Theoretical Design of Low Band Gap Conjugated Polymers through Ladders with Acetylenic Crosspieces

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Received April 4, 2007; Revised Manuscript Received May 29, 2007

ABSTRACT: Building ladder polymers provides an alternative way to design intrinsically low band gap conjugated polymers. Using conventional conjugated polymers, polyacetylene, polydiacetylene and polytriacetylene as sidepieces, we propose a series of novel types of ladder polymers with conjugated acetylenic blocks $(-C\equiv C-)_m$ serving as crosspieces. Periodic boundary conditions density functional calculations are performed to investigate the effect of the acetylenic cross-couplings between the two sidepieces. We predict the band gap of the acetylenic coupled (AC) ladder polymers can be reduced to less than 0.3 eV without doping, significantly reduced compared with the parent sidepiece polymers at the same theoretical level. The effect of varying the length and spacing of the crosspieces along the sidepieces is investigated in order to maximize the effect of the gap reduction. Unusual electronic and optical properties are expected from these series of ladder conjugated polymers.

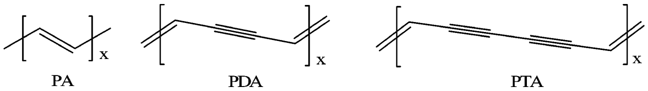
1. Introduction

The search for *intrinsically* low band gap conjugated polymers has been of great interests in the last two decades.[1] Despite numerous efforts from both experimental and theoretical work in the past, the lowest band gap conjugated polymer which has been confirmed to be stable in the undoped form is still poly(isothienonaphthene) (PITN) and its derivatives,[2] with a band gap of about 1.0 eV. There have been reports of conjugated polymers with significantly lower band gaps in the literature,[3] but most of them are believed to be unstable, doped, or contaminated.

Building ladders is an important concept of designing intrinsically low band gap conjugated polymers,[1a,d,e,4] although examples exist in which a completely conjugated ladder polymer exhibits a relatively large band gap.[5] In conjugated polymers, the interaction of π-orbitals of all the repeating units splits the highest-occupied molecular orbital (HOMO) of the corresponding monomer into the highest valence band, and the lowest-unoccupied molecular orbital (LUMO) of the monomer into the lowest conduction band. This interaction reduces the energy gap starting from the monomer, moving to the dimer, trimer, etc., and finally to the polymer. The dual-linked inter-unit cell interactions present in ladder polymers often lead to a much stronger conjugation effect than in the corresponding linear polymers where only a single linkage is present between unit cells. Consequently, the band gap of a ladder polymer may be greatly reduced relative to that of the isolated sidepiece polymer. A famous example for a low band gap ladder-type polymer is polyacene (PAc)[6] which can be viewed as two parallel polyacetylene chains cross-coupled through interchain bonding. However, PAc is an unstable system that has never been made, and therefore, more stable alternatives are being sought.

In this work, we introduce a new family of conjugated ladder polymers which utilize conjugated acetylenic units as crosspieces connecting two parallel sidepiece conjugated polymers. The rigid and sterically undemanding acetylenic rungs in the so-constructed ladder polymers provide strong cross-chain coupling and additional conjugation pathways. In this paper, we performed periodic boundary conditions density functional theory calculations to theoretically explore acetylenic coupled (AC) ladder polymers. Three types of conjugated polymers, polyacetylene (PA), polydiacetylene (PDA), and polytriacetylene (PTA) are used as sidepieces which are shown in Scheme 1. The band gap reduction mechanism of the AC ladder polymers compared with the parent isolated sidepiece polymers are examined.

Scheme 1. Sidepiece Conjugated Polymers: Polyacetylene (PA), Polydiacetylene (PDA), and Polytriacetylene (PTA)



2. Theoretical Calculations

All calculations were carried out using the Gaussian03 program.[7] Periodic boundary conditions (PBC) calculations were performed for the polymers; molecular calculations were performed for the finite oligomers or molecules. We have shown[8,9] that Becke's half and half hybrid scheme[10] of density functional theory (DFT) in the form of BHandHLYP,[7] and the KMLYP hybrid scheme[11] are preferred to accurately predict geometry for carbon chain-like conjugated polymers, such as PA and PDA, over Becke's three parameter hybrid scheme (B3),[12] which underestimates the bond length alternation in these cases.[8,9] Conversely, for conjugated polymers consisting of aromatic repeating units, the B3 hybrid density functional theory provides superior predictions for both the geometry and the energy band gap. This is evident in Table 1, where we used the B3LYP form of the B3 hybrid scheme with the Becke 88 exchange functional[13] and the Lee, Yang, and Parr correlation functional (LYP).[14] The selected test group of conjugated polymers with aromatic repeating units is shown in Scheme 2, including poly(*p*-phenylene) (PPP), polythiophene (PTh), polypyrrole (PPy), poly(*p*-phenylenevinylene) (PPV), poly(thienylvinylene) (PThV), and poly(3,4-ethylenedioxythiophene) (PEDOT). The root-mean-square (rms) deviation of B3LYP theory from experimental band gap values[15a−f] is only 0.099 eV for the selected testing set, which is much better than the

