

Multichannel Conductance of Folded Single-Molecule Wires Aided by Through-Space Conjugation**

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Abstract: Deciphering charge transport through multichannel pathways in single-molecule junctions is of high importance to construct nanoscale electronic devices and deepen insight into biological redox processes. Herein, we report two tailor-made folded single-molecule wires featuring intramolecular π - π stacking interactions. The scanning tunneling microscope (STM) based break-junction technique and theoretical calculations show that through-bond and through-space conjugations are integrated into one single-molecule wire, allowing for two simultaneous conducting channels in a single-molecule junction. These folded molecules with stable π - π stacking interaction offer conceptual advances in single-molecule multichannel conductance, and are perfect models for conductance studies in biological systems, organic thin films, and π -stacked columnar aggregates.

The rational design of robust molecular wires that are able to construct reliable single-molecule junctions is fundamental to nanoscale electronics.^[1,2] The conductance study of single-molecule wires is also conducive to understanding the diverse electronic properties in biological systems. So far, the widely studied artificial single-molecule wires can be roughly classified into two broad categories according to totally different conjugation patterns. One is through-bond conjugated rod-

like molecules,^[3-9] such as fully conjugated oligo(phenylene vinylene)s (OPVs)^[10] or less conjugated oligophenylenes,^[11,12] and the other is represented by paracyclophanes^[13-16] featuring through-space conjugation between π -stacked benzene rings. Most single-molecule junctions in the literatures are of single-channel conductance realized by either through-bond or through-space conjugated molecules. However, those with complementary multiple conducting channels, which can improve the conductance and stability of molecular devices, are really rare, due to the lack of capable molecular wires.

The multichannel single-molecule wires are inspired by a folded molecule (*Z*)-*o*-BPTPE containing a pair of well π -stacked biphenyls tethered by a vinyl group.^[17] In comparison with the spontaneously formed π - π stacking in molecular junctions,^[18-20] whose stacking geometry is extremely difficult to control, the π - π stacking in (*Z*)-*o*-BPTPE is rigidified and greatly stabilized, and shows advantage to produce more reliable and reproducible single-molecule junctions. The π -stacked region in (*Z*)-*o*-BPTPE is extended, being about two-fold larger than that in paracyclophane. And the vinyl group that holds two biphenyls together is more favorable than the alkyl chain in paracyclophane in terms of electronic conductivity. These merits encourage us to design new single-molecule wires utilizing (*Z*)-*o*-BPTPE as a core part. Grafting two pyridines as terminal anchors onto (*Z*)-*o*-BPTPE enables the molecule to efficiently attach to metal electrodes, usually gold, and form a metal-molecule-metal junction.^[21] The chemical structures of generated folded molecules *f*-TPE-PPy and *f*-TPE-PEPy are shown in Figure 1a. Two linear counterparts *l*-TPE-PPy and *l*-TPE-PEPy are also prepared and investigated as control (Scheme S1).

Crystallographic analyses on single crystals of *f*-TPE-PPy and *f*-TPE-PEPy grown from THF/methanol mixtures reveal that both molecules adopt a folded conformation (Figure 1b), inherited from (*Z*)-*o*-BPTPE-based intermediates (Figure S1). Taking *f*-TPE-PPy for example, its two biphenyls are located in a face-to-face, slightly displaced manner, and the shortest distances between two stacked phenyl rings are about 3.1 Å, which are much shorter than the typical distance for π - π stacking interactions (3.5 Å), implying efficient π -orbitals overlap and electronic coupling between π -stacked biphenyls. Such well-defined folded structures that bring two π -conjugated fragments into close proximity are well indicative of through-space conjugation.^[13-16] The central vinyl bridge that links to the *ortho*-positions of two biphenyls is highly twisted out of the planes of biphenyls, which should impair the efficient π -orbital overlap between biphenyl and central vinyl groups. The through-bond conjugation of the

