Model for Triplet State Engineering in Organic Light Emitting Diodes

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Engineering the position of the lowest triplet state ($T_1$) relative to the first excited singlet state ($S_1$) is of great importance in improving the efficiencies of organic light emitting diodes and organic photovoltaic cells. We have carried out model exact calculations of substituted polyenes to understand the factors that affect the energy gap between $S_1$ and $T_1$. The factors studied are backbone dimerisation, different donor-acceptor substitutions and twisted geometry. The largest system studied is an eighteen carbon polyene which spans a Hilbert space of about 991 million. We show that for reverse intersystem crossing (RISC) process, the best system involves substituting all carbon sites on one half of the polyene with donors and the other half with acceptors.

I. INTRODUCTION

Conjugated polymers have become one of the prominent candidates in flexible, solid state organic light emitting diode (OLED) devices. They are now employed in commercial displays and lighting applications. Emission properties in these devices are primarily based on injection of an electron and hole from electrodes into the device. These charges migrate under the influence of the electric field and could finally recombine, giving rise to a singlet or a triplet exciton on the conjugated system. Although simple spin statistics predicts generation of at most 25% singlet excitons due to independent injection of electron and hole, this is not borne out experimentally. The spin statistics does not account for the rate of formation of the excitons, and the rate depends upon the binding energies of excitons. The singlet exciton binding energy being smaller than that of the triplet exciton, more singlets are formed in a unit time than triplets. The exciton binding purely a consequence of electron-electron interactions and the 25% upper bound for singlet exciton formation is valid only in the noninteracting picture. Notwithstanding this, the actual yield of singlets is still small and low internal efficiency of electroluminescence in OLEDs beckons alternate routes such as harnessing triplet excited states. Inclusion of heavy metal atoms like platinum (Pt) or iridium (Ir) in the conjugated polymer enhances spin-orbit coupling which breaks the spin symmetry, thus allowing what is notionally a singlet-triplet transition, indeed electrophosphorescent devices have been developed using this principle. However, the longer lifetime of phosphorescence results in saturation of triplet state population of the emitter and promotes triplet-triplet annihilation (TTA). TTA could give rise to a lower energy nonemissive state which will not contribute to light emission. Hence, the alternate pathway i.e. population enhancement via conversion of triplets into singlet states seems to be a promising option for harnessing triplets to enhance electroluminescence quantum yield. The position of triplet $T_1$ relative to the singlet $S_1$ is also of importance in other applications such as photodynamic therapy, where collision between triplet oxygen and $S_1$ will give rise to $T_1$ and singlet oxygen, the latter being the reactive species in the therapy.

In organic systems $T_1 \rightarrow S_1$ population transfer can be achieved either through triplet-triplet annihilation or through reverse intersystem crossing (RISC). Triplet-triplet annihilation can theoretically maximize yield up to $\sim 11\%$ based on the simplistic argument that two spin-1 species can give rise to one spin two, one spin one and one spin zero species, resulting in a theoretical maximum yield of 1/9. This picture will change in interacting models depending upon the exciton binding energy of the species. However, there are claims that TTA can enhance OLED efficiency up to $\sim 62.5\%$. The excited singlet population can also be enhanced by the RISC mechanism. Although $E(T_1) < E(S_1)$ by Kasha rule, normally $E(T_1)$ is far less than $E(S_1)$ and triplets are lost. The RISC idea is to find systems in which the $S_1 - T_1$ gap is of order $k_B T$ under ordinary conditions. Thermal equilibrium may then repopulate $S_1$ and depending upon competing processes, make fluorescence the dominant decay mode for $T_1$ as well. Even better would be violation of Kasha rule, molecules with $E(T_1) > E(S_1)$. Thus reduction of energy gap between singlet excited state and triplet excited state and utilization of environmental thermal energy for RISC appears to be an attractive alternate path for enhancing the efficiency of electroluminescent devices.