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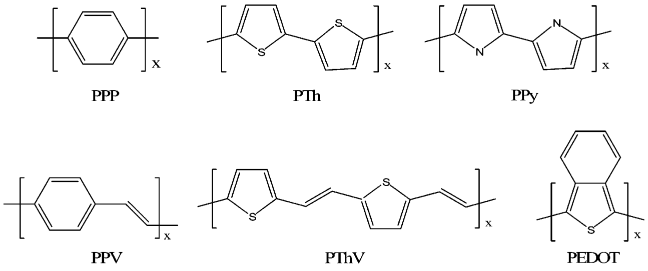
10.1021/ma0708040 CCC: $37.00

Table 1. Theoretical Band Gap (in eV) Predictions for Some Typical Conjugated Polymers Possessing Aromatic Groups at B3LYP and BHandHLYP Levels

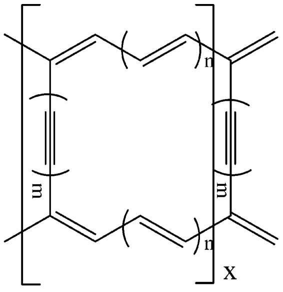
methodology[a]	PPP	PTh	PPy	PPV	PThV	PEDOT	rms
B3LYP//B3LYP	3.076	2.054	2.882	2.443	1.705	1.837	0.099
B3LYP//BHandHLYP	3.153	2.302	3.071	2.588	2.000	2.089	0.296
BHandHLYP//BHandHLYP	4.864	3.930	4.812	4.305	3.631	3.665	1.952
experiment	3.0[15a]	2.0[15b]	2.8[15c]	2.3-2.4[15d]	1.7[15e]	1.6-1.7[15f]	

[a] Methods labeled as "A//B" refer to full geometry optimization at "B" level followed by energy level calculations at "A" level. 6-31G* basis sets are used in all calculations. Numbers of k points in the irreducible Brillouin zones are 79, 44, 48, 52, 30, and 44 for PPP, PTh, PPy, PPV, PThV, PEDOT, respectively.

Scheme 2. Selected Conjugated Polymers Testing Set with Various Aromatic Repeat Units: PPP: Poly(*p*-phenylene); PTh, Polythiophene; PPy, Polypyrrole; PPV, Poly(phenylenevinylene); PThV, Poly(thienylenevinylene); PEDOT, Poly(3,4-ethylenedioxythiophene)



Scheme 3. Schematic Representation of Acetylenic Coupled Polyacetylene Ladder Polymers with Varying Length of Acetylenic Crosspieces (*m*) and Varying Linking Intervals on the Sidepieces (*n*)



[m,n]-ACPAL

performance of the BHandHLYP theory (rms = 1.952 eV) or the combination B3LYP//BHandHLYP (B3LYP band gap calculation at BHandHLYP optimized geometry; rms = 0.296 eV). The acetylenic coupled PA, PDA, and PTA ladder polymers studied in this paper are essentially fused dehydro-[4n+2]-annulene ring systems which are aromatic.[16−18] Therefore, we report all theoretical calculations on AC ladder polymers at the B3LYP/6-31G* level. This selection is further justified in the next section. The k-mesh in all PBC calculations is automatically determined by the Gaussian03 program and is checked to be adequate. Details are listed along with computational results.

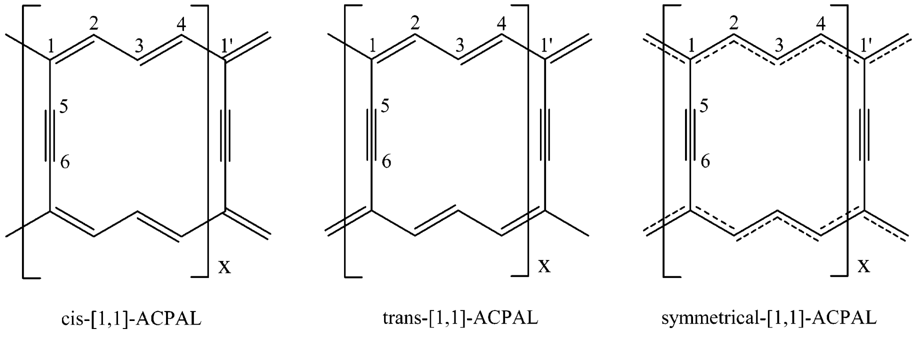
3. Results and Discussions

3.1. Acetylenic Coupled Polyacetylene Ladders (ACPAL).

Polyacetylene (PA) is one of the most studied conjugated polymers. The carbon chain backbone of PA possesses a bond length alternation (BLA) of 0.07−0.09 Å[19] due to Peierls distortion (the distortion of a regular one-dimensional structure with a partially occupied band to give bond alternation or dimerization),[20] leading to an energy band gap of about 1.5−1.8 eV.[19] Acetylenic coupled polyacetylene ladders (Scheme 3, [*m*,*n*]-ACPAL) are fused [4n+2]dehydroannulene polymers which are formed by cross-coupling two parallel PA chains with acetylenic $(-C{\equiv}C-)_m$ bridges at various regular positions. Polyacene might be viewed as a limiting member of the family which can be labeled [0,0]-ACPAL although PAc does not contain any AC unit.