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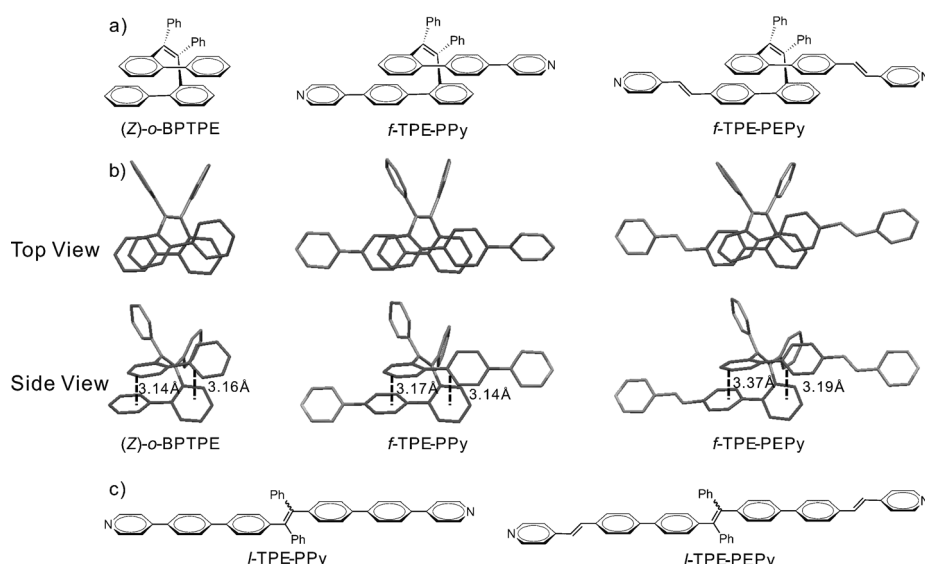


Figure 1. a) Chemical structures and b) top and side views of crystal structures of (Z)-o-BTPE (CCDC 955718), *f*-TPE-PPy (CCDC 1030245) and *f*-TPE-PEPy (CCDC 1030246). Hydrogens are omitted for clarity. c) Chemical structures of *l*-TPE-PPy and *l*-TPE-PEPy.

entire molecular backbones of *f*-TPE-PPy and *f*-TPE-PEPy is thus weakened in the position of central vinyl.

The comparative study on absorption property of folded and linear molecules supports our hypothesis (Figure 2a). For example, *f*-TPE-PPy shows a most significant absorption band peaking at 282 nm, and a low-energy absorption tail, which is similar to paracyclophanes.^[22,23] However, the absorption spectrum of *l*-TPE-PPy is strongly red-shifted, with a main absorption peak at 301 nm and a shoulder at 342 nm. In general, the origins of short- and long-wavelength absorption bands are associated to the transitions from ground (S_0) state to second (S_2) and first (S_1) excited states, respectively.^[22] The S_2 state of *f*-TPE-PPy is primarily localized on the biphenyl-pyridine fragment, whereas the S_1 state is delocalized onto the entire molecular backbone, attributed to the electronic communication across the vinyl group and/or transannular gap. Likewise, *f*-TPE-PEPy shows a main absorption peak at

323 nm, which is close to the absorption maximum of the biphenyl-vinyl-pyridine fragment (325 nm),^[24] suggesting this absorption band is associated with the S_0 – S_2 transition. The low-energy absorption from S_0 – S_1 transition is hardly detectable for *f*-TPE-PEPy. This is presumably attributed to the extended conjugation of the biphenyl-vinyl-pyridine fragment; thus a lower energy level of the S_2 state. The absorption band of weak S_0 – S_1 transition could be covered by strong S_0 – S_2 one in the absorption spectrum by virtue of a smaller energy difference between the S_1 and S_2 states in *f*-TPE-PEPy than in *f*-TPE-PPy. Owing to the lower energy of the S_1 state, absorption into the S_2 state is followed by internal conversion to the S_1 state; thus the emission from S_1 – S_0 transition is dominated by the contribution of entire folded molecules.

Excited by absorption maximum, *f*-TPE-PPy and *f*-TPE-PEPy display photoluminescence (PL) peaking at 485 and 488 nm in THF solutions, being blue-shifted by only 17 and 14 nm compared to those of *l*-TPE-PPy (502 nm) and *l*-TPE-PEPy (502 nm; Figure 2b). The extremely large Stokes shifts of 203 and 165 nm for *f*-TPE-PPy and *f*-TPE-PEPy further evidence their weak through-bond conjugation but efficient through-space conjugation.^[22,23] Since the folded molecules are much more rigid than the linear counterparts,^[25] their PL efficiencies are greatly enhanced in solutions (Table 1), owing to the suppression of intramolecular motions.

