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Benzobisthiadiazole-based high-spin donor-acceptor conjugated polymers with localized spin distribution†

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Stable organic semiconductors (OSCs) with a high-spin ground-state can profoundly impact emerging technologies such as organic magnetism, spintronics, and medical imaging. Over the last decade, there has been a significant effort to design π-conjugated materials with unpaired spin centers. Here, we report new donor-acceptor (D–A) conjugated polymers comprising cyclopentadithiophene and cyclopentadiselenophene donors with benzobisthiadiazole (BBT) and iso-BBT acceptors. Density functional theory calculations show that the BBT-based polymers display a decreasing singlet–triplet energy gap with increasing oligomer chain length, with a degenerate singlet and triplet states for $N = 8$ repeat unit. Furthermore, a considerable distance between the unpaired electrons with a pure diradical character disrupts the π-bond covalency and localizes the unpaired spins at the polymers ends. However, replacing the BBT acceptor with iso-BBT leads to a closed-shell configuration with a low-spin ground-state and a localized spin density on the polymers cores. This study shows the significance of the judicious choice of π-conjugated scaffold in generating low- ($S = 0$) and high-spin ($S = 1$) ground-state in the neutral form, by modulation of spin topology in extended π-conjugated D–A polymers for emergent optoelectronic applications.

Introduction

High-spin ($S \geq 1$) organic molecules with a pure diradical character possess a wide variety of intriguing molecular and electronic properties and have potential applications for numerous advanced optoelectronic devices. The unpaired electrons in the high-spin molecules may impart strong ferromagnetic interactions, making them useful as a building block for the all-organic magnet[14] or magnetic sensors,[2] charge-storage[13] and rewritable memory devices.[11] Although a large number of works have been conducted in designing and synthesizing high-spin organic molecules,[12] only a handful of polymeric systems are reported, which invert the spin pairing in the singlet state ($S = 0$) and stabilize a high-spin ($S = 1$) ground-state in the neutral form.[16]–[20]

Organic semiconductors (OSCs) with two unpaired electrons residing in two degenerate or nearly degenerate non-bonding frontier molecular orbitals (FMOs) possess a reduced antiferromagnetic (AFM) coupling between the unpaired electrons than the closed-shell molecules. These molecules show a small highest occupied MO (HOMO)–lowest unoccupied MO (LUMO) energy gap, and significantly reduce the energetic difference between the low-to-high spin states (AE)10,16,21–29. The unpaired electrons in the open-shell OSCs impart exotic spin-correlated functionalities. The spin distribution along the polymer chain modulates ground-state spin multiplicity and magnetic properties of the materials.[11,16]–[18] Although the presence of unpaired electrons is a requisite for the open-shell diradicals,[12] localization of unpaired electrons on different sites in the π-conjugated scaffold has been rather difficult.[18]–[11] Localized spin distribution has been achieved in radical-functionalized graphene nanoribbons (GNRs) or zigzag GNRs (ZGNRs) with crystallographic edge orientations, where the radical sites act as spin-bearing units, generating magnetic edge states (Fig. 1a–b).[12] However, in the case of modified (Z)GNRs, the spin in these systems is a result of spin-bearing side-chain functionalization rather than an intrinsic property of these materials[20] Polyacenes (Fig. 1c), on the other hand, show disjoint non-bonding molecular orbitals leading to spin distributions localized at the core.[12,17,21] The previous studies on high-spin state materials indicates a complete delocalization of the unpaired electrons on the π-conjugated backbone, providing thermodynamic stabilization of the molecules (Fig. 1d–e).[16]–[17] Therefore, the development of new materials with intrinsic localized electron den-

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Fig. 1 Archetypal examples of π-conjugated materials with variable spin localization and ground-states. (a) zigzag graphene nanoribbons (ZGNRs) with crystallographic edge orientations, (b) radical-functionalized GNRs show magnetic edge states, (c) polyacenes show disjoint MOs with core localized spin density distribution, (d–e) high-spin ($S = 1$) ground-states D–A polymers with delocalized spin density distributions, and (f–i) the tailored BBT- and iso-BBT-based D–A polymers used to tune the spin topology, show low- ($S = 0$) to high-spin ($S = 1$) states in the neutral form. Energy values ($\Delta E_{ST} = E_S - E_T$) are provided in kcal/mol and diradical character ($y_0$) is a dimensionless quantity. All $y_0$ values and $\Delta E_{ST}$ of (f–i) from computational calculation at $N = 8$ repeat unit.

Fig. 1f–i Here, we present new donor-acceptor (D–A) conjugated polymers based on alternating cyclopentadithiophene (CPDT) and cyclopentadiselenophene (CPDS) donors, which are π-conjugated with benzobis[1,2-c;4,5-c’]bis[1,2,5]thiadiazole (BBT) and benzo[1,2-d:4,5-d’]bis[1,2,3]thiadiazole (iso-BBT)22 acceptors, respectively (Fig. 1f–i), where the BBT-based polymers show a high-spin ($S = 1$) ground-state with a pure diradical character ($y_0 = 1$); however, the iso-BBT-based polymers have a closed-shell ($y_0 = 0$) configuration with a low-spin ($S = 0$) ground-state. These types of D–A topologies offer opportunity to tailor molecular structures to tune electronic properties, while having solution processability and backbone flexibility, making D–A polymers as a suitable building block for numerous optoelectronic technologies.20–23

We employed the structurally symmetric BBT and iso-BBT acceptors to manipulate the spin density distribution to have open-shell and closed-shell configurations, respectively.22 The diradical nature of the BBT acceptor is well-known along with its high electron affinity due to the hypervalent sulfur and strong pro-quinoid character, leading to the quinoidal molecular backbone and a small singlet–triplet gap ($\Delta E_{ST}$).39,49–54 The lower LUMO energy level inherent to the BBT unit decreases the HOMO–LUMO energy gap, which facilitates admixing of HOMO and LUMO to the ground electronic state.55 Also, the thiadiazole units of the BBT recover aromatic stabilization energy in the open-shell ground-state, a driving force facilitating double-bond breaking.22,53,56 As a result, the CPDT-BBT and CPDS-BBT polymers show a pure diradical character and a degenerate $\Delta E_{ST}$ at the neutral state, which would facilitate magnetic switching from the low-spin to high-spin ground-state.
the high-spin ground-state. However, a large HOMO–LUMO energy gap in the iso-BBT-based polymers and lack of thiadiazole units create a highly aromatic backbone, leading to a closed-shell configuration with localized spin density in the polymers cores.

Computational details

Selection of appropriate functional

Geometry optimization is performed with Gaussian 16 software package, without any symmetry constraints. Molecular geometries for the electronic singlet ($S = 0$) and the triplet ($S = 1$) states of the model oligomers ($N = 1$ to $8$) are optimized using hybrid density functional, B3LYP. For the Se and Si atoms, LANL2DZ basis set is used along with associated effective core potentials and 6-31G(d,p) basis set is used for other atoms. All parameters for geometry optimization are set to default. For larger oligomers, geometries are considered optimized once the forces on all atoms converged to zero.

We have performed benchmark calculations on dimer ($N = 2$) of CPDT-BBT polymer using different functionals with variable amount of Hartree-Fock (HF) exchange at 6-31G(d,p) basis set (see Table S1). Calculations are performed with pure functional, BLYP (HF exchange = 0.0 %), hybrid functionals with low HF exchange, B3LYP (HF exchange = 20.0 %) and PBE1PBE (HF exchange = 25.0 %), hybrid functionals with intermediate HF exchange