Three canonical forms of ACPAL could contribute to the real structure of the ladder polymer based on the alternating pattern of the PA sidepieces (note that only the *cis* form is illustrated in Scheme 3). The three forms, *cis*, *trans*, and *symmetrical* forms of ACPAL, are exemplified by [1,1]-ACPAL shown in Scheme 4. Computationally we found two minima of [1,1]-ACPAL at B3LYP/6-31G* level near the *cis* and *symmetrical* canonical forms, respectively, as listed in Table 2. We extensively experimented with various starting geometries and all converged to one of the two reported structures. Note that PBC frequency calculations cannot be performed at this level of theory in order to further confirm the two minima. As can be expected, *cis*- and *trans*-[1,1]-ACPAL should have about the same total energy. This can be rationalized by comparing with the case of PAc. The only factor that contributes to the very small energy difference between *cis*- and *trans*-polyacene comes from the third neighbor through space C−C interactions between the two PA sidepieces.[6c] In the case of [1,1]-ACPAL, this factor becomes less important fifth neighbor through space C−C interactions. It is a surprise to find out that the *symmetrical* form of [1,1]-ACPAL also has about the same total energy as the *cis* form, considering the fact that equidistant PA is less stable than its alternating counterpart due to the Peierls distortion. The introduction of a second conjugation dimension to the PA sidepiece with cross-linking apparently leads to the suppression of Peierls distortion. This can be explained as follows. The

Scheme 4. Canonical Forms of the *cis*, *trans*, and *symmetrical* Ladder Polymer [1,1]-ACPAL



cis-[1,1]-ACPAL trans-[1,1]-ACPAL symmetrical-[1,1]-ACPAL

Table 2. Bond Distances and Band Gaps for the Three Minima of [1,1]-ACPAL Ladder Polymer Obtained after Full Geometry Optimization at the B3LYP/6-31G* Level[a]

canonical form	$r_{1,2}$	$r_{2,3}$	$r_{3,4}$	$r_{4,1'}$	$r_{1,5}$	$r_{5,6}$	$\delta r = (r_{2,3} + r_{4,1'} - r_{1,2} - r_{3,4})/2$ (Å)	total energy (au)	band gap (ev)
cis	1.405	1.403	1.379	1.432	1.423	1.221	0.026	−384.5922	0.412
trans	n/a[b]								
symmetrical	1.417	1.392	1.390	1.420	1.422	1.221	0.002	−384.5922	0.312

[a] For PA at the same theoretical level with 138 irreducible *k* points: $r_{1,2} = 1.370$; $r_{2,3} = 1.425$; $\delta r = r_{2,3}-r_{1,2} = 0.055$ Å; band gap is 1.203 eV. Number of *k* points in the irreducible Brillouin zone is 69 for all three configurations. [b] The *trans*- form was optimized to the *cis*- or *symmetrical* forms depending on the initial geometry.

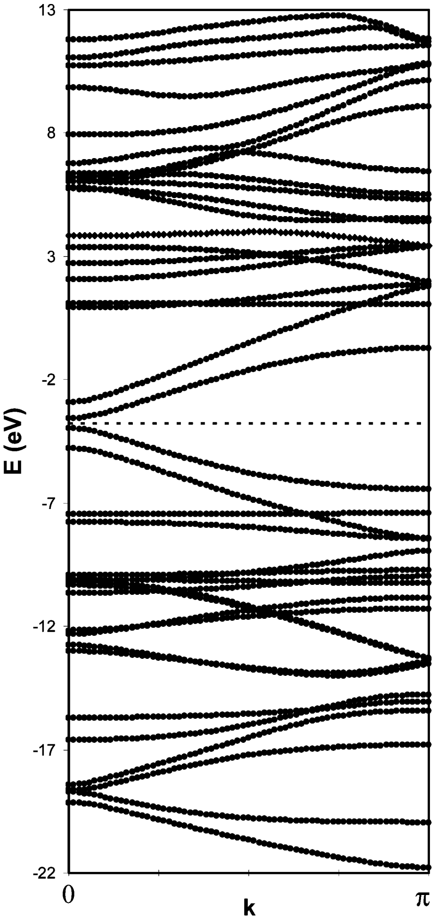


Figure 1. Energy band structure of *cis*-[1,1]-ACPAL at B3LYP/6−31G* theoretical level, with 69 *k* points in the irreducible Brillouin zone. The dotted line in the middle represents the Fermi level.

