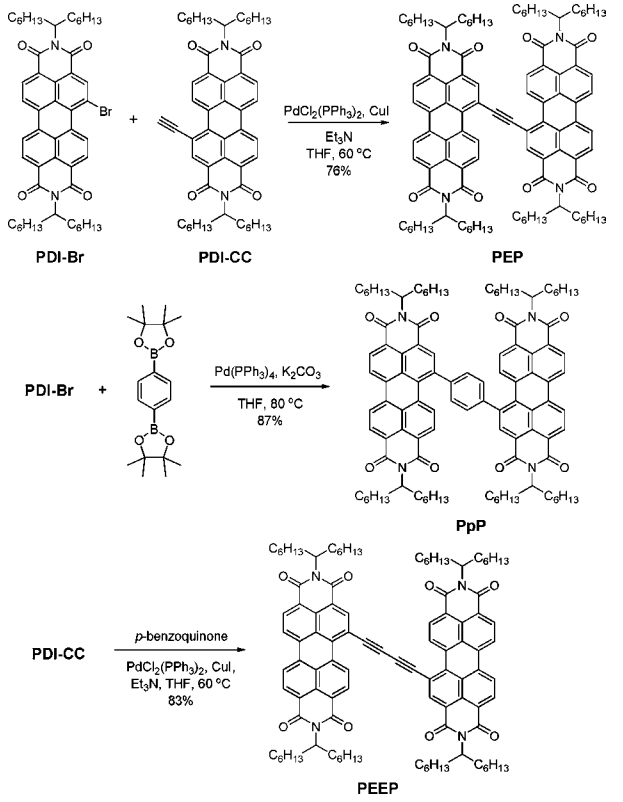
via the bay-positions into elongated conjugative oligomers of defined structures. By employing suitable linkers the LUMO level can be effectively lowered in the oligomer relative to that in the monomer. Additionally, PDI units are known to display a longitude and/or transverse offset when stacking intermolecularly.[1a] With the extended aromatic scaffold the oligomers may accommodate similar displacement while still maintaining significant intermolecular overlapping, which is important for semiconducting performance. Lastly, the oligomers of defined structures may exhibit novel self-assembly behaviors and impart ordered morphology during solution processing. In the current study, three different conjugative linkers, phenylene, ethynylene, and butadiynylene, were examined (Scheme 1). The C−C triple

Scheme 1. Syntheses of PDI Dimers



bond was particularly selected, as compared to the alternative linker, e.g., phenylene, it imposes less steric interaction when tethered to the bay position of PDI and should thus be more favorable for creating conjugated structures.

The three dimers, **PpP**, **PEP**, and **PEEP**, were designed to be prepared from bay-position brominated PDI via Suzuki, Sonogashira, and Glaser coupling[8] reactions, respectively (Scheme 1). Although various palladium-catalyzed cross-coupling involving brominated PDIs were previously reported by a number of research groups,[2m,3f,6,9] our efforts at these dimers were not without challenges. Two important intermediates, 1-bromo-PDI (**PDI-Br**) and 1-ethynyl-PDI (**PDI-CC**), were obtained according to the previously reported literature procedures.[9d] However, our attempts at preparing and isolating oligomers having *N*-cyclohexyl or *N*-2-ethylhexyl side chains were not quite successful. The reason was attributed to the low solubility of the intermediates and products. Thus, "swallow-tailed" 1-hexylhetpyl substituents were then introduced to the imide nitrogen atoms. These side chains indeed greatly improved the solubility and eventually helped realize the syntheses of the target molecules. All three synthesized dimers were soluble in common organic solvents, which also allowed

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(7) A method was recently reported for fusing two or three PDI units via the bay positions, resulting in effectively lowered LUMO: (a) Qian, H.; Wang, Z.; Yue, W.; Zhu, D. *J. Am. Chem. Soc.* **2007**, *129*, 12664. (b) Qian, H.; Qian, Z.; Negri, F.; Wang, C.; Wang, Z. *J. Am. Chem. Soc.* **2008**, *130*, 17970.

(8) A modified Glaser coupling condition as previously reported was used: Williams, V. E.; Swager, T. M. *J. Polym. Sci. Part A: Polym. Chem.* **2000**, *38*, 4669.

(9) For examples, see: (a) Rohr, U.; Schlichting, P.; Böhm, A.; Gross, M.; Meerholz, K.; Bräuchle, C.; Müllen, K. *Angew. Chem., Int. Ed.* **1998**, *37*, 1434. (b) Müller, S.; Müllen, K. *Chem. Commun.* **2005**, 4045. (c) Jiménez, A. J.; Spänig, F.; Rodríguez-Morgade, M. S.; Ohkubo, K.; Fukuzumi, S.; Guldi, D. M.; Torres, T. *Org. Lett.* **2007**, *9*, 2481. (d) Rajasingh, P.; Cohen, R.; Shirman, E.; Shimon, L. J. W.; Rybtchinski, B. *J. Org. Chem.* **2007**, *72*, 5973.