Experimental and theoretical investigations of RISC are being carried out through the last decade, both in metal-containing and all-organic (metal-free) conjugated molecules and oligomers. Kohler et al. studied $S_1 - T_1$ gap using fluorescence and delayed-fluorescence techniques in platinum containing phenylene ethylene...
polymers with spacers of different size and in their all-organic analogs; corresponding energy gaps are of the order $0.7 \pm 0.1$ eV irrespective of the organic ligand used. In spite of this success, interest in metal containing polymers has waned since the metals in these systems are usually rare-earth. Metal-free thiophenylene based copolymers with (i) para-phenylene, (ii) ethylene, (iii) phenylene vinylene and (iv) thiophene vinylene moieties in their structure are synthesized by Chaudhuri et al. The lowest achievable $S_1 - T_1$ gap reported is as small as 0.02 eV, as determined by the difference in the peak position of the fluorescence and phosphorescence spectra. Endo et al. developed molecular luminophores where minimal spatial overlap of frontier molecular orbitals (HOMO and LUMO), residing on donor and acceptor moieties results in a gap of 0.11 eV, while Uoyama and coworkers have reported better molecular system with lower than 100 meV gap. In both reports, it is proposed that, introduction of steric hindrance results in very low spatial overlap between HOMO and LUMO of the corresponding molecules and consequently reduced gap between the excited states. This assumes that the energy difference between $S_1$ and $T_1$ is governed by the exchange integral involving the HOMO and LUMO orbitals, which to a first approximation is governed by the differential overlap of the HOMO and LUMO orbitals. Goushi et al. developed electroluminescent devices based on exciplex formation between donor and acceptor molecules, corresponding energy separation between $S_1$ and $T_1$ in these systems being $\sim 50$ meV. Recently, Adachi et al. synthesized molecules belonging to carbazole-triazine family with smaller $S_1 - T_1$ gaps (0.04 eV) and they have come up with some systems having comparable gaps, in the amine-sulphone family.

Theoretical modelling of excited singlet-triplet gap in molecular systems having a donor and acceptor moiety is done in configuration interaction picture with only single particle-hole excitations. Gierschner et al. investigated carbazole-paraterphenyl systems with different substituents on donor and acceptor parts and with different linkers between parent moieties using TD-DFT technique. However, TD-DFT still suffers from lack of accurate functionals for the calculations. Kohler et al. studied $S_1 - T_1$ gap in planar and twisted conformations of long $\pi$-conjugated oligomers of poly(p-phenylene vinylene) (PPV), poly(p-phenylene) (PP) and poly(p-phenylene ethynylene) (PPE). These calculations were performed in single CI space within the intermediate neglect of differential overlap (INDO) model. They found that the energy gap between singlet excited state ($S_1$) and triplet state ($T_1$) is independent of structure and consistent with the value of 0.7 eV, as they argued that the exchange interaction is short ranged in character, depends only on the electron-hole wavefunction overlap and therefore will be invariant in longer chains. The twist of each monomer about its neighboring monomer also does not affect much as twist in general remains in the range of $\leq 40^\circ$. Their calculation are based on the crude single CI approximation whose validity is in question in the twisted conformation. There is also work of Karsten et al. who have reported oligomers of 5,7-bis(thiophen-2-yl)thieno[3,4-b]pyrazine where the $S_1 - T_1$ gap reduces from $\sim 0.9$ eV to $\sim 0.5$ eV in the pentamers. The theoretical calculation at the INDO level, predicts the gap to be of the order of $\sim 0.8$ eV in the pentamers. Although, a number of materials with low singlet-triplet gaps are studied, most of them are molecular or oligomeric systems. Organic electronic devices use both small molecules and large oligomers. Both have their own advantages and disadvantages. Processing of large oligomers is an advantage but variation in oligomer structure from batch to batch is a disadvantage. On the other hand, molecules have well-defined structure but their processing is not as simple as those of oligomers and they also tend to crystallize, degrading the device performance. In the case of small molecules intermolecular charge separation or exciplex formation is necessary for obtaining smaller gap systems and this is possible only on introducing very strong donors and acceptors.