energy gain of [1,1]-ACPAL through the presumable π-electron Peierls distortion is offset by the energy loss in compressing and stretching of the σ frame, as can be witnessed in Figures 1 and SI-1 by the slight decrease of the sum of occupied π-orbital levels accompanied by the slight increase of the sum of occupied σ-orbital levels when going from the *symmetrical* form to the *cis* or *trans* forms. A similar reason keeps benzene in the high D_{6h} symmetry form relative to the D_{3h} structure.[21,22]

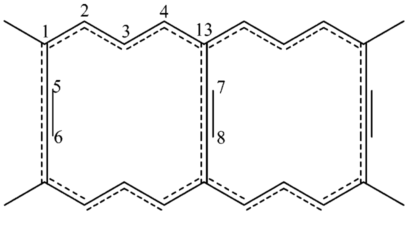
It is interesting to note that all three minima can be located for the [1,*n*]-ACPAL series *only* when $n > 1$ at the B3LYP level. The *symmetrical* form of [1,1]-ACPAL can be located on the potential energy surface at nonhybrid DFT and B3LYP hybrid DFT levels, but not at levels with higher amounts of exact exchange such as hybrid HandHLYP and Hartree−Fock (HF) theory. Detailed results of calculations from other levels of theory are not presented here, because of the higher reliability of B3LYP. For those interested in the modeling of these fused annulenes we note that the *trans* form of [1,1]-ACPAL cannot be found at the B3LYP level but can be located at the HandHLYP level. This implies a rather delicate dependency of small energy differences between these valence isomers on the precise level of theory, especially on the amount of exact exchange incorporated in the various DFT methods used in our calculations. The *symmetrical* form might be artificially favored in the pure (nonhybrid) DFT theory without any addition of exact exchange, or might be artificially disfavored by the pure HF theory which does not account for electron correlation. This strong dependence on the level of theory motivated us to perform further validation of the theoretical methods used. Since ACPAL ladders are not available experimentally, the validation was based on the X-ray structural data of trisdehydro-[10.10.2][14]annuleno[14]annulene (Cambridge Structural Database code: TDHANN),[23] which can be seen as a "dimer" of [1,1]-ACPAL. The results are listed in Table 3, where the labeling refers to Scheme 5. For computational efficiency, methyl groups are used in the theoretical calculations to replace the *tert*-butyl substituents in the experiment. TDHANN has an approximate D_{2h} symmetry both in the experimental data and in the theoretically optimized geometry. In general, all presented theoretical geometries agree well with the experiment data, except that the Møller−Plesset perturbation theory (MP2) is incorrect in the prediction of the bond length alternation pattern

Table 3. Theoretical and Experimental Bond Length (in Å) of Trisdehydro[10.10.2][14]annuleno[14]annulene (TDHANN)[a]

bond	weight	expt	HF	BHandHLYP	B3LYP	BLYP	MP2
$r_{1,2}$	4	1.382	1.345	1.370	1.391	1.407	1.405
$r_{2,3}$	4	1.416	1.444	1.410	1.410	1.415	1.395
$r_{3,4}$	4	1.362	1.339	1.359	1.376	1.388	1.388
$r_{4,13}$	4	1.434	1.462	1.429	1.432	1.441	1.416
$r_{1,5}$	4	1.418	1.434	1.400	1.397	1.400	1.383
$r_{5,6}$	2	1.215	1.197	1.215	1.231	1.244	1.251
$r_{13,7}$	2	1.406	1.345	1.382	1.399	1.410	1.421
$r_{7,8}$	1	1.205	1.235	1.220	1.228	1.238	1.233
$r_{1,23}$	4	1.539	1.510	1.505	1.515	1.527	1.511
A_x (%)			100	50	20	0	n/a
rms (unweighted)			0.033	0.017	0.015	0.020	0.026
rms (weighted)			0.031	0.017	0.015	0.019	0.026

[a] Numbering refers to Scheme 5. Methyl groups are used in the calculations in the place of *tert*-butyl substituents in the experiment. The symmetry group is approximately D_{2h}. Experimental data with weights over 1 are averages. A_x is the percentage of exact exchange incorporated in the theory.

Scheme 5. Structure of Trisdehydro[10.10.2][14]annuleno[14]annulene (TDHANN)

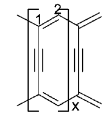
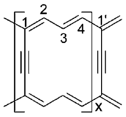
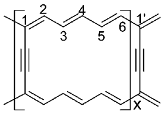


TDHANN

of $r_{1,2}$ and $r_{2,3}$. The B3LYP predictions have the lowest rms deviation, further validating our selection of that level of theory.

