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Through-Space Conjugation: A Thriving Alternative for Optoelectronic Materials

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Efficient electronic coupling is the key to constructing optoelectronic functional π systems. Generally, the delocalization of π electrons must comply with the framework constructed by covalent bonds (typically σ bonds), representing classic through-bond conjugation. However, through-space conjugation offers an alternative that achieves spatial electron communication with closely stacked π systems instead of covalent bonds thus enabling multidimensional energy and charge transport. Because of the ever-accelerating advances of through-space conjugation studies, researchers are inspired greatly by the beauty of through-space conjugated systems and their potential in high-tech applications. In this mini review, we introduce some representative and newly developed π systems having the through-space conjugation feature. In addition to discussing the profound impacts of through-space conjugation on the luminescence properties and charge transport, we will review some impressive findings of distinctive molecules with attractive characteristics, such as aggregation-induced

emission, thermally activated delayed fluorescence, bipolar charge transport, and multichannel. These achievements may bring about new breakthroughs of theory, materials, and devices in the fields of organic electronics and molecular electronics.



Keywords: aggregation-induced emission, energy and charge transfer, single-molecule wires, thermally activated delayed fluorescence, through-space conjugation

Introduction

Through-space conjugation, one of the most significant properties of π electron delocalization, can lead to noncovalent inter-ring interaction among closely face-toface overlapped aromatic rings. Unlike traditional through-bond conjugation in which the π electrons are delocalized along with a framework built with σ bonds, through-space conjugation possesses more flexibility and possibilities due to its noncovalent structure and spatial delocalization of π electrons. Fascinated by its novel mechanism and potential applications in optoelectronics¹⁻³ and bioscience,⁴ numerous researchers have devoted themselves to deep

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Figure 1 (*a*) Chemical structure, crystal structure, and HOMO and LUMO orbital distribution of [2.2]pCp and chemical structures of [2.2]pCp derivatives. (b) Cisoid and transoid conformations of chromophoric tier in the stacked polymer, pg-poly(PV₃), and chemical structure of pp-poly(F-CP-TDZ) with a schematic figure of charge transfer within the polymer. Reprinted with permission from ref. 8 Copyright 2012 AIP Publishing; ref. 12 Copyright 2012 Wiley-VCH; ref. 13 Copyright 2010 American Chemical Society; ref. 14 Copyright 2012 Royal Society of Chemistry; and ref. 15 Copyright 2011 Royal Society of Chemistry.

exploration of through-space conjugated molecules for decades.

The very first report on [2.2]paracyclophane ([2.2] pCp) in 1949⁵ symbolized the inception of through-space conjugation research. [2.2]pCp enables π electrons to delocalize between two close parallel phenyl rings as the central distances between two stacked phenyl rings is approximately 3.1 Å (Figure 1a), a typical through-space conjugated conformation.^{6,7} The special structure of [2.2] pCp leads to distinctive optical and electronic properties. Based on experimental investigation and theoretical calculation, researchers have gained much information on the unique features of [2.2]pCp and its derivatives. For instance, the charge delocalization and energy-transfer dynamics in electronically coupled π systems have been thoroughly elucidated. Theoretical results indicate that the energy band gap between the highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) of [2.2]pCp (3.72 eV) is about 1.4 eV smaller than that of benzene (5.15 eV), demonstrating [2.2]pCp has a more effective and expansive π -conjugated structure than benzene because of the strong through-space conjugation.⁸ By characterizing π - π interaction and quantifying through-space charge

transfer, it is found that the quenching of resonant photoluminescence processes is stronger in [2.2]pCp than in [4.4]paracyclophane ([4.4]pCp), which has a larger inter-ring separation of 4.0 Å.⁹ There is much faster electron delocalization in [2.2]pCp because of the better through-space coupling. As a result, photoexcited energy transfer occurs efficiently from donor-to-acceptor π -electron systems with energy transfer efficiency over 99.9% and a rate constant of about 10^{12} s⁻¹ when [2.2]pCp is applied to polymers as a skeleton to construct singlemolecular wires.^{10,11} Another representative characteristic of [2.2]pCp and its derivatives is their remarkable photophysical properties. The presence of a shoulder in the UV-vis spectrum arising from the lower energy level compared with isolated analogue is observed in both oligomers, such as pg-CP(PV₂)₂ and pg-CP(PV₃)₂,¹² with [2.2]pCp cores and polymers such as pg-poly(PE₃)¹³ (Figure 1a) with a through-space conjugated [2.2]pCp backbone. Their photoluminescence spectra usually display a broad, structureless, and largely redshifted peak, consistent with the excited states of these compounds undergoing rapid energy transfer to relax and forming a lower energy "phane" electronic state. In a transoidcisoid diad, pg-poly(PV₃) (Figure 1b) has been shown to

experience an energy transfer process along the wellstacked [2.2]pCp skeleton,¹⁴ resulting in a larger Stokes shift than the unstacked model. This kind of energy transfer can be limited by a break of through-space conjugation due to different conformation of the monomers. Other than the energy transfer via a through-space pathway in ladder-like stacked structures, it is also found that energy transfer can be achieved in linear structures linked via through-space interaction (Figure 1b).¹⁵ pp-Poly(F-CP-TDZ) possesses a donor and acceptor π -conjugated system that are linked by through-space conjugated [2.2]pCp in a single-polymer main chain. Spectroscopic results demonstrate Förster-type intramolecular energy transfer from the donor to the acceptor, as the photoluminescence spectrum of the donor overlaps with the absorption spectrum of the chargetransfer band of the acceptor.

Because of their intriguing photoluminescence and charge transport properties, through-space conjugated molecules have been adopted to build various functional materials with desirable multidimensional energy and charge-transfer capabilities. As through-space conjugation has high sensitivity to geometric and electronic structures,¹⁶ the moieties generally need to overcome steric hindrance to form a favorable face-to-face geometry with an inter-ring separation of less than 3.5 Å.¹⁷ Based on this general principle, many molecules with diverse optical and electronic properties have been designed by exploiting through-space conjugation, such as carbazole hexaphenylbenzene (CzHPB),¹⁸ naphthalene-1,8:4,5-bis (dicarboximide) dimer ((-)-2NDI),¹⁹ o-phenylene hexamer (oP⁶(H)⁶),²⁰ 1,8-triarylamino naphthylene (N-1,8TAA),²¹ paracyclophane analogue (CP[(NBP)₂F]),²² etc. Active studies on these molecules have propelled further development of through-space conjugation theory and has shown them to be highly promising for a series of optoelectronic materials and devices.

In this mini review, we focus on the latest advances of through-space conjugated molecules. Emphases will be placed on introducing two major kinds of performance: photoluminescence and charge transport, which we will give through-space conjugated systems a promising future in optoelectronic devices. We present some important findings aided by through-space conjugation, such as aggregation-induced emission (AIE), thermally activated delayed fluorescence (TADF), and intramolecular energy and charge-transfer dynamics. Based on molecular design and characterization, we then unveil the structure-property correlation, fundamental implications, and feasible applications of the newly emerging through-space conjugated foldamers bearing a tetraphenylethene (TPE) core and elucidate their great potential in bipolar charge transport and multichannel conductance. These insights should be meaningful for researchers to understand and design new molecules with specific optoelectronic functions.