Our goal in the present paper is to explore various factors such as the strength of electron correlations, role of donor and acceptor substitutions, length of $\pi$-conjugation and the geometry of the conjugated backbone on the $S_1 - T_1$ gap in simple substituted and unsubstituted polyenes. Attributing the $S_1 - T_1$ gap to the strength of the exchange integral involving HOMO and LUMO orbitals is equivalent to single CI approximation, which is grossly inadequate in strongly correlated systems such as the conjugated $\pi$-systems. Instead, in our approach we carry out full CI calculation on model polyenes to explore the relative importance of different factors that control the $S_1 - T_1$ gap. We have employed the Pariser-Parr-Pople model to study the $S_1 - T_1$ gap. We have also employed the Hubbard model study to verify the accuracy of our extrapolations. In the PPP model, the ground state $S_0$ of an unsubstituted polyene consists of predominantly singly occupied $p_z$ orbitals, while the singlet $S_1$ state, if it is dipole allowed, has more contribution from a pair of doubly occupied and empty $p_z$ orbitals. If $S_1$ is a two-photon state, as is the case of long polyenes, it has more probability for singly occupied states than even the ground state. The triplet $T_1$ state is much like the $S_0$ state, except that the electron delocalisation is reduced due to Pauli blocking for electron transfer between neighboring orbitals having the same spin. In this study, we explore ways of increasing ionicity of the $T_1$ state to raise its energy close to that of the $S_1$ state, when $S_1$ is dipole allowed.

This paper is organized as follows. In the next section we introduce the model Hamiltonian and the methodology of our study. In the third, we discuss the role of (i) conjugation length, (ii) dimerisation strength, (iii) donor-acceptor strength in push-pull systems and (iv) the role of molecular geometry on the $S_1 - T_1$ gap respectively. In section 4, we summarize and conclude our study.
II. MODEL HAMILTONIAN AND COMPUTATIONAL METHOD

In present model system calculation, we consider linear even polyene chains of length varying between 4 – 18 sites in steps of 2 carbon sites, so as to have even number of electrons in the π system. In substituted polyenes, three type of substitutions are considered; in one, the donor and acceptor effects are introduced alternately along all carbon atoms in the chain, while in the second we have considered the donor and acceptor substitutions at the terminal carbon atoms and have rotated the molecule about the middle bond, in 4n + 2 (n integer) polyene chain. In the third, we have substituted one half of the 4n site polyene chain by donors and the other half by acceptors. The basic idea, behind considering alternate donor-acceptor substitutions is to reduce the effect of strong electron-electron interaction, for it is known that donor-acceptor substitutions is to reduce the effect of acceptors. The basic idea, behind considering alternate donor-acceptor substitutions is to reduce the effect of strong electron-electron interaction, for it is known that donor-acceptor substitutions is to reduce the effect of acceptors.

The Hamiltonian employed for interacting π-electronic systems is the Pariser–Parr-Pople (PPP) Hamiltonian, which considers long-range Coulombic interaction along with on-site Hubbard interaction (U):

\[
H_{PPP} = \sum_{i,\sigma} t_0 (1 - (-1)^{\delta} \delta \frac{(\tilde{c}_{i,\sigma}^{\dagger} \tilde{c}_{i+1,\sigma}^{\dagger} + \text{H.C.})}{2} + \sum_{i} \epsilon_i \hat{n}_i \\
+ \sum_{i} \frac{U_i}{2} \hat{n}_i \hat{n}_i - 1 + \sum_{i>j} V_{ij} (\hat{n}_i - z_i) (\hat{n}_j - z_j)
\]

(1)

\(\epsilon_i\) is the site energy at site \(i\), \(t_0\) is the mean nearest-neighbor hopping integral, \(U\) is the on-site Coulomb interaction energy. The intersite interaction energies, \(V_{ij}\) are obtained from Ohno interpolation scheme, assuming a mean C-C bond distance of 1.4Å. The quantity \(\delta\) is the fraction of dimerisation which we varied between 0 to 0.25, the C-C distance accordingly varies as 1.4(1 ± \(\delta\))Å, with \(\delta\). The \(\tilde{c}_{i,\sigma}^{\dagger}\) (\(\tilde{c}_{i,\sigma}\)) operators create (annihilate) an electron with spin \(\sigma\) in the \(p_z\) orbital at the \(i^{\text{th}}\) carbon atom; \(\hat{n}_i\) is the corresponding number operator and \(z_i\) is the local chemical potential given by the number of electrons in orbital ‘\(i\)’ that leave the \(i^{\text{th}}\) site neutral; for carbon in π-conjugation \(z = 1\). The standard PPP Hamiltonian parameters for carbon, namely \(t_0 = 2.4\) eV and \(U = 11.26\) eV are chosen for our study. Neglecting the last term, which is the intersite interaction term leads to the Hubbard model, the parameter \(U/t\) is usually varied to model different interaction strengths in this model.