As shown earlier in Table 2, the *cis*- and *trans*-[1,1]-ACPAL also have a common band gap of about 0.4 eV, slightly larger than that of the *symmetrical* form which is about 0.3 eV. The band structures of *cis*-[1,1]-ACPAL, *trans*-[1,1]-ACPAL, and *symmetrical* [1,1]-ACPAL at B3LYP/6-31G* level are very similar, with that of the *cis* form shown in Figure 1. Introducing acetylenic cross-coupling as in [1,1]-ACPAL effectively reduces the band gap from 1.2 eV for isolated PA chains at the same theoretical level[8,9] to about 0.3−0.4 eV for the ladder. This reduction is partly due to the geometry relaxation of the PA sidepieces as a response to the cross-coupling, and partly due to the orbital mixing between the sidepieces and the AC steps of the ladder. The former is evident in Table 2 as the bond length alternation is significantly reduced from PA to ACPAL. The latter is illustrated in Scheme 6, where the development of the gap for *cis*-[1,1]-ACPAL is illustrated in the orbital interaction diagram. There are four frontier orbitals originating from the highest occupied crystal orbital (HOCO) and the lowest unoccupied crystal orbital (LUCO) of two parallel PA sidepieces. By bringing the two isolated PA sidepieces closer as in the ladder, and due to the introduction of the acetylenic cross-coupling, these orbitals evolve into HOCO-1, HOCO, LUCO and LUCO+1 of [1,1]-ACPAL. The small energy differences within each of the two pairs on the right are due to the small through space interactions between the two PA sidepieces before the rungs are inserted. The HOCO of ACPAL is destabilized due to the out-of-phase interaction between the fragment orbitals of acetylenic bridges and those of the sidepieces. Conversely, the LUCO of ACPAL is stabilized due to the in-phase interaction between them. Therefore, the band gap of ACPAL is reduced relative to that of PA with the bond length alternation at the relaxed geometry of ACPAL.

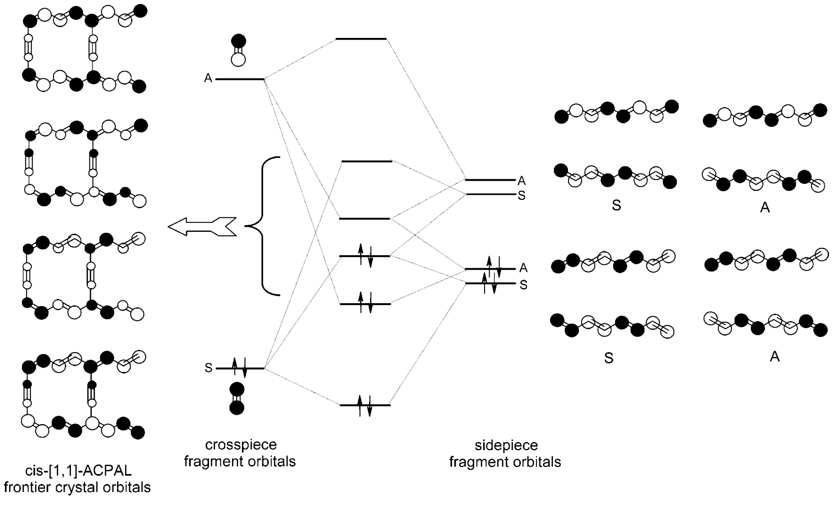
Table 4. Optimized Geometry and Energy Band Gap of *cis*-[1,*n*]-ACPAL ($n = 0,1,2$) at B3LYP/6-31G* Theoretical Level[a]

System	Bond length (Å)	δr (Å)	Band gap (eV)
 [1,0]-ACPAL	$r_{1,2}$=1.433 $r_{2,3}$=1.435	0.002	0.403
 [1,1]-ACPAL	$r_{1,2}$=1.405 $r_{2,3}$=1.403 $r_{3,4}$=1.379 $r_{4,1'}$=1.432	0.026	0.412
 [1,2]-ACPAL	$r_{1,2}$=1.397 $r_{2,3}$=1.409 $r_{3,4}$=1.378 $r_{4,5}$=1.418 $r_{5,6}$=1.370 $r_{6,1'}$=1.441	0.041	0.596

[a] When $n \to \infty$, the system becomes essentially polyacetylene, δr= 0.055 Å and band gap is 1.203 eV, at the same theoretical level. Numbers of k points in the irreducible Brillouin zones are 134, 69, and 47 for n = 0, 1, 2, respectively. δr is the average bond length difference between adjacent single and double bonds along the side polyacetylene chain.