Aggregation-Induced Emission

AIE luminogens (AIEgens) refer to luminogenic molecules that are nonluminescent or weakly luminescent when molecularly dissolved in solvents but emit intensely in the aggregated state.²³ These intriguing luminescent materials are of great importance for practical applications in optoelectronic devices and bioimaging because of their high solid-state photoluminescence quantum yields (PLQYs). Generally, when AIEgens aggregate, the free intramolecular motions such as rotation and vibration are restricted by spatial constraint and collective forces from weak intermolecular interactions, and thus the nonradiative decay channels can be blocked.²⁴ Instead, the radiative decay of the excited state will dominate, which enables AIEgens to emit efficiently. Normally, the through-bond conjugated framework forms the structural basis of AIEgens by the development of electronic delocalization among the building blocks through covalent bonds. But AlEgens often require a highly twisted conformation in which the aromatic rings can spatially interact with each other and effective through-space conjugation is possible.

The propeller-shaped TPE is a classic through-bond conjugated AIEgen.²⁵ However, 1,1,2,2-tetraphenylethane $(s-TPE)^{26}$ without a typical π -conjugated structure is also reported to be AIE-active (Figure 2a). It exhibits a weak emission peak in nonvisible region (297 nm) in pure tetrahydrofuran (THF) solution, associated with the emission of individual phenyl ring. But a strong, longwavelength emission peaking at 460 nm, accompanied by a greatly decreased emission intensity at 297 nm, is observed in THF-water mixture (water fraction of 90%) caused by the formation of s-TPE aggregates due to its hydrophobic nature. Although it is weakly through-bond conjugated, it can emit strong visible light at 467 nm with a high solid-state PLQY of up to 69% under 280 nm excitation, which is an unexpected and unique phenomenon. As shown in Figure 2a, the four phenyl rings in s-TPE are linked by C-C single bonds, and thus they freely rotate in dilute solutions, which causes nonradiatively deactivation of the excited state. In the aggregated state, the rotation of these phenyl rings is restricted, and the phenyl rings can form a fixed and well-stacked conformation in which the π electron clouds overlaps and results in a spatial delocalization effect. In that case, the band gap of s-TPE is severely narrowed, thus leading to a largely redshifted emission. Namely, the through-space conjugation of s-TPE is promoted in the aggregated state and contributes significantly to its AIE property and strong long-wavelength emission.

Similar through-space conjugation-related AIE phenomenon is observed in other AIE systems. For example, an unorthodox luminogen with poor through-bond conjugation, the racemic C6-unsubstitued tetrahydropyrimidine (THP),²⁷ is highly emissive in the crystalline state with a high PLQY of 93%, which is in sharp contrast to its

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Figure 2 (a) Through-space conjugation among phenyl rings in s-TPE and photoluminescence spectra of s-TPE in THF/water mixture with different water fractions (f_w). Inset: Chemical structure and fluorescent photos of s-TPE solid, taken under 365 nm UV light irradiation. (b) Schematic illustration of the unconventional clusteroluminogens. Reprinted with permission from ref. 26 Copyright 2017 American Chemical Society and refs. 28 and 29 Copyright 2018 American Chemical Society.

nonfluorescent property in the solution state. The efficient through-space conjugation formed among closelyaligned, electron-rich aromatic rings and heteroatoms in crystals is rationalized to account for the interesting AIE effect and strong solid-state emission. Along with these interesting discoveries, a new concept of clusteroluminogen^{28,29} is proposed and has drawn considerable attention. As illustrated in Figure 2b, strong through-space conjugation and multiple lone-pair electronic interactions within a single molecule enable formation of a through-space conjugated luminescent material. The chain entanglement and intra/interchain interactions in polymers will further enhance electronic communication among heteroatoms and aromatic rings, which facilitates the molecular clustering, conformational rigidity and, finally, strong photoluminescence. Therefore, clusteroluminogens can be considered as a new kind of nonconventional chromophores and may serve as light-emitting materials for optoelectronic devices and biotechnology. These inspiring achievements can provide us some insights into throughspace conjugation and clustering-induced emission, but deciphering their underlying mechanism is still in its infancy and requires more scientific effort.

Thermally Activated Delayed Fluorescence

TADF emitters have recently drawn increasing interests because of their theoretical 100% exciton utilization,³⁰

which enables them to compete with phosphorescent materials in comparable electroluminescence (EL) efficiency but at a greatly reduced cost. For TADF emitters, one of the vital issues is how to simultaneously achieve a small singlet-triplet energy splitting (ΔE_{ST}) to trigger up conversion from the triplet state (T₁) to the singlet state (S₁) by efficient reverse intersystem crossing process and a large enough transition dipole moment to guarantee a high PLQY.³¹⁻³³ Most TADF emitters have a highly twisted noncoplanar connection between electron donors and acceptors to acheive effective separation of HOMO and LUMO and thus a small ΔE_{ST} . However, in this situation, the transition dipole moment is also decreased, leading to a weak oscillator strength and a low PLQY.

To address this issue, a twisted structural model of an electron acceptor and donor linked by an aryl backbone has recently been proposed in which through-space conjugation between donor and acceptor groups is utilized to activate the reverse intersystem crossing process without causing a large loss of PLQY. The nearly perpendicular linkage with large torsion angles can minimize the overlap of HOMO on electron donor and LUMO on electron acceptor, resulting in a small ΔE_{ST} , whereas the closely parallel arrangement of donor and acceptor ensures strong through-space conjugation, which can improve electronic coupling to enhance PLQY. Therefore, these TADF molecules built on a through-space conjugated skeleton can achieve nearly 100% internal quantum

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Figure 3 (a) Chemical structures of through-space conjugated TADF emitters. (b) Crystal structures of B-oTC and XPT, and photoluminescence transient spectra of P-Ac50-TRZ50 in toluene under nitrogen and air at 298 K. Reprinted with permission from ref. 34 Copyright 2018 Royal Society of Chemistry; ref. 35 Copyright 2017 Wiley-VCH; and refs. 36–44 Copyright 2017 American Chemical Society.

efficiency. Figure 3a illustrates a typical through-space conjugated TADF emitter, *cis*-Bz-PCP-TPA,³⁴ based on a [2.2]pCp skeleton with stacked donor-acceptor groups. The through-space charge transfer from donor to acceptor is detected by the appearance of a high-intensity absorption band at 311 nm. The *cis*-Bz-PCP-TPA has a small $\Delta E_{\rm ST}$ of 0.13 eV and a prominent blue delayed fluorescence at 480 nm with a lifetime of 1.8 µs, thus demonstrating its TADF character.

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Two additional typical TADF emitters based on through-space conjugated skeletons are B-oTC³⁵ and XPT,³⁶ which have even better EL performance. In both emitters, the donor groups are nearly parallel to the acceptor groups with short distances of 2.8-3.4 Å (Figure 3b), leading to intramolecular donor-acceptor interactions. The combined through-bond and throughspace charge-transfer paths simultaneously allow small $\Delta E_{\rm ST}$ values and large transition dipole, bringing about strong TADF property and high emission efficiencies. Microsecond delayed lifetimes and high PLQYs in films (94% and 65% for B-oTc and XPT, respectively) have been obtained. Moreover, it has been observed that the through-space conjugated donor-acceptor structure results in further restriction of intramolecular vibration and rotation in the aggregated state and thus enhanced emission, which can be considered as aggregationinduced delayed fluorescence (AIDF). When applying these two emitters to organic light-emitting diodes as light-emitting layers, both devices show good EL performance. The device using XPT as emissive dopant radiates green light at 584 nm with a maximum external quantum

efficiency (EQE) of 10%, which exceeds the theoretical limit of a simple fluorescent OLED. More importantly, the nondoped OLED using B-oTc neat film as light-emitting layer can achieve blue light at 474 nm with a remarkable EQE of 19.1%. This result demonstrates the feasibility of nondoped OLEDs with brilliant performance by applying AIDF materials, and many other breakthroughs have been achieved in different AIDF systems.³⁷⁻⁴⁴