The PPP Hamiltonian being non-relativistic, conserves total spin. Since we are interested in the singlet and triplet states, it is best to solve for the eigenvalues in a spin adapted basis. This has the twin advantage of dealing with smaller Hilbert space as well as labelling the eigenstates by the total spin. We have employed the diagrammatic valence bond (DVB) basis as the spin adapted basis and the Rumer-Pauling rule to weed out linear dependence. The resulting basis is linearly independent but non-orthogonal. The Hamiltonian matrix in this representation is non-symmetric. We use the Retrupper’s modification of the Davidson’s algorithm for obtaining a few low-lying states. Since we express the Hamiltonian matrix in a complete basis, the results obtained are exact or the full CI results. The major drawback with this method is that the full CI space becomes exponentially large with increase in system size. The largest space we have worked with in this paper is the triplet state of a polyene with 18 carbon atoms which spans a space of dimension 901, 955, 588. The use of electron-hole (e-h) symmetry and \(C_2\) symmetry leads to subspaces of dimensionality about one-fourth of this. However, both symmetries are killed if we introduce non-zero site energies to simulate donor (acceptor) behavior at the sites. Nonetheless, if we introduce non-zero site energies as in Fig. II \(C_2 \otimes e-h\) symmetry is retained and exploiting this results in dimensionality of the subspaces which are half the dimensionality of the unsymmetrized space. It should be remarked here that although the size of the resultant matrices are large, the matrices are extremely sparse and with Retrupper’s algorithm, we can obtain a few low lying states in each of the subspaces.

III. RESULTS AND DISCUSSION

Spin is conserved in all the model systems that we discuss, but other symmetries vary from model to model. The spin gap is always the singlet-triplet gap, \(E_{ST} = E(T_1) - E(S_0)\); We consider two singlet-singlet gaps \(E_1 = E(S_1) - E(S_0)\) and \(E_2 = E(S_2) - E(S_0)\) and the crucial \(S_1 - T_1\) gap, \(E(S_1) - E(T_1)\), which becomes negative when Kasha rule is violated.

FIG. 1. Schematic diagram of a polyene chain; \(+\epsilon\) and \(-\epsilon\) represent the donor and acceptor substitutions respectively, \(\delta\) is the dimerisation parameter and the transfer integral is modulated as \((1 + \delta) t_0\) for the double bond and \((1 - \delta) t_0\) for the single bond.
Singlet gap and two photon singlet state \[ E_{S} \] (1)

Following: Singlet gap \( \Delta_E \) between the gap between (triangles); gap between triplet and one photon singlet state (A. Unsubstituted uniform models

The Hubbard model in the limit, independent of the symmetry of the uniform Heisenberg chain, the spin gap \( \Delta_S \) is zero. This also holds for the uniform Hubbard model in the polymer limit. In Fig. 2 we see that the gap between the two photon state and the lowest triplet are vanishingly small, with the small extrapolated value indicating the magnitude of error in extrapolation from finite systems to the polymer limit. However, the gap between the one-photon state and \( T_1 \) remains finite. Our Hubbard model calculation are carried out at \( U/t = 4 \) and the two photon state is below the one photon state. For this interaction strength, the Hubbard chain will not be fluorescent, by Kasha rule. The Hubbard model extrapolations of excited state energies give results consistent with the physical picture.

In Fig. 4 we show the dependence of \( S_1 - T_1 \) gap on chain length for uniform \( (\delta = 0) \) polyenes in the PPP model. We see that the \( S_1 - T_1 \) gap remains finite in the polymer limit and reflects the fact that in the PPP model, as the chain length increases, the Hamiltonian incorporates interactions of longer range. Besides the \( S_1 \) state in the PPP model is the two photon state and the RISC process can only populate the nonemissive state, even if this gap is small. Therefore, we see that in unsubstituted correlated models, the vanishing of \( S_1 - T_1 \) gap will not result in a RISC process that can be useful in light emission.