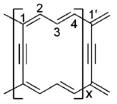
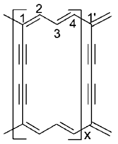
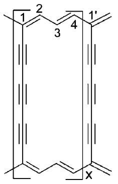
To study the effect of the spacing of the acetylenic crosspieces on the band gap of the ladder, we investigated a series of [1,*n*]-ACPAL (n = 0, 1, 2) ladders with various linking intervals. We only present the *cis* forms of the ladders in Table 4 since the *trans* and *symmetrical* forms have similar band gaps. The first of this series, *cis*-[1,0]-ACPAL, could be unstable and subject to neighboring acetylene-to-acetylene cross-linking as a result of the short distance between them. Nevertheless, study of this series can shed some light on the effect of changing coupling positions along the PA sidepieces. With n increasing there are less acetylenic bridges that couple the PA sidepieces, and as a result the coupling effect decreases. The reduction of bond length alternation from isolated PA sidepieces becomes less significant. In addition, due to the increase in the number of PA chain atoms in the unit cell of the ladder with increasing n, the orbital coefficient of the PA chain atoms at the cross-coupling (atom 1 in Table 4) position decreases. This results in less efficient orbital overlap between the sidepieces and the crosspieces, and in turn less band gap reduction through orbital interaction, as shown in Scheme 6. When $n \to \infty$, the coupling effect is negligible and the ladder system becomes essentially

Scheme 6. Orbital Interaction Diagram of *cis*-[1,1]-ACPAL Corresponding to the $k = 0$ Point of the Brillouin Zone (see Figure 1)[a]



[a] S and A refer to the symmetry relative to the reflection through the plane bisecting the two side chains.

Table 5. Optimized Geometry and Energy Band Gap of *cis*-[m,1]-ACPAL (m = 1,2,3) at B3LYP/6-31G* Theoretical Level[a]

System	$r_{1,2}$ (Å)	$r_{2,3}$ (Å)	$r_{3,4}$ (Å)	$r_{4,1'}$ (Å)	$\delta r=(r_{2,3}+r_{4,1'}-r_{1,2}-r_{3,4})/2$ (Å)	Band gap (eV)
 [1,1]-ACPAL	1.405	1.403	1.379	1.432	0.026	0.412
 [2,1]-ACPAL	1.398	1.411	1.374	1.438	0.038	0.497
 [3,1]-ACPAL	1.396	1.412	1.373	1.440	0.042	0.557

[a] When $m \rightarrow \infty$, the crosspieces become essentially isolated polyyne chains with a band gap of 1.487 eV, and the sidepieces become essentially isolated PA chains with a bond length alternation of 0.055 Å and a band gap of 1.203 eV, at the same theoretical level.[9] Number of k points in the irreducible Brillouin zone is 69 for all three systems.

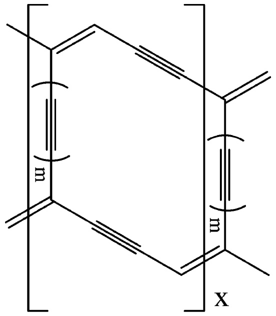
two individual PA chains with bond length alternation δr = 0.055 Å and band gap 1.203 eV, at the same theoretical level.[9] In conclusion, with the smallest n in this series, *cis*-[1,0]-ACPAL maximizes the acetylenic coupling effect with a maximally reduced band gap of about 0.4 eV. However, the more realistic *cis*-[1,1]-ACPAL has a similarly small band gap.

The same argument can be applied to the *cis*-[m,1]-ACPAL series listed in Table 5 which shows the dependency of the band gap on the length of the oligoacetylenic crosspieces (m = 1, 2, 3). In analogy to the *cis*-[1,n]-ACPAL series, the strength of the cross-coupling is maximal when m is the shortest, m = 1. *Cis*-[1,1]-ACPAL has the smallest bond length alternation of 0.026 Å and a lowest band gap of 0.412 eV in this series. On the other hand, at minimal cross-coupling limit when $m \rightarrow \infty$, the crosspieces become essentially isolated polyyne chains with a band gap of 1.487 eV,[9] and the sidepieces become essentially isolated PA chains with a bond length alternation of 0.055 Å and a band gap of 1.203 eV,[9]at the same theoretical level.

In summary, the acetylenic coupling strength is maximized with smallest m and n of [m,n]-ACPAL ladders. Polyacene or-[0,0]-ACPAL is the low band gap limit of [m,n]-ACPAL series. Because of the stability concerns of PAc and [1,0]-ACPAL, we propose [1,1]-ACPAL as the most promising low band gap acetylenic coupled polyacetylene ladder polymers in this series. Note that the acetylenic coupling effect is very efficient in reducing the gap for all [m,n]-ACPAL studied here. The bond length alternation along the sidepiece chain and the band gap of the ladders do not vary much with m and n which provides flexibility in pursuing low band gap ACPAL ladders experimentally.