Unlike the molecules discussed above with π -conjugated backbones that allow the coexistence of through-space and through-bond conjugation, a new type of polymer, P-Ac(1-x)-TRZx,⁴⁵ comprised of a saturated hydrocarbon backbone and aromatic electron donors and acceptors as pendants (Figure 3a), possesses only through-space conjugation yet exhibits an interesting blue TADF property. The saturated hydrocarbon backbone avoids the strong electronic coupling between donors and acceptors to achieve blue emission and a small ΔE_{ST} . On the other hand, the efficient through-space conjugation between donor and acceptor is conducive to charge transport and light emission. Therefore, polymer P-Ac50-TRZ50 shows typical TADF features of a longdelayed fluorescence lifetime of 1173.0 ns in toluene under nitrogen (Figure 3b), a blue emission peak at 498 nm, and a high PLQY of 60% in film. The solutionprocessed OLED based on P-Ac95-TRZ05 can perform efficiently, affording a strong blue EL emission at 472 nm with a high EQE of 12.1% and a low efficiency roll-off of 4.9% (at 1000 cd m^{-2}). The achievement of a high EQE mainly arises from extracting light from both triplet and singlet excitons involving through-space charge transfer.

Expanding the study of molecular design based on through-space conjugation may be the key to further improve the performance of blue TADF emitters.

Energy and Charge Transfer

Energy and charge transfer often occur simultaneously between electron donors and acceptors that are in close proximity.46 The through-space intervalence chargetransfer (IVCT) phenomenon originating from mixed valency has been found in metal-organic frameworks (MOFs), such as $[Zn_2(BPPTzTz)_2(tdc)_2]_n$ (Figure 4a),⁴⁷ for which both experiment and theory have confirmed the presence of two closely aligned BPPTzTz ligands with a short interchain distance of 3.80 Å. Visual inspection of the molecular orbitals reveals that two kinds of energy transitions occur originating from a singly occupied molecular orbital localized on one BPPTzTz unit to LUMO+1 localized on the adjacent ligand or to LUMO+2 localized on the same ligand. Both transitions display substantial IVCT character (Figure 4b). According to the IVCT between BPPTzTz^{•-} and BPPTzTz[°], the reduction of one ligand induces a resonance effect in the other that decreases the stacking offset and increases the overall donor-acceptor orbital overlap, thereby facilitating the IVCT process. The relative intensity of the underlying IVCT transitions is also highly dependent on the distances between ligands. Specifically, the IVCT behavior intensifies with the shorter distances between the stacked ligands. This interesting through-space, mixedvalence interaction can lead to long-range delocalization throughout the entire framework (Figure 2c), which is essential for the conductivity in MOFs.48-50

Similarly, a multichromophoric tetracationic cyclophane DAPPBox⁴⁺ exhibiting efficient intramolecular energy and electron transfer is reported by Gong et al.⁵¹ The asymmetric, rigid, and box-like cyclophane is comprised of an ExBIPY²⁺ unit and a DAPP²⁺ unit linked together by two p-xylylenes (Figure 5a). Two types of through-space interactions occur in DAPPBox⁴⁺, which has been confirmed via crystallography analysis and spectroscopy measurement.⁵² The first type is intramolecular throughspace conjugation between ExBIPY²⁺ and DAPP²⁺, and the second type is intermolecular through-space conjugation between two closely aligned ExBIPY²⁺ units. An apparent redshift is observed in the absorption maximum of DAPPBox⁴⁺ in comparison to corresponding methylated compounds (Figure 5b),^{53,54} thus verifying the existence of through-space electronic interaction. Efficient energy transfer within the cyclophane can be expected from the emission spectrum dominated by green emission at 517 nm, under excitation at 339 nm of DAPPBox⁴⁺ (Figure 5c). The quenching of ExBIPY²⁺ emission at 380 nm, accompanied by the enhancement of DAPP²⁺ emission at 510 nm, suggests quantitative energy transfer from ExBIPY²⁺ to DAPP²⁺. The emission spectrum of DAPPBox⁴⁺ is not a simple collection of multiple emission bands from different subunits, but a structureless broad band associated with the DAPP²⁺ unit, which confirms the existence of through-space energy transfer. Ultrafast intramolecular charge transfer happens from DAPP²⁺ to ExBIPY²⁺ to yield DAPP^{3+•}-ExBIPY^{+•} radical ion pair in 1.5 ps, verified by the appearance of the 1150 nm absorption originating from a DAPP^{3+•}-ExBIPY^{+•} radical ion pair (Figure 5d). These results demonstrate the positive effect of through-space conjugation on the intra- and



Figure 4 | (a) Chemical structures of the cofacial pair of BPPTzTz ligands showing reduction to the mixed-valence state, which facilitates the through-space IVCT interaction. (b) Molecular orbitals involved in the transitions in the nearinfrared region for the cofacial mixed-valence dimer $(BPPTzTz^{0/^{\bullet}})_2$ extracted from the crystal structure of $[Zn_2(BPPTzTz)_2(tdc)_2]_n$. (c) Crystal structure of $[Zn_2(BPPTzTz)_2(tdc)_2]_n$ showing the cofacial alignment of the BPPTzTz ligands marked by red rectangle. Reprinted with permission from ref. 47 Copyright 2018 American Chemical Society.

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Figure 5 | (a) Chemical structure of DAPPBox⁴⁺. The energy-transfer and charge-transfer processes of DAPPBox⁴⁺ are displayed. (b) Absorption spectra of DAPPBox⁴⁺, Me-ExBIPY²⁺, and Me-DAPP²⁺ in MeCN at room temperature. (c) Emission spectra of DAPPBox⁴⁺, Me-ExBIPY²⁺, Me-DAPP²⁺, and a physical mixture of Me-ExBIPY²⁺ and Me-DAPP²⁺ in MeCN (1.6 μ M) upon excitation at 339 nm. (d) Visible and near-infrared femtosecond spectra with excitation at 330 nm of DAPPBox⁴⁺ in MeCN at room temperature. Reprinted with permission from ref. 51 Copyright 2017 American Chemical Society.

intermolecular charge transfer. This kind of constitutionally asymmetric cyclophane is believed to have a promising future in integration into solar energy conversion and organic electronics.

New Through-Space Conjugated System

Because of their unique charge transfer properties, through-space conjugated molecules are equipped with not only fascinating photophysical features such as AIE and TADF but also show promise for charge mobility and electronic communication, which are of great importance for the fabrication of efficient optoelectronic devices. Therefore, numerous systems with novel structures, properties, and applications utilizing throughspace conjugated molecules have been investigated. However, the thoroughly studied and well-established through-space conjugated systems are surprisingly rare. To the best of our knowledge, only studies of the [2.2] pCp system are relatively mature and widely used to construct through-space conjugated materials. In our recent work, we have systematically studied a new class of foldamers containing a TPE core and uncovered their intriguing through-space conjugation and optoelectronic functions. The archetypal foldamer, Z-o-BPTPE, has been

confirmed by crystallographic analysis to be a cis-isomer. The specific phenyl rings, Φ_1 and Φ_2 , are stacked in a nearly parallel manner, with a plane overlap of about 50% and inter-ring distances of 3.147 and 3.166 Å (Figure 6),⁵⁵⁻⁵⁷ indicating the existence of efficient electronic coupling between the stacked phenyl rings. Compared with the conventional [2.2]pCp, Z-o-BPTPE performs better in photoluminescence and charge transport. Because it has four closely packed phenyl rings that can interact noncovalently, Z-o-BPTPE has better through-space conjugation than [2.2]pCp, which only has two phenyl rings involved in through-space conjugation. Furthermore, through-space and through-bond conjugation can occur in Z-o-BPTPE with vinyl-linked two phenyl fragments simultaneously, while there is only through-space conjugation in [2.2]pCp. Based on this archetypal architecture, we have developed a library of foldamers with interesting properties and studied the structure-property correlation and possible applications.