The theory calculation discloses that the frontier electronic orbitals of folded molecules are mainly confined to the biphenyl-pyridine or biphenyl-vinyl-pyridine fragments but the central vinyl group shows almost no contribution (Fig-

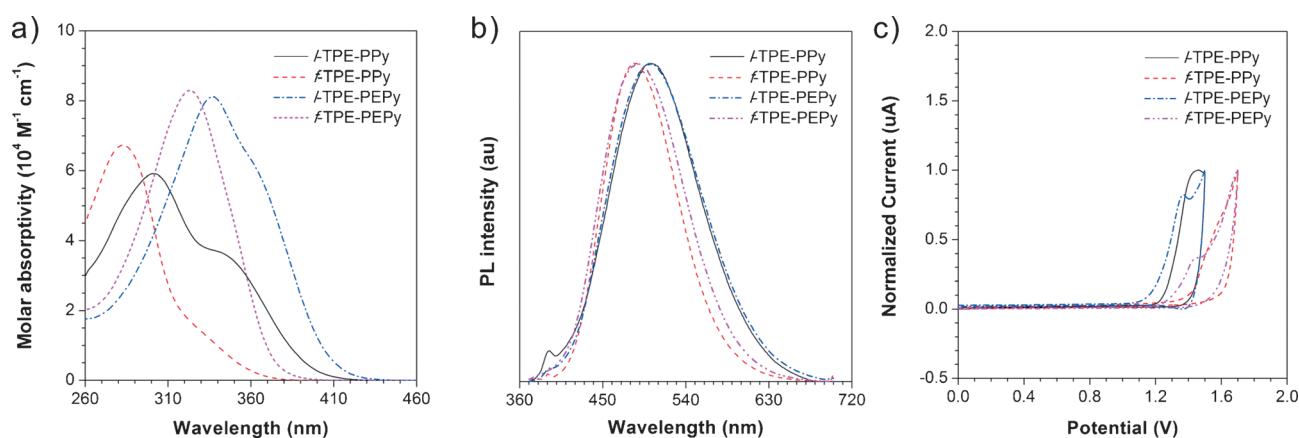


Figure 2. a) Absorption and b) PL spectra, and c) cyclic voltammograms of folded and linear molecules. Absorption and PL spectra were measured in THF (10^{-6} M).

Table 1: Photophysical properties, energy levels, and single-molecule conductance of *f*-TPE-PPy, *f*-TPE-PEPy, *l*-TPE-PPy, and *l*-TPE-PEPy.

Compound	λ_{abs} [nm]	λ_{em} [nm]	$\Phi^{\text{[a]}}$ [%]	Theoretical energy level			Experimental energy level [eV] ^[c]			Conductance [nS]
				HOMO	LUMO	E_g	HOMO	LUMO	$E_g^{\text{[d]}}$	
<i>f</i> -TPE-PPy	282	485	45.7	−5.77	−1.81	3.96	−5.80	−2.61	3.19	1.40
<i>f</i> -TPE-PEPy	323	488	46.2	−5.73	−2.25	3.48	−5.70	−2.68	3.02	0.50
<i>l</i> -TPE-PPy	301 (342)	502	1.2	−5.66	−2.06	3.60	−5.66	−2.82	2.84	1.50
<i>l</i> -TPE-PEPy	337 (360)	502	1.5	−5.59	−2.34	3.25	−5.59	−2.85	2.74	0.55

[a] Absolute fluorescence quantum yield, measured in THF solution (10^{-6} M) by an integrating sphere.

[b] Calculated by B3LYP/6-31G(d). [c] Determined by cyclic voltammetry. [d] Optical band gaps calculated from the absorption onset.

ure S2), which confirms that the through-bond conjugation of the entire twisted backbone is lowered. Hence, *f*-TPE-PPy and *f*-TPE-PEPy show lower HOMO energy levels and larger HOMO–LUMO gaps than the linear counterparts (Table 1), which agrees with the experimental data determined by cyclic voltammetry (Figure 2c). To deepen the insight into through-space conjugation in a more quantitative fashion, calculation is further carried out on the central (*Z*)-*o*-BPTPE segment that serves as the kernel for *f*-TPE-PPy and *f*-TPE-PEPy. The frontier orbitals ranging from HOMO−2 to LUMO+2 are presented in Figure 3a. The HOMO of (*Z*)-*o*-BPTPE is dominated by the orbitals of two biphenyls and the vinyl group. In contrast, the LUMO+1 is formed only by the orbitals of two biphenyls, without contribution from the vinyl group, clearly demonstrating considerable bonding character in the inter-ring region of two biphenyls, which can be referred as through-space conjugation.