3.2. Acetylenic Coupled Polydiacetylene Ladders (ACPDAL). Similar as ACPAL, acetylenic coupled polydiacetylene ladders (ACPDAL) can be designed by using polydiacetylene (PDA) polymers as sidepieces. Scheme 7 illustrates [m]-ACPDAL with varying length of the oligoacetylenic crosspieces, m. They are all fused [4n+2]dehydroannulene polymers with larger degrees of dehydrogenation than their ACPAL counterparts. On the basis of the above analysis, the band gap of the ACPDAL ladders will be greatly reduced relative to PDA by the acetylenic cross-couplings. [1]-ACPDAL is expected to have the smallest bond length alternation in the PDA sidepieces and have the lowest band gap. This is verified in Table 6, where theoretical calculations on [m]-ACPDAL ladders with m = 1, 2, 3 are listed together with PDA. The energy band structure and the four frontier crystal orbitals of [1]-ACPDAL are shown in Figure 2. At the B3LYP/6-31G* level, the band gap is 0.683 eV, compared with 1.690 eV for the isolated PDA chain at the same theoretical level. As in the ACPAL ladders, the frontier orbitals of [1]-ACPDAL are also strongly affected by the acetylenic coupling: the HOCO is destabilized while the LUCO is stabilized due to the fragment orbital interactions between sidepieces and crosspieces. This, together with a reduced bond length alternation from that of the PDA sidepieces, leads to a dramatically reduced band gap.

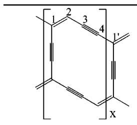
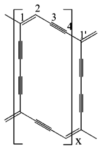
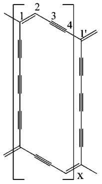
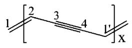
Scheme 7. Schematic Representation of Acetylenic Coupled Polydiacetylene Ladder (ACPDAL) Polymers with Varying Lengths of Acetylenic Crosspieces (m)



[m]-ACPDAL

We are encouraged to find that [2]-ACPDAL has been synthesized by Okada et al.[24] through spontaneous solid-state polymerization of tetracontahexayne at ambient temperature, which they called LPDA (ladder PDA). The ladder formation was not complete, and the band gap was not determined. The absorption spectrum of the ladder polymer shows various features down to about 1 eV which was the lower limit of the experiment, thus an even smaller intrinsic gap cannot be ruled out. The spins in these ladder polymers have been extensively

Table 6. Optimized Geometry and Energy Band Gap of [*m*]-ACPDAL (*m* = 1, 2, 3) and PDA at B3LYP/6-31G* Theoretical Level[a]

System	$r_{1,2}$ (Å)	$r_{2,3}$ (Å)	$r_{3,4}$ (Å)	$r_{4,1'}$ (Å)	$\delta r = (r_{2,3} + r_{4,1'} - r_{1,2} + r_{3,4})/2$ (Å)	Band gap (eV)
 [1]-ACPDAL	1.391	1.389	1.225	1.409	0.091	0.683
 [2]-ACPDAL	1.390	1.390	1.224	1.412	0.094	0.792
 [3]-ACPDAL	1.390	1.391	1.224	1.411	0.094	0.858
 PDA	1.368	1.401	1.224	1.401	0.106	1.690

[a] Number of *k* points in the irreducible Brillouin zone is 70 for all systems.

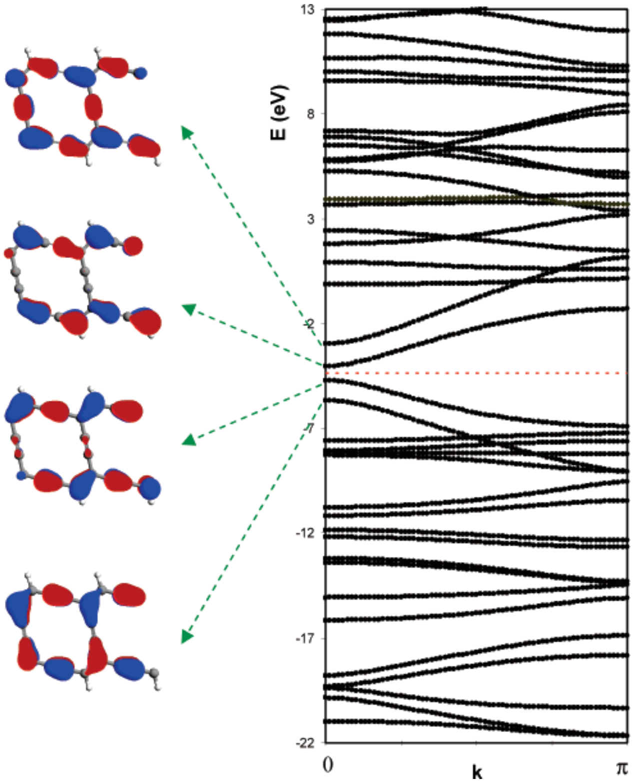
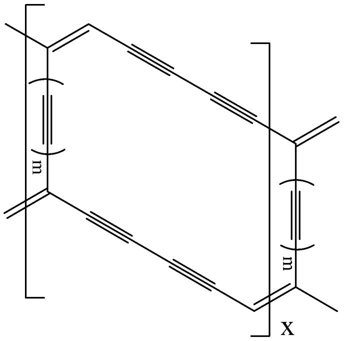


Figure 2. Band structure and frontier orbitals (including two unit cells) of [1]-ACPDAL at B3LYP/6−31G* theoretical level, with 69 *k* points in the irreducible Brillouin zone. The dotted line in the middle represents the Fermi level.

studied using various electron paramagnetic resonance (EPR) methods for its novel magnetic properties.[25] At B3LYP/6-31G* level, we predict that the band gap of [2]-ACPDAL is 0.792 eV, slightly larger than [1]-ACPDAL but much smaller than that of the parent single chain PDA.