We have expanded our studies on the TPE-based foldamers and constructed more complicated foldamers bearing two through-space conjugated oligo-*p*-phenylene chains (Figure 7a).⁵⁸ The crystallographic results confirm their folded structures and *cis*-conformation, wherein two linear through-bond conjugated oligo-*p*phenylene chains are closely aligned in an offset and



Figure 6 (a) Schematic figure showing the better conjugation in Z-o-BPTPE compared with [2.2]pCp. (b) Molecular structure and crystal structure of Z-o-BPTPE with the shortest distances between Φ_1 and Φ_2 . (c) Calculated molecular orbitals ranging from HOMO-1 to LUMO+1 of Z-o-BPTPE. Reprinted with permission from refs. 55-57 Copyright 2016 Elsevier.

facing each other in a roughly parallel manner. The shortest distances between two chains are between 3.16 and 3.46 Å, and intense electron clouds of frontier molecular orbitals are observed in the interchain regions, demonstrating efficient through-space conjugation. Absorption spectra reveal that Z-o-BPTPE has two main absorption peaks at around 240 and 300 nm (Figure 7b). The longwavelength absorption peaks become less distinguishable as tails in the absorption spectra of Z-o-BBPTPE and f-3Ph. These peaks even disappear for f-4Ph, f-5Ph, and f-TPE-PVP, for which the short-wavelength absorption peaks are enhanced and redshifted correspondingly. When the oligo-*p*-phenylene chains are elongated, the absorption bands of higher energy become stronger and redshifted, whilst the absorption bands of lower energy are relatively weakened. By combining experimental and theoretical results, it is deduced that the enhanced through-space conjugation mainly contributes to the

short-wavelength absorptions associated with the high-energy $S_{\rm O}-S_n$ transition, and the weaker throughbond conjugated central TPE unit leads to the small, long-wavelength absorption of the low-energy $S_{\rm O}-S_{\rm 1}$ transition.⁵⁸

Concerning f-3Ph, f-4Ph, and f-5Ph (Figure 7b),⁵⁹ the observation that the absorption maxima become redshifted with an increase in the folded chains is similar to the tendency of their corresponding oligo-*p*-phenylenes. This phenomenon suggests that the main contributions for absorption of these foldamers are from the oligo-pphenylene chains rather than the entire folded molecules. Contrary to the chain-length-sensitive absorption property, the photoluminescence peaks of these foldamers in solution are only slightly altered in the range of 489-498 nm, which are very close to that of Z-o-BPTPE (493 nm) but much longer than those of linear oligop-phenylenes, such as p-terphenyl (340 nm) and p-quaterphenyl (368 nm). This result suggests that the emissions originate from the central folded part (Z-o-BPTPE moiety) rather than from the entire molecule or the oligo-p-phenylene moieties. Therefore, it is reasonable to deduce that intramolecular energy transfer occurs within these foldamers, namely the energy absorbed by oligo-p-phenylenes is transferred to the central folded part for light emission. Because of this intramolecular energy transfer process, the Stokes shifts of these foldamers are uncharacteristically large (190-214 nm) in view of the molecular structures without typical electron donor-acceptor interaction.

Moreover, by exploring other TPE-cored foldamers with different branched chains, we have concluded that the substituents with a different electronic nature and heterocycles can regulate the stacking geometry and optical properties, but show no apparent impact on the formation of a folded architecture. These foldamers exhibit an efficient through-space conjugation and aggregationenhanced emission (AEE)^{55-58,60-63} property because of the increased molecular rigidity. In view of this observation, regulating the geometric and electronic structures of the foldamers to control the degree of through-space conjugation should be helpful for manipulating photophysical properties and potential functions.

Bipolar Charge Transport

By incorporating carbazole or biphenylamine groups into Z-o-BBPTPE, two novel foldamers (Z-o-BCaPTPE and Z-o-BTPATPE) are obtained (Figure 8a).⁶⁴ These novel foldamers possess a regular through-space conjugated structure, which rigidifies molecular conformations and gives rise to AEE characteristics. The folded structure with efficient through-space conjugation provides Z-o-BCaPTPE and Z-o-BTPATPE with a unique bipolar charge transport ability. As revealed by the time-of-flight transient photocurrent technique, comparable mobilities





Figure 7 (a) Molecular structures and the electron cloud distribution of LUMO+1 orbitals of Z-o-BBPTPE, f-TPE-PV, and f-TPE-PVP. (b) Molecular structures of the foldamers and the schematic representation of energy transfer. Experimental absorption spectra of f-3Ph, f-4Ph, f-5Ph, Z-o-BBPTPE, f-TPE-PV, and f-TPE-PVP, and normalized absorption and fluorescence spectra of f-3Ph, f-3Ph(Me), f-4Ph, f-4Ph(Me), f-5Ph, and f-5Ph(Me). Reprinted with permission from ref. 58 Copyright 2017 Wiley-VCH; and ref. 60 Copyright 2015 American Chemical Society.

of holes (4.9 × 10⁻⁴ cm² V⁻¹ s⁻¹) and electrons (4.3 × 10⁻⁴ cm² V⁻¹ s⁻¹) are detected in Z-o-BCaPTPE (Figure 8b) at an applied electric field of 60 V µm⁻¹. Z-o-BTPATPE also shows a similar bipolar charge transport property, with hole and electron mobilities of 3.7×10^{-4} and 3.3×10^{-4} cm² V⁻¹ s⁻¹, respectively, at a 60 V µm⁻¹ electric field. Currently thinking suggests that both foldamers should be favored for hole transport, that is, their electron mobilities should be much worse than hole mobilities because they are comprised of electron-donating groups. It is believed that the through-space conjugated folded structure can stabilize the injected electron by spatially delocalizing the negative charge which thus accounts for this unusual phenomenon. This has also validated only by a linear isomer with hole mobility.

The intriguing bipolar charge transport ability and AEE properties make these foldamers good candidates for performing different functions in optoelectronic devices. To investigate this potential, three kinds of OLEDs based on the foldamers are fabricated. The first kind of device uses both foldamers as light-emitting and hole-transporting layers, the second type of device employs both foldamers as light-emitting and electron-transport-ing layers, and the foldamers in the last class of device serve as light-emitting layers only. All three kinds of devices show sky blue EL at 488–492 nm with comparable performance, demonstrating that they can serve as multifunctional materials in OLEDs. Given that there are no conventional electron-transporting groups in both molecules, the through-space conjugation should be

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Figure 8 (a) Chemical structures and crystal structures of Z-o-BCaPTPE and Z-o-BTPATPE. (b) Transient photocurrents in hole transport (the left panel) and electron transport (the right panel) configurations for film (10 μ m) of Z-o-BCaPTPE:PS:C₆₀ (50:48.5:1.5 wt%) composite. Inset: log-log plot of the photocurrent as a function of time. Reprinted with permission from ref. 64. Copyright 2011 Wiley-VCH.

responsible for multiple functions. These achievements show us that through-space conjugation can enable molecules to have certain unique electroactivity. By combining excellent emission efficiency, high thermal stability, and good bipolar charge transport ability and with further optimization, these through-space conjugated foldamers can become a promising material for optoelectronic devices.