The conductance of these molecules in single-molecule junctions was measured by the STM-based break-junction technique.^[26] In Figure 4, the curves of conductance versus

displacement show plateaus during elongation below the quantum conductance G_0 ($G_0 = 2e^2h^{-1}$, in which e is the charge on an electron, and h is Planck's constant), which provides a signal of junction formation. To determine the conductance of each molecule in a statistically significant manner, a one-dimensional (1D) histogram is created for traces measured. A pronounced conductance peak that indicates the most prevalent molecular junction con-

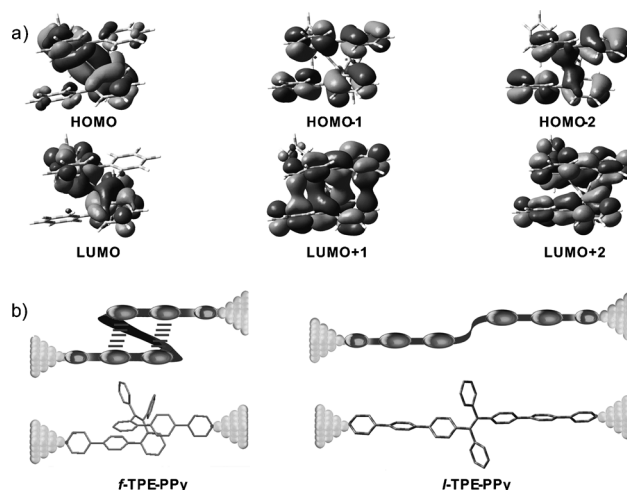


Figure 3. a) Frontier molecular orbitals ranging from HOMO−2 to LUMO+2 of (*Z*)-*o*-BPTPE. b) Representation of circuits of *f*-TPE-PPy and *l*-TPE-PPy anchored onto gold electrodes.