B. Dependence of \( S_1 - T_1 \) gap on strength of dimerisation, \( \delta \)

In the noninteracting limit, even for nonzero \( \delta \), the \( S_1 - T_1 \) gap will be zero, although the \( S_0 - S_1 \) and \( S_0 - T_1 \) gaps remain finite. At intermediate correlation strengths in the Hubbard model, the \( S_1 - T_1 \) gap corresponds to the gap between the one photon state and the triplet state, since the gap will be dominated by the transfer energy contribution to the excited state. However, at \( U = 4t \),
FIG. 5. Variation of singlet gap \( [E(S_1) - E(S_0); \text{filled symbols}] \) and triplet gap \( [E(T_1) - E(S_0); \text{open symbols}] \) with inverse chain length \( N^{-1} \) in unsubstituted and substituted regular PPP chain. The symbol code for strength of the substitution is shown in the figure. The chain length at which singlet gap is less than the triplet gap is marked by arrow for \( \epsilon = 1 \). Inset: \( S_1 - T_1 \) gap vs \( \epsilon \) in the polymer limit.

where we have studied, the lowest singlet is the two photon state. The gap between the two photon singlet and triplet state increases for \( \delta = 0.1 \), compared to the uniform chain at every system size and in the polymer limit gives a finite gap of \( \sim 0.25t \) (Fig. 2). Thus the \( S_1 - T_1 \) gap for the dimerised chain is finite, unlike with the uniform Hubbard model.

In the PPP model also the \( S_1 - T_1 \) gap increases with dimerisation \( \delta \) (Fig. 4). We see from the figure that both in the large oligomers and in the polymer limit, there is a crossover in the 2A\(_g\) and 1B\(_u\) states for \( \delta \gtrsim 0.1 \), as we noted in\(^{22}\). The gap between the lowest excited singlet and the \( T_1 \) state is shown in the polymer limit (bottom curve). The gap between \( S_1 \) and \( T_1 \) states is nearly constant for \( 0.1 < \delta < 0.25 \). These results show that dimerisation alone is not a useful parameter for engineering the \( S_1 - T_1 \) gap.

C. Dependence of \( S_1 - T_1 \) gap on substitution

We have studied the dependence of the \( S_1 - T_1 \) gap on the strength of substitution. We have simulated alternate substitution of donor and acceptor groups of equal strength by introducing site energies; positive site energy \((+\epsilon)\) at donor site and negative site energy \((-\epsilon)\) at acceptor sites, \( \epsilon > 0 \), both of same strength \((\epsilon_D = -\epsilon_A)\). We have assumed four different donor (acceptor) strengths by varying \( \epsilon \) from 1 eV to 4 eV. For the uniform chain we find that in the polymer limit (Fig. 4), the \( S_1 - T_1 \) gap nearly vanishes for \( \epsilon = 3 \) eV and 4 eV. The \( S_1 - T_1 \) gap is positive \((E(S_1) > E(T_1))\) for \( \epsilon = 0 \) (unsubstituted) case but for \( \epsilon = 1 \) eV, the triplet \( T_1 \) energy is lower than the singlet \( S_1 \) energy, in the polymer limit, although \( E(N,S_1) > E(N,T_1) \) for \( N \) value ranging from 8 to 18 that we have studied. Indeed, the fact that for oligomers of length \( \gtrsim 30 \) sites (see Fig. 9), the Kashra rule is not obeyed is an advantage as \( T_1 \) to \( S_1 \) conversion will not need any thermal energy. Thus such oligomers would be ideally suited as high efficiency OLED materials. These results show that donor-acceptor substitution is a very sensitive way to control the \( S_1 - T_1 \) gap.

To explore the role of dimerisation in substituted chains, we have studied the \( S_1 - T_1 \) gap as a function of dimerisation of the PPP chains with different substitution strengths. One of the important features we note is that the \( S_1 - T_1 \) gap in the polymer limit is always positive, except in the case of \( \delta = 0.1 \) and \( \epsilon = 2 \) eV, where the extrapolated gap is slightly below zero (Fig. 4). For all values of \( \delta \), the \( S_1 - T_1 \) gap extrapolates to the least value for \( \epsilon = 2 \) eV. This shows that just moderately strong donor-acceptor substitution is sufficient to bring the \( S_1 \) and \( T_1 \) states close in energy.