Multichannel Conductance

Single-molecule-level electronic devices are of high importance to break through the intrinsic limitation of silicon-based electronic devices.⁶⁵ Single-molecule wires, which can link with electrodes for charge transport and electron interaction via through-space⁶⁶ or throughbond⁶⁷ pathways, are an indispensable, fundamental element for molecular electronic devices.⁶⁸ Although through-space conjugated single-molecular wires were developed later and are much rarer than the throughbond conjugated ones, the ever-accelerating improvement in exploring various through-space conjugated systems such as [2.2]pCp derivatives and self-assembled cages⁶⁹ enclosing stacked aromatic rings uncover the promising future of electron transport in a through-space manner. In most cases, single-molecule wires are of single channel conductance, namely they realize electric conductance by virtue of either the through-bond channel or the through-space channel. Recently, we have suggested a new design strategy for single-molecule wires with multichannel conductance by integrating through-bond and through-space channels into one molecule.

By grafting pyridine groups at two ends of a Z-o-BPTPE core as terminal anchors to attach to the gold

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Figure 9 (a) Chemical structures and top and side views of crystal structure of f-TPE-PPy and f-TPE-PEPy together with the chemical structures of I-TPE-PPy and I-TPE-PEPy. (b) Schematic representation of circuits anchored onto gold electrodes of f-TPE-PPy and I-TPE-PPy. Reprinted with permission from ref. 69 Copyright 2015 Wiley-VCH.

electrode efficiently, f-TPE-PPy and f-TPE-PEPy have been thoroughly investigated as candidates of singlemolecular wires (Figure 9a).47 Their through-space conjugation coupled with twisted through-bond conjugated backbones has been confirmed by spectroscopy and theoretical calculation. The conductivity of *f*-TPE-PPy and *f*-TPE-PEPy and two linear counterparts (*I*-TPE-PPy and /-TPE-PEPy) are measured by the scanning tunneling microscopy-based break junction (STM-BJ) technique for comparison. Experimental results reveal that the conductance of *f*-TPE-PPy is 1.40 nS, which is close to that of /-TPE-PPy (1.50 nS). A similar phenomenon is also observed for *f*-TPE-PEPy (0.50 nS) and *l*-TPE-PEPy (0.55 nS). However, due to the much better through-bond conjugation and closer HOMO energy levels to the Fermi energy level of Au, /-TPE-PPy and /-TPE-PEPy should

possess conductance one or two order magnitude higher than those of *f*-TPE-PPy and *f*-TPE-PEPy. A reasonable explanation for the close conductance is that throughspace conjugation of *f*-TPE-PPy and *f*-TPE-PEPy can function as an additional conductance channel and compensate for the conductance loss because of the poor through-bond conjugation. This conceptually new model of multichannel conductance via through-bond and through-space channels (Figure 9b) paves the way for to advance the conductance of single-molecule wires.

Because of an insufficient contribution from the through-space conducting channel, folded singlemolecular wires only provide close conductance in comparison with the conventional linear counterparts. In view of this, a series of novel single-molecular wires created by integrating a through-space conjugated



Figure 10 | (a) Molecular structures of HPB-SM, HPB(OM)-SM, and HPB(OM)₃-SM with indicated torsion angles (φ) between the central benzene and its adjacent one on the backbone in optimized molecular structures, and their crystal structures with indicated shortest distances between face-to-face aligned neighboring phenyls. (b) Schematic representation of circuits of HPB(OM)₃-SM and PP-SM anchored onto gold electrodes. Reprinted with permission from ref. 70 Copyright 2018 American Chemical Society.

hexaphenylbenzene (HPB) core and a through-bond conjugated *p*-oligophenylene backbone (Figure 10a) have been developed.⁷⁰ Grafting two 4-(methylthio) phenyls as terminal anchors onto HPB enables the molecular wires to efficiently interact with gold electrodes. And, methoxy groups are introduced in four peripheral phenyls in HPB(OM)-SM and HPB(OM)₃-SM to tune the through-space conjugation degree. The crystal structures reveal that the peripheral phenyls in HPB are face-to-face aligned, with the shortest distances of 2.87-2.95 Å between neighboring phenyls, indicative of a strong electronic coupling interaction. The torsion angles are increased from HPB-SM (59°) to HPB(OM)-SM (67°) and then HPB(OM)-SM (87°), revealing that the through-bond conjugation of the molecular backbones is progressively decreased. On the other hand, the degree of through-space conjugation is enhanced with increasing quantities of methoxy groups in the molecules, as the addition of methoxy groups can enrich the π -electron cloud and promote the electronic coupling interaction. The STM-BJ data reveal that HPB-SM, HPB

(OM)-SM, and HPB(OM)₃-SM have conductance values of 3.88, 7.75, and 12.28 nS, respectively, which are superior to the linear referential molecule based on p-oligophenylene, PP-SM (2.45 nS). Given the weaker through-bond conjugation but stronger through-space conjugation, it is reasonable that through-space conjugation in HPBbased molecular wires is able to exceedingly offset the conductance loss of the weakened through-bond conjugation. Moreover, this conclusion can be further proven by the increasing conductance from HPB-SM to HPB(OM)-SM and then to HPB(OM)₃-SM, being consistent with the tendency of the through-space conjugation enhancement. Therefore, we propose a novel model of multichannel conductance of HPB(OM)₃-SM in a single-molecule junction (Figure 10b), which can be more functional and robust than the traditional single channel conductance of PP-SM. Such multichannel conductance demonstrates a promising and conceptually new strategy to design single-molecule wires that is conducive to the development of molecular electronics.

Conclusion

Through-space conjugation is considered a promising complement to conjugation theory because electronic communication and energy transition are allowed to occur among noncovalently linked moieties in throughspace conjugated molecules, which has high academic value and profound practical implication. The inter/ intramolecular charge and energy transfer form the foundation of many interesting optical and electronic phenomena, which can contribute to the development of many different types of functional materials and devices. In this mini review, we have systematically demonstrated the significant impact of through-space conjugation on luminescence property and charge transport by introducing latest advances in representative molecular systems. Through-space conjugation provides unorthodox molecules such as s-TPE with AIE features and brings about fundamental insights into the concept of clusteroluminogens. By combining electron donors and acceptors in through-space conjugated frameworks, efficient blue TADF materials are achieved, which has promising applications in OLEDs. Highly efficient energy transfer and ultrafast charge transport also become more feasible via a through-space mechanism in certain systems, such as asymmetric cyclophanes and MOFs, making them potential candidates for electronic devices. With thorough molecular design based on the newly emerging through-space conjugated foldamers bearing a TPE core, we unveil the structure-property correlation, fundamental implications, and feasible applications. Through-space conjugation can exert profound impact on the absorption and emission, intramolecular energy transfer, and bipolar charge transport properties of the foldamers. Aided by through-space conjugation and multifunctionality, these foldamers can serve different roles in OLEDs, such as lightemitting layers and hole/electron-transporting layers. More importantly, by integrating the through-space and through-bond conducting channels, robust singlemolecular wires with multichannel conductance can be created, which is highly conducive to improving the conductance and stability of molecular wires and provides many opportunities for novel functional single-molecule devices. Although still in its infancy, the burgeoning development of molecular systems with through-space conjugation has inspired more and more researchers to embark on this interesting research area. We believe that further study may lead to an in-depth systematic understanding of the through-space conjugation mechanism and result in breakthroughs in the fields of optoelectronic materials and devices.