3.3. Acetylenic Coupled Polytriacetylene Ladders (ACPTAL). Utilizing polytriacetylene as sidepiece backbones, acetylenic coupled polytriacetylene ladders ([*m*]-ACPTAL) can be designed as shown in Scheme 8, with *m* representing the length of the oligoacetylenic steps. The band structure and frontier orbitals of the first member [1]-ACPTAL are shown in Figure 3. At the B3LYP/6-31G* theoretical level, the band gap of [1]-ACPTAL is predicted to be 0.999 eV, a value significantly lower than the band gap of 1.799 eV for an isolated PTA chain at the same theoretical level. This gap reduction is in line with the rest of the presented calculations. The gap of [1]-ACPTAL is larger than the corresponding value for [1]-ACPDAL in concordance with the larger spacing of the acetylenic coupling units.

Scheme 8. Schematic Representation of Acetylenic Coupled Polytriacetylene Ladder (ACPTAL) Polymers with Varying Lengths of Acetylenic Crosspieces (*m*)



[m]-ACPTAL

4. Conclusions

We proposed a new series of low band gap PA, PDA, and PTA conjugated ladder polymers which are formed by cross-coupling the above conjugated polymers through acetylenic steps. The band gap of the acetylenic coupled ladder polymers are greatly reduced relatively to those of the parent sidepiece polymers, while the large bandwidths necessary for electron and hole delocalization are maintained. This strategy is different

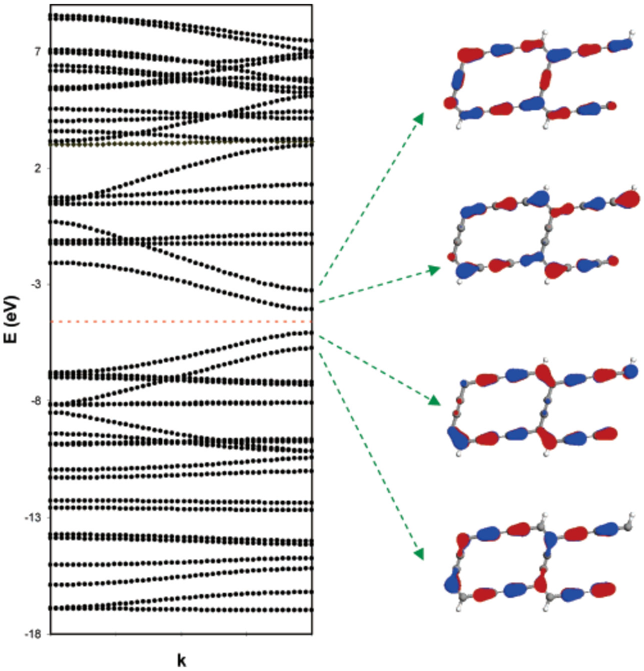


Figure 3. Band structure and frontier orbitals (including two unit cells) of [1]-ACPTAL at the B3LYP/6−31G* theoretical level, with 46 *k* points in the irreducible Brillouin zone. The dotted line in the middle represents the Fermi level.

from the design and synthesis of planarized conjugated polymers.[26] The presented design of acetylenic cross-coupling leads to geometry relaxation on the sidepiece polymers resulting in a reduction of the bond length alternation, and leads to the increase of HOCO and decrease of LUCO energy levels through sidepiece-crosspiece orbital interactions. Both contribute to the reduction of the band gap. The effect shows systematic variations as a function of the spacing and length of the lining units. The stronger the acetylenic cross-coupling, the more significant is the reduction of the band gap from the sidepiece polymers to the corresponding ladders. This dependence can be utilized to fine-tune the band gaps and other properties of the resulting ladder polymers.

The success in the synthesis of one member of the AC ladder polymer series,[2]-ACPDAL,[25] indicates the viability of our theoretical design. The AC ladder conjugated polymers are expected to have small band gaps and other associated unusual electronic[27] and optical[28] properties, which could be further modified through substitutions.

Acknowledgment. Support from the National Science Foundation (Grant No. DMR-0331710) is gratefully acknowledged.

Supporting Information Available: Figure SI-1, showing the energy differences between all the 33 occupied σ and π energy levels of *cis*-[1,1]-ACPAL and *symmetrical* [1,1]-ACPAL at the Γ point, and tables of calculation results including total energies and Cartesian coordinates of all studied materials. This material is available free of charge via the Internet at http://pubs.acs.org.

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MA0708040