D. Dependence of \( S_1 - T_1 \) gap on structure

In correlated systems it is conjectured that the singlet excitation is a charge like excitation which creates a pair of positive and negative charges while triplet excitation involves creation of a radical pair. This simple picture leads to the belief that if the geometry of a polyene system is twisted, we can separate the charges in the singlet exciton and spins in the triplet exciton, resulting in a situation where these separated entities do not overlap. In such a situation, it can be argued that the triplet state and the excited singlet state should be very nearly degenerate. To test this paradigm, we have studied the excited singlet and triplet states of twisted polyenes with \( 4n+2 \) carbon atoms with a donor and an acceptor of equal strengths substituted at the end sites of the chain, as a
function of the twist angle. The twist is effected about the central double bond and the transfer integral is taken as $t \cos \theta$ where $\theta$ is the twist angle and $t$ is the transfer integral which is $2.568$ eV, corresponding to a polycene double bond. In Fig. 7 we have presented the $S_1 - T_1$ gap as a function of the twist angle for a polycene chain of 14 carbon sites, and for different site energies. We find that the $S_1 - T_1$ gap is large and remains so as the central bond is twisted. The dependence, though weak is non-monotonic and shows a minimum around $40^\circ$ twist angle. This result can be explained by the fact that the charge separation leads to lower singlet excitation energy but to vanishing triplet excitation energy. At $\theta = 90^\circ$, the gap between the ground state and the triplet excited state is zero, but the gap between the ground state and the singlet excited state though near a minimum is still very large since the interaction between the charges at either ends ($U - V_{12N}$) is quite large. Thus in strongly correlated systems, it is not possible to reduce the $S_1 - T_1$ gap by blocking the transfer between two halves of the system, with the type of substitution that we have so far considered.

If the substitution on the polycene chain is such that both the excited singlet and excited triplet states are ionic in the same way, we can in principle reduce the $S_1 - T_1$ gap. To test this, we have studied the $S_1 - T_1$ gap in $4n$ (n integer) carbon polyenes when on one half of the chain we have donors and on another half we have acceptors (Fig. 8). The chain is twisted about the middle bond by $90^\circ$ so that the transfer between the two halves of the chain is zero. In this geometry, we have obtained the $S_1 - T_1$ gap for various donor/acceptor strengths, $\epsilon$. We find that the $S_1 - T_1$ gap vanishes for a range $1.8 \leq \epsilon \leq 2.5$ and follows from the fact that the two halves of the chain are ion-radicals and the hopping integral being zero between the two halves, the $S_1$ and $T_1$ states become degenerate. When $| \epsilon |$ is less than $1.8$ eV, then the two halves are not ion radicals and $S_1$ and $T_1$ are not degenerate. For $| \epsilon |$ greater than $2.5$ eV, there is one electron transfer in the ground state and $S_0$ and $T_1$ are degenerate, while in $S_1$, there is negligible transfer of electron from one half to the other and $S_1 - T_1$ degeneracy is again lost. This can be seen in Fig. 8 inset, where we have shown the number of $\pi$-electrons in the left half of chain as a function of $\epsilon$, for 16-site polycene chain. Indeed, some of the experimental systems have the feature of donor substituted sites and acceptor substituted sites connected through a twisted bond with very small transfer integral between the two substituted parts.

IV. CONCLUSION

Engineering the energy gap between the triplet ($T_1$) state and the excited singlet ($S_1$) state is of importance in improving the efficiency of organic electronic devices such as OLEDs and OPV cells. The aim of this paper has been to find the factors that affect the gap between excited singlet ($S_1$) and the lowest triplet ($T_1$) state of a $\pi-$conjugated molecule. We have carried out exact or Full CI calculations on polyene chains with up to 18 carbon atoms. We find that the usual factors such as change in dimerisation and rotation about the central double bond do not materially affect this gap. However, substitution by donor and acceptor groups at alternate carbon sites has a strong effect on the $S_1 - T_1$ gap and the gap nearly vanishes for some values of the donor (acceptor) strength and dimerisation parameter. Substitution with donor/acceptor groups renders the triplet $T_1$ state more ionic in character and therefore raises its energy closer to that of the singlet $S_1$ state which is known to
be ionic in character. This study provides a basis for systematically controlling the $S_1 - T_1$ gap and will be useful in designing molecules with small $S_1 - T_1$ gap. Fig. 9 summarizes the dependence of $S_1 - T_1$ gap on the factors such as dimerisation and substitution by push-pull groups at alternate sites. However, the most promising case is when we have donors substituted at all sites on one half of the chain and acceptor substituted at the other half. In this case the $S_1 - T_1$ gap vanishes for a range of donor (acceptor) strengths, when the chain is twisted around the middle bond separating the donors and acceptors. It should be possible to synthesize such systems for device applications.

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