Conflicts of Interest

The authors declare no competing financial interests.

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References

1. Brédas, J.-L.; Beljonne, D.; Coropceanu, V.; Cornil, J. Charge-Transfer and Energy-Transfer Processes in Π-Conjugated Oligomers and Polymers: A Molecular Picture. *Chem. Rev.* **2004**, *104*, 4971-5004.

2. Warshel, A.; Karplus, M. Calculation of Ground and Excited State Potential Surfaces of Conjugated Molecules. I. Formulation and Parametrization. *J. Am. Chem. Soc.* **1972**, *94*, 5612–5625.

3. Pace, C. J.; Gao, J. Exploring and Exploiting Polar- π Interactions with Fluorinated Aromatic Amino Acids. *Acc. Chem. Res.* **2013**, *46*, 907-915.

4. Wang, H.; Zhao, E.; Lam, J. W.; Tang, B. Z. Aie Luminogens: Emission Brightened by Aggregation. *Mater. Today* **2015**, *18*, 365-377.

5. Brown, C.; Farthing, A. Preparation and Structure of Di-P-Xylylene. *Nature* **1949**, *164*, 915.

6. Cram, D. J.; Steinberg, H. Macro Rings. I. Preparation and Spectra of the Paracyclophanes. *J. Am. Chem. Soc.* **1951**, *73*, 5691–5704.

7. Cram, D. J.; Allinger, N. L.; Steinberg, H. Macro Rings. VII. The Spectral Consequences of Bringing Two Benzene Rings Face to Face. *J. Am. Chem. Soc.* **1954**, *76*, 6132-6141.

8. Bai, M.; Liang, J.; Xie, L.; Sanvito, S.; Mao, B.; Hou, S. Efficient Conducting Channels Formed by the π - π Stacking in Single [2,2] Paracyclophane Molecules. *J. Chem. Phys.* **2012**, *136*, 104701.

9. Batra, A.; Kladnik, G.; Vázquez, H.; Meisner, J. S.; Floreano, L.; Nuckolls, C.; Cvetko, D.; Morgante, A.; Venkataraman, L. Quantifying Through-Space Charge Transfer Dynamics in π -Coupled Molecular Systems. *Nat. Commun.* **2012**, *3*, 1086.

10. Morisaki, Y.; Kawakami, N.; Nakano, T.; Chujo, Y. Energy-Transfer Properties of a [2.2] Paracyclophane-Based Through-Space Dimer. *Chem. Eur. J.* **2013**, *19*, 17715–17718.

11. Morisaki, Y.; Shibata, S.; Chujo, Y. [2.2] Paracyclophane-Based Single Molecular Wire Consisting of Four π -Electron Systems. *Can. J. Chem.* **2016**, *95*, 424-431.

12. Mukhopadhyay, S.; Jagtap, S. P.; Coropceanu, V.; Brédas, J. L.; Collard, D. M. π -Stacked Oligo(Phenylene Vinylene)s Based on Pseudo-Geminal Substituted [2.2] Paracyclophanes: Impact of Interchain Geometry and Interactions on the Electronic Properties. *Angew. Chem. Int. Ed.* **2012**, *51*, 11629–11632.

DOI: 10.31635/ccschem.019.20180020 CCS Chem. **2019**, *1*, 181–196

13. Jagtap, S. P.; Collard, D. M. Multitiered 2d π -Stacked Conjugated Polymers Based on Pseudo-Geminal Disubstituted [2.2]Paracyclophane. *J. Am. Chem. Soc.* **2010**, *132*, 12208–12209.

 Jagtap, S. P.; Collard, D. M. 2D Multilayered π-Stacked Conjugated Polymers Based on a U-Turn Pseudo-Geminal [2.2] Paracyclophane Scaffold. *Polym. Chem.* **2012**, *3*, 463-471.
Morisaki, Y.; Chujo, Y. Through-Space Conjugated Polymers Consisting of [2.2] Paracyclophane. *Polym. Chem.* **2011**, *2*, 1249-1257.

16. Sirringhaus, H.; Tessler, N.; Friend, R. H. Integrated Optoelectronic Devices Based on Conjugated Polymers. *Science* **1998**, *280*, 1741-1744.

17. Sariciftci, N. S.; Smilowitz, L.; Heeger, A. J.; Wudl, F. Photoinduced Electron Transfer from a Conducting Polymer to Buckminsterfullerene. *Science* **1992**, *258*, 1474–1476.

18. Sun, D.; Rosokha, S. V.; Kochi, J. K. Through-Space (Cofacial) π -Delocalization Among Multiple Aromatic Centers: Toroidal Conjugation in Hexaphenylbenzene-Like Radical Cations. *Angew. Chem.* **2005**, *117*, 5263–5266.

19. Wu, Y.; Frasconi, M.; Gardner, D. M.; McGonigal, P. R.; Schneebeli, S. T.; Wasielewski, M. R.; Stoddart, J. F. Electron Delocalization in a Rigid Cofacial Naphthalene-1, 8:4, 5-Bis(Dicarboximide) Dimer. *Angew. Chem. Int. Ed.* **2014**, *53*, 9476-9481.

20. Hartley, C. S. Folding of Ortho-Phenylenes. *Acc. Chem. Res.* **2016**, *49*, 646–654.

21. Schmidt, H. C.; Spulber, M.; Neuburger, M.; Palivan, C. G.; Meuwly, M.; Wenger, O. S. Charge Transfer Pathways in Three Isomers of Naphthalene-Bridged Organic Mixed Valence Compounds. *J.Org. Chem.* **2016**, *81*, 595–602.

22. Takase, M.; Inabe, A.; Sugawara, Y.; Fujita, W.; Nishinaga, T.; Nomura, K. Donor-Acceptor Segregated Paracyclophanes Composed of Naphthobipyrrole and Stacked Fluoroarenes. *Org. Lett.* **2013**, *15*, 3202–3205.

23. Luo, J.; Xie, Z.; Lam, J. W.; Cheng, L.; Chen, H.; Qiu, C.; Kwok, H. S.; Zhan, X.; Liu, Y.; Zhu, D. Aggregation-Induced Emission of 1-Methyl-1,2,3,4,5-Pentaphenylsilole. *Chem. Commun.* 2001, 1740–1741.

24. Mei, J.; Hong, Y.; Lam, J. W.; Qin, A.; Tang, Y.; Tang, B. Z. Aggregation-Induced Emission: The Whole Is More Brilliant Than the Parts. *Adv. Mater.* **2014**, *26*, 5429–5479.

25. Wang, J.; Mei, J.; Hu, R.; Sun, J. Z.; Qin, A.; Tang, B. Z. Click Synthesis, Aggregation-Induced Emission, E/Z Isomerization, Self-Organization, and Multiple Chromisms of Pure Stereoisomers of a Tetraphenylethene-Cored Luminogen. *J. Am. Chem. Soc.* **2012**, *134*, 9956-9966.

26. Zhang, H.; Zheng, X.; Xie, N.; He, Z.; Liu, J.; Leung, N. L.; Niu, Y.; Huang, X.; Wong, K. S.; Kwok, R. T. Why Do Simple Molecules with "Isolated" Phenyl Rings Emit Visible Light? *J. Am. Chem. Soc.* **2017**, *139*, 16264–16272.