them to be purified with flash column chromatography. It is also noteworthy that although diisopropylamine was an effective base in the Sonogashira reaction preparing 1-trimethylsilylethynyl-PDI (**PDI-CC-TMS**) from **PDI-Br** and trimethylsilylacetylene, offering a nearly quantitative yield as reported in the literature,[9d] when it was used as a base for generating **PEP** and **PEEP** under similar conditions, the reactions gave only moderate yields of 61% and 58%, respectively. Based on a previous study,[10] the reason for the low conversions was suspected to be the nucleophilic substitution of the secondary amine at the brominated PDI at elevated temperatures. Replacing *i*-Pr_2NH with tertiary amine Et_3N indeed improved the reaction yields noticeably (Scheme 1).

Electronic spectra of these dimers in dichloromethane[11] showed that the onset of the absorption bands displayed a bathochromic shift compared to that of the reference compound **PDI** (Figure 1). This suggested effective electronic coupling between the two PDI units in each dimer. Specifically, ethynylene linkage imparted the largest extent of red shift, while the phenylene unit exhibited the minimum effect. Subsequently, cyclic voltammetry (CV) was conducted to assess the LUMO energy of each dimer (Figure 2 and Table 1). Remarkably, the first reductive wave was noticeably shifted toward higher potential value for both **PEP** and **PEEP** compared to that of **PDI**, whereas **PpP** displayed a negligible change.[12] In order to unambiguously confirm that the higher electron affinity of **PEP** and **PEEP** was a result of substantial electronic coupling between the constituting PDI units, rather than merely from attachment of the ethynylene unit, the electrochemical behavior of intermediate **PDI-CC-TMS** was examined. The CV showed that the reductive potential of this intermediate exhibited a much less significant change compared to that of **PEP**. This clearly supports the argument that electronic coupling between the PDI units is substantial and indispensable for the observed electrochemical property change in the oligomers.

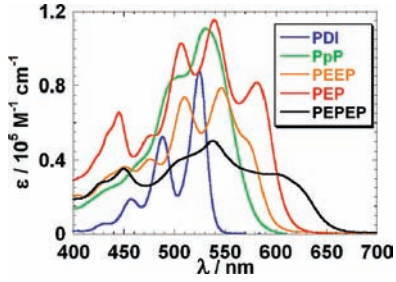

Figure 1. Absorption spectra of **PDI** and its oligomers in dichloromethane (1.0×10^{-6} M).

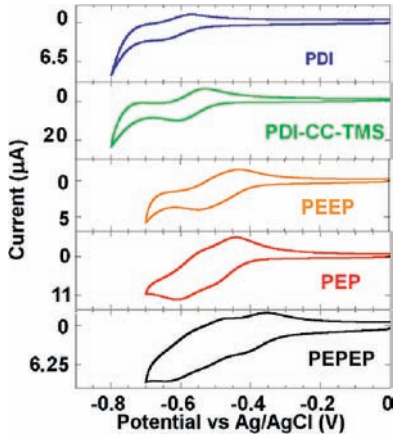

Figure 2. Reductive cyclic voltammograms of PDI oligomers in dichloromethane (1.0×10^{-4} M).

Table 1. Summary of Optical and Electrochemical Data

compd	λ_{abs} (log ε)	reductive half-wave potential (V)[a]
PDI	525 (4.9), 488 (4.7), 457 (4.3)	−0.58
PDI-CC-TMS	536 (5.8), 498 (4.6), 467 (4.2)	−0.56
PpP	531 (5.0), 501 (4.9)	−0.58
PEEP	574 (4.6), 546 (4.9), 510 (4.9)	−0.47
PEP	582 (4.9), 539 (5.1), 507 (5.0)	−0.45
PEPEP	600 (4.5), 538 (4.7)	−0.37

[a] Relative to the Ag/AgCl reference electrode.

Evidently, the ethynylene and butadiynylene linkers lowered the LUMO level relative to that of the monomer, whereas the phenylene spacer was ineffective in decreasing the LUMO. Previous investigations have also found various spacers to differ in their capacity in electronic coupling.[13] The reason for this may be complex. In our system, it was speculated that steric effects may be a particularly important cause for the difference between the phenylene and C−C triple bond(s) linkages. The steric interactions between the attached phenyl ring and the bay-positioned hydrogen atom in its vicinity most likely prohibited the coplanar conformation between the linker and PDI units, resulting in partial disruption of electronic coupling. In contrast, the slimmer C−C triple bond imposed less significant steric repulsion and was thus able to effectively extend the conjugation. Consequently, **PEP** and **PEEP** achieved delocalized frontier orbitals (FOs) and exhibited lowered LUMO level.

This speculation was substantiated by theoretical studies. Based on calculations, the phenylene ring assumed a

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(11) Absorption spectra of the oligomers were recorded at varied concentrations ranging from ca. 10^{-6} to 10^{-4} M in dichloromethane (Figures S9−S12, Supporting Information), and little change was observed with the band shape and extinction coefficient, indicating minimal intermolecular aggregation occurred under such conditions.