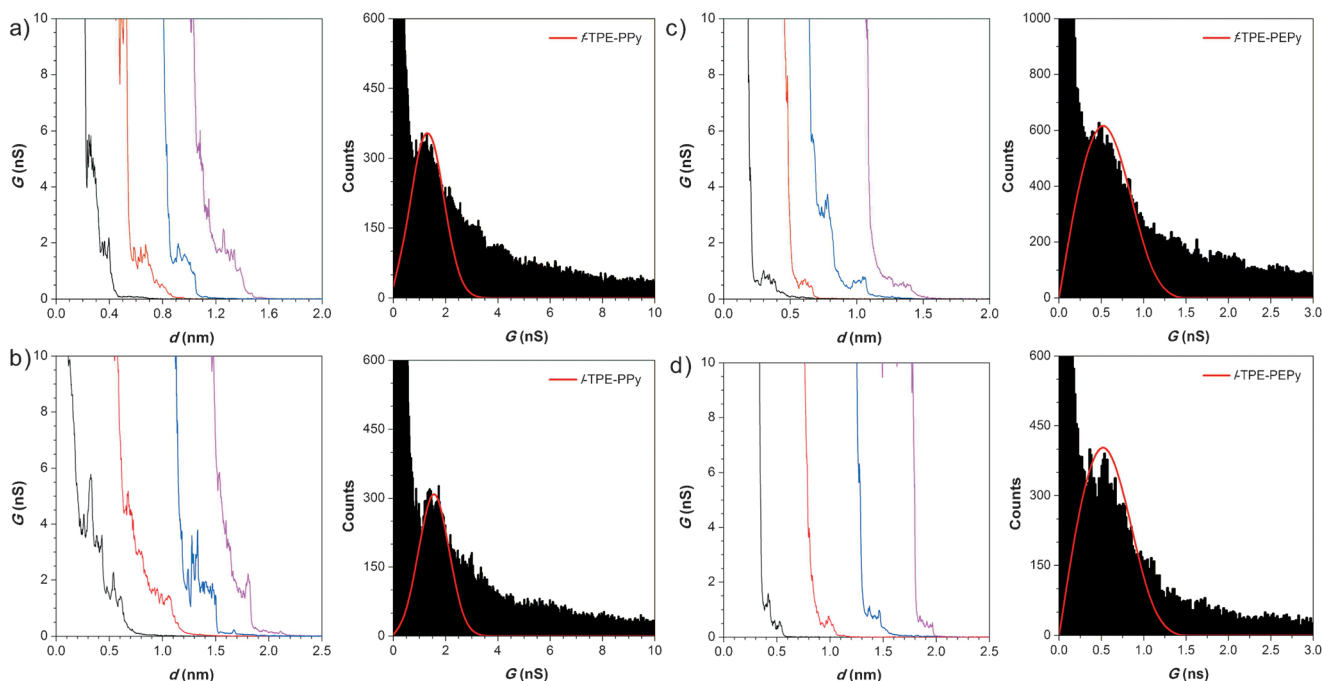


Figure 4. Conductance–distance curves, and 1D conductance histograms of a) *f*-TPE-PPy, b) *l*-TPE-PPy, c) *f*-TPE-PEPy, and d) *l*-TPE-PEPy.

ductance appears at 1.40 nS in the 1D histogram of *f*-TPE-PPy, which is comparable to that of better conjugated *l*-TPE-PPy (1.50 nS). Analogously, *f*-TPE-PEPy shows a nearly equal conductance (0.50 nS) to that of *l*-TPE-PEPy (0.55 nS). Similar results can also be found in the two-dimensional histograms (Figure S3).

The nonresonant tunneling process^[7–9] is generally considered as the main electrical conduction mechanism in π -conjugated rod-like rigid molecules, an important feature of which is the length dependence of the conductance.^[3] The lengths of through-bond conjugation of *f*-TPE-PPy and *f*-TPE-PEPy are 2.45 and 2.92 nm, being slightly shorter than those of *l*-TPE-PPy and *l*-TPE-PEPy (2.66 and 3.13 nm). According to the length *L* and conductance *G* of two linear molecules in $G = Ae^{-\beta L}$, a decay constant β as the increase of vinyl groups can be roughly determined as 2.1 nm⁻¹. The datum is consistent with those of carotenoid polyenes (≈ 2.2 nm⁻¹)^[28] and OPVs (1.7 nm⁻¹)^[27] confirming that our measurements are reliable. The value is also close to the β of OPVs measured by ultrafast cyclic voltammetry (1.9 nm⁻¹) established from kinetic rate constants for reduction,^[29] but larger than that of OPVs with ethoxy substituents determined by an indirect laser-induced temperature jump (0.6 nm⁻¹)^[10] probably caused by the ethoxy substituents and/or different effective reorganization energies in the experiment.^[29]

Since the single-molecule conductance depends more critically on the delocalization of π -orbitals,^[5] the conductance of poorly π -conjugated *f*-TPE-PPy and *f*-TPE-PEPy could be decreased in one or two orders of magnitude relative to that of linear counterparts.^[30,31] In addition, the energy band gap also governs the charge-transport property through a single-molecule junction. The lower HOMO energy levels and larger HOMO–LUMO gaps of the folded molecules may further lower their conductance.^[32] Although the folded molecules are of these unfavorable factors for electronic conductivity by a through-bond pathway, their practical conductance is comparable to the better-conjugated linear molecules. This interesting phenomenon encourages us to believe, in addition to the through-bond tunneling channel, the through-space tunneling channel between π -stacked biphenyls exists simultaneously, which improves the charge-transfer probability and partially compensates the loss of through-bond conjugation. The models of multichannel conductance of *f*-TPE-PPy and single-channel conductance of *l*-TPE-PPy in single-molecule junctions are illustrated in Figure 3b.

In conclusion, two folded molecules with intramolecular π – π stacking interaction between a pair of biphenyls are synthesized, and used to construct single-molecule junctions for the first time. The experimental and calculation results demonstrate apparent through-space conjugation appearing in the inter-ring region of two π -stacked biphenyls, which acts as an efficient conducting channel in a single-molecule junction and offsets the lower through-bond conjugation. The conductance of folded molecules, measured by the STM-based break-junction technique, is comparable to that of better-conjugated linear counterparts. The folded molecules that combine through-bond and through-space conjugation

are expected to be of a broad usage in novel single-molecule wires with multichannel conductance.

Keywords: conductance · folded molecules · single-molecule wire · π – π stacking · scanning tunneling microscopy

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