27. Zhu, Q.; Zhang, Y.; Nie, H.; Zhao, Z.; Liu, S.; Wong, K. S.; Tang, B. Z. Insight into the Strong Aggregation-Induced Emission of Low-Conjugated Racemic C6-Unsubstituted Tetrahydropyrimidines through Crystal-Structure-Property Relationship of Polymorphs. *Chem. Sci.* **2015**, *6*, 4690-4697. 28. Han, T.; Deng, H.; Qiu, Z.; Zhao, Z.; Zhang, H.; Zou, H.; Leung, N. L. C.; Shan, G.; Elsegood, M. R. J.; Lam, J. W. Y.; Tang, B. Z. Facile Multicomponent Polymerizations toward Unconventional Luminescent Polymers with Readily Openable Small Heterocycles. *J. Am. Chem. Soc.* **2018**, *140*, 5588-5598.

29. He, Z.; Ke, C.; Tang, B. Z. Journey of Aggregation-Induced Emission Research. *ACS Omega* **2018**, *3*, 3267-3277. 30. Cai, Z.; Zhang, N.; Awais, M. A.; Filatov, A. S.; Yu, L. Synthesis of Alternating Donor-Acceptor Ladder-Type Molecules and Investigation of Their Multiple Charge-Transfer Pathways. *Angew. Chem. Int. Ed.* **2018**, *57*, 6442-6448.

31. Im, Y.; Kim, M.; Cho, Y. J.; Seo, J.-A.; Yook, K. S.; Lee, J. Y. Molecular Design Strategy of Organic Thermally Activated Delayed Fluorescence Emitters. *Chem. Mater.* **2017**, *29*, 1946–1963.

32. Yang, Z.; Mao, Z.; Xie, Z.; Zhang, Y.; Liu, S.; Zhao, J.; Xu, J.; Chi, Z.; Aldred, M. P. Recent Advances in Organic Thermally Activated Delayed Fluorescence Materials. *Chem. Soc. Rev.* **2017**, *46*, 915-1016.

33. Kaji, H.; Suzuki, H.; Fukushima, T.; Shizu, K.; Suzuki, K.; Kubo, S.; Komino, T.; Oiwa, H.; Suzuki, F.; Wakamiya, A. Purely Organic Electroluminescent Material Realizing 100% Conversion from Electricity to Light. *Nat. Commun.* **2015**, *6*, 8476. 34. Spuling, E.; Sharma, N.; Samuel, I. D.; Zysman-Colman, E.; Bräse, S. (Deep) Blue Through-Space Conjugated TADF Emitters Based on [2.2] Paracyclophanes. *Chem. Commun.* **2018**, *54*, 9278-9281.

35. Chen, X. L.; Jia, J. H.; Yu, R.; Liao, J. Z.; Yang, M. X.; Lu, C. Z. Combining Charge-Transfer Pathways to Achieve Unique Thermally Activated Delayed Fluorescence Emitters for High-Performance Solution-Processed, Non-Doped Blue OLEDs. *Angew. Chem. Int. Ed.* **2017**, *56*, 15006–15009.

36. Tsujimoto, H.; Ha, D.-G.; Markopoulos, G.; Chae, H. S.; Baldo, M. A.; Swager, T. M. Thermally Activated Delayed Fluorescence and Aggregation Induced Emission with Through-Space Charge Transfer. *J. Am. Chem. Soc.* **2017**, *139*, 4894–4900.

37. Guo, J.; Fan, J.; Lin, L.; Zeng, J.; Liu, H.; Wang, C. K.; Zhao, Z.; Tang, B. Z. Mechanical Insights into Aggregation-Induced Delayed Fluorescence Materials with Anti-Kasha Behavior. *Adv. Sci.* **2018**, *6*, 1801629.

 Guo, J.; Zhao, Z.; Tang, B. Z. Purely Organic Materials with Aggregation-Induced Delayed Fluorescence for Efficient Nondoped OLEDs. *Adv. Opt. Mater.* **2018**, *6*, 1800264.
Liu, H.; Zeng, J.; Guo, J.; Nie, H.; Zhao, Z.; Tang, B. Z. A Versatile Molecular Design for High-Performance Nondoped OLEDS with ~100% Exciton Utilization and Negligible Efficiency Roll-Off. *Angew. Chem. Int. Ed.* **2018**, *57*.

40. Huang, J.; Nie, H.; Zeng, J.; Zhuang, Z.; Gan, S.; Cai, Y.; Guo, J.; Su, S. J.; Zhao, Z.; Tang, B. Z. Highly Efficient Nondoped OLEDs with Negligible Efficiency Roll-Off Fabricated from Aggregation-Induced Delayed Fluorescence Luminogens. *Angew. Chem. Int. Ed.* **2017**, *56*, 12971–12976.

41. Guo, J.; Li, X. L.; Nie, H.; Luo, W.; Gan, S.; Hu, S.; Hu, R.; Qin, A.; Zhao, Z.; Su, S. J. Achieving High-Performance Nondoped

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OLEDs with Extremely Small Efficiency Roll-Off by Combining Aggregation-Induced Emission and Thermally Activated Delayed Fluorescence. *Adv. Funct. Mater.* **2017**, *27*, 1606458.

42. Guo, J.; Li, X.-L.; Nie, H.; Luo, W.; Hu, R.; Qin, A.; Zhao, Z.; Su, S.-J.; Tang, B. Z. Robust Luminescent Materials with Prominent Aggregation-Induced Emission and Thermally Activated Delayed Fluorescence for High-Performance Organic Light-Emitting Diodes. *Chem. Mater.* **2017**, *29*, 3623-3631.

43. Gan, S.; Zhou, J.; Smith, T. A.; Su, H.; Luo, W.; Hong, Y.; Zhao, Z.; Tang, B. Z. New AlEgens with Delayed Fluorescence for Fluorescence Imaging and Fluorescence Lifetime Imaging of Living Cells. *Mater. Chem. Front.* **2017**, *1*, 2554–2558.

44. Zeng, J.; Guo, J.; Liu, H.; Lam, J. W.; Zhao, Z.; Chen, S.; Tang, B. Z. Aggregation-Induced Delayed Fluorescence Luminogens for Efficient Organic Light-Emitting Diodes. *Chem. Asian J.* **2018**, *14*, 828-835.

45. Shao, S.; Hu, J.; Wang, X.; Wang, L.; Jing, X.; Wang, F. Blue Thermally Activated Delayed Fluorescence Polymers with Nonconjugated Backbone and Through-Space Charge Transfer Effect. *J. Am. Chem. Soc.* **2017**, *139*, 17739-17742.

46. Kirner, S.; Sekita, M.; Guldi, D. M. 25th Anniversary Article: 25 Years of Fullerene Research in Electron Transfer Chemistry. *Adv. Mater.* **2014**, *26*, 1482–1493.

47. Hua, C.; Doheny, P. W.; Ding, B.; Chan, B.; Yu, M.; Kepert, C. J.; D'Alessandro, D. M. Through-Space Intervalence Charge Transfer as a Mechanism for Charge Delocalization in Metal-Organic Frameworks. *J. Am. Chem. Soc.* **2018**, *140*, 6622–6630.

48. AlKaabi, K.; Wade, C. R.; Dincă, M. Transparent-to-Dark Electrochromic Behavior in Naphthalene-Diimide-Based Mesoporous Mof-74 Analogs. *Chem* **2016**, *1*, 264-272.