(12) For **PEP** and **PEPEP** due to significant overlap of the first and second reductive waves, deconvolution and accurate determination of the half-wave potentials were difficult; these values were estimated from the approximate peak position based on our best judgement and may thus present large errors, but the increasing trend relative to the value of **PDI** was evident.

(13) Barlow, S.; Marder, S. R. *Chem. Commum.* **2000**, 1555. In this review electronic coupling through phenylene groups was shown to be weaker than that through ethynylene units in ferrocene-related systems.

pronounced dihedral angle with the PDI units in the optimized conformation of **PpP**, and the LUMO of the molecule was localized on each individual PDI unit (Figure 3). Quite the opposite for **PEP** and **PEEP**, both LUMO and

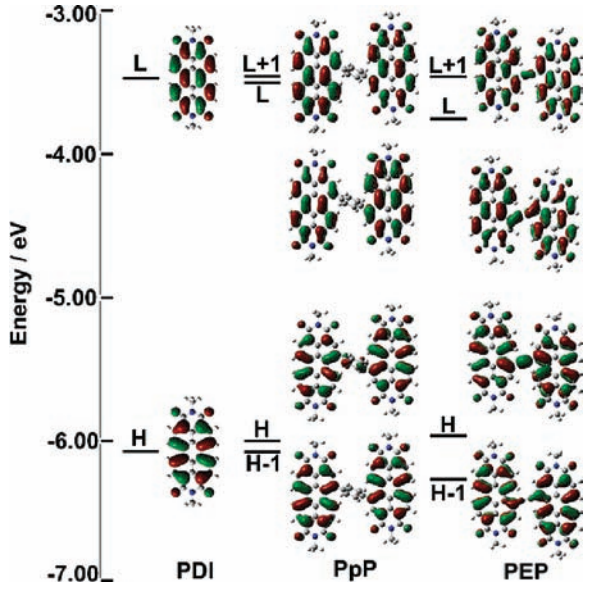
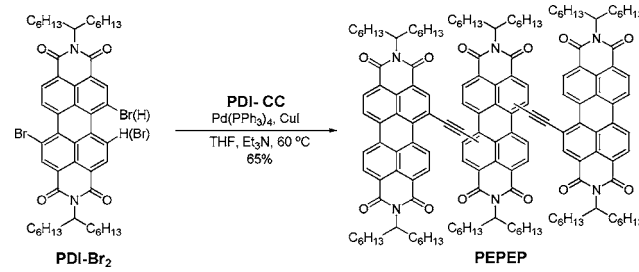


Figure 3. B3LYP/3-21G*-computed FOs of **PDI**, **PpP**, and **PEP** (*N*-hexylheptyl were replaced with *N*-methyl groups in calculations).

HOMO were delocalized over both PDI units and the linker (Figure 3 and Figure S3, Supporting Information). Furthermore, a much larger energy separation was found between the LUMO and LUMO+1 in **PEP** than that in **PpP**. As these orbitals roughly represent the combinations of the LUMOs of the PDI subunits with some linker contributions, a larger splitting also evidenced a more effective interaction. According to the calculations, the corresponding energy separation in **PEEP** is larger than that in **PpP** but smaller than that in **PEP**. Additionally, the fact that the *sp*-hybridized carbon being more electronegative than the sp^2 carbon likely further contributed to the decrease of the LUMO in **PEP** and **PEEP**.

Encouraged by these results, trimer **PEPEP** (Scheme 2) was then synthesized via a double Sonogashira cross-coupling of **PDI-CC** with a regioisomeric mixture of 1,7-

Scheme 2. Synthesis of PDI Trimer



and 1,6-dibromo-PDI.[9d,14] Again, triethylamine gave a higher yield than diisopropylamine in this reaction (65% vs 43%). Based on the absorption spectra and CV (Figures 1 and 2), the LUMO level of **PEPEP** was further decreased relative to that of **PEP**. This result proves that oligomerization of PDI units by conjugatively coupling the bay positions is a viable approach to attaining molecules of lowered LUMO level.

In summary, a number of dimeric and trimeric molecules of PDI units linked by conjugative spacers via the bay positions were prepared. An evident decrease in the LUMO level was achieved with the ethynylene- and butadiynylene-linked oligomers. Both experimental and theoretical studies showed that ethynylene and butadiynylene are suitable linkages to extend the effective conjugation length and delocalize frontier orbitals, while a phenylene unit was disruptive to conjugation, at least partially due to steric effects.

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Supporting Information Available: Syntheses, spectroscopy, CV, thermal stability, and calculation details. This material is available free of charge via the Internet at http://pubs.acs.org.

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(14) 1,7- and 1,6-dibromo-**PDI**s exhibit very similar solubility and polarity and are thus currently unseparable; efforts are being made at indentifying suitable conditions for separating the regioisomers of **PDI-Br$_2$** and **PEPEP**.