49. Zhang, Z.; Awaga, K. Redox-Active Metal-Organic Frameworks as Electrode Materials for Batteries. *MRS Bull.* **2016**, *41*, 883–889.

50. Aubrey, M. L.; Long, J. R. A Dual-Ion Battery Cathode Via Oxidative Insertion of Anions in a Metal-Organic Framework. *J. Am. Chem. Soc.* **2015**, *137*, 13594–13602.

51. Gong, X.; Young, R. M.; Hartlieb, K. J.; Miller, C.; Wu, Y.; Xiao, H.; Li, P.; Hafezi, N.; Zhou, J.; Ma, L. Intramolecular Energy and Electron Transfer Within a Diazaperopyrenium-Based Cyclophane. *J. Am. Chem. Soc.* **2017**, *139*, 4107-4116.

52. Hunter, C. A.; Sanders, J. K. M. The Nature of π - π Interactions. *J. Am. Chem. Soc.* **1990**, *112*, 5525–5534.

53. Dyar, S. M.; Barnes, J. C.; Juríček, M.; Stoddart, J. F.; Co, D. T.; Young, R. M.; Wasielewski, M. R. Electron Transfer and Multi-Electron Accumulation in Exbox4+. *Angew. Chem. Int. Ed.* **2014**, *53*, 5371-5375.

54. Barnes, J. C.; Fahrenbach, A. C.; Dyar, S. M.; Frasconi, M.; Giesener, M. A.; Zhu, Z.; Liu, Z.; Hartlieb, K. J.; Carmieli, R.; Wasielewski, M. R.; Stoddart, J. F. Mechanically Induced Intramolecular Electron Transfer in a Mixed-Valence Molecular Shuttle. *Proc. Natl. Acad. Sci. U.S.A.* **2012**, *109*, 11546–11551. 55. Shen, P.-C.; Zhuang, Z.-Y.; Zhao, Z.-J.; Tang, B. Z. Recent Advances of Folded Tetraphenylethene Derivatives Featuring through-Space Conjugation. *Chin. Chem. Lett.* **2016**, *27*, 1115–1123.

56. Zhuang, Z.; Shen, P.; Ding, S.; Luo, W.; He, B.; Nie, H.; Wang, B.; Huang, T.; Hu, R.; Qin, A. Synthesis, Aggregation-Enhanced Emission, Polymorphism and Piezochromism of TPE-Cored Foldamers with through-Space Conjugation. *Chem. Commun.* **2016**, *52*, 10842–10845.

57. Zhao, Z.; He, B.; Nie, H.; Chen, B.; Lu, P.; Qin, A.; Tang, B. Z. Stereoselective Synthesis of Folded Luminogens with Arene-Arene Stacking Interactions and Aggregation-Enhanced Emission. *Chem. Commun.* **2014**, *50*, 1131-1133.

58. Luo, W.; Nie, H.; He, B.; Zhao, Z.; Peng, Q.; Tang, B. Z. Spectroscopic and Theoretical Characterization of through-Space Conjugation of Foldamers with a Tetraphenylethene Hinge. *Chem. Eur. J.* **2017**, *23*, 18041–18048.

59. He, B.; Nie, H.; Chen, L.; Lou, X.; Hu, R.; Qin, A.; Zhao, Z.; Tang, B. Z. High Fluorescence Efficiencies and Large Stokes Shifts of Folded Fluorophores Consisting of a Pair of Alkenyl-Tethered, π -Stacked Oligo-P-Phenylenes. *Org. Lett.* **2015**, *17*, 6174–6177.

60. He, B.; Nie, H.; Luo, W.; Hu, R.; Qin, A.; Zhao, Z.; Tang, B. Z. Synthesis, Structure and Optical Properties of Tetraphenylethene Derivatives with Through-Space Conjugation between Benzene and Various Planar Chromophores. *Org. Chem. Front.* **2016**, *3*, 1091-1095.

61. Zhuang, Z.; Bu, F.; Luo, W.; Peng, H.; Chen, S.; Hu, R.; Qin, A.; Zhao, Z.; Tang, B. Z. Steric, Conjugation and Electronic Impacts on the Photoluminescence and Electroluminescence Properties of Luminogens Based on Phosphindole Oxide. *J. Mater. Chem. C* **2017**, *5*, 1836–1842.

62. He, B.; Luo, W.; Hu, S.; Chen, B.; Zhen, S.; Nie, H.; Zhao, Z.; Tang, B. Z. Synthesis and Photophysical Properties of New through-Space Conjugated Luminogens Constructed by Folded Tetraphenylethene. *J. Mater. Chem. C* **2017**, *5*, 12553–12560.

63. Zhang, Y.; Shen, P.; He, B.; Luo, W.; Zhao, Z.; Tang, B. Z. New Fluorescent Through-Space Conjugated Polymers: Synthesis, Optical Properties and Explosive Detection. *Polym. Chem.* **2018**, *9*, 558–564.

64. Zhao, Z.; Lam, J. W.; Chan, C. Y.; Chen, S.; Liu, J.; Lu, P.; Rodriguez, M.; Maldonado, J. L.; Ramos-Ortiz, G.; Sung, H. H. Stereoselective Synthesis, Efficient Light Emission, and High Bipolar Charge Mobility of Chiasmatic Luminogens. *Adv. Mater.* **2011**, *23*, 5430–5435.

65. Xiang, D.; Wang, X.; Jia, C.; Lee, T.; Guo, X.; Molecular-Scale Electronics: From Concept to Function. *Chem. Rev.* **2016**, *116*, 4318-4440.

66. Morisaki, Y.; Ueno, S.; Saeki, A.; Asano, A.; Seki, S.; Chujo, Y. π-Electron-System-Layered Polymer: Through-Space Conjugation and Properties as a Single Molecular Wire. *Chem. Eur. J.* **2012**, *18*, 4216-4224.

67. Miguel, D.; Alvarez de Cienfuegos, L.; Martín-Lasanta, A.; Morcillo, S. P.; Zotti, L. A.; Leary, E.; Bürkle, M.; Asai, Y.; Jurado, R.; Cárdenas, D. J. Toward Multiple Conductance Pathways with Heterocycle-Based Oligo

© 2019 Chinese Chemical Society

(Phenyleneethynylene) Derivatives. *J. Am. Chem. Soc.* **2015**, *137*, 13818-13826.

68. Qi, S.; Iida, H.; Liu, L.; Irle, S.; Hu, W.; Yashima, E. Electrical Switching Behavior of a [60]. Fullerene-Based Molecular Wire Encapsulated in a Syndiotactic Poly (Methyl Methacrylate) Helical Cavity. *Angew. Chem. Int. Ed.* **2013**, *52*, 1049–1053.

69. Chen, L.; Wang, Y.-H.; He, B.; Nie, H.; Hu, R.; Huang, F.; Qin, A.; Zhou, X.-S.; Zhao, Z.; Tang, B. Z. Multichannel Conductance of Folded Single-Molecule Wires Aided by Through-Space Conjugation. *Angew. Chem. Int. Ed.* **2015**, *54*, 4231-4235.

70. Zhen, S.; Mao, J.-C.; Chen, L.; Ding, S.; Luo, W.; Zhou, X.-S.; Qin, A.; Zhao, Z.; Tang, B. Z. Remarkable Multichannel Conductance of Novel Single-Molecule Wires Built on Through-Space Conjugated Hexaphenylbenzene. *Nano Lett.* **2018**, 18, 4200-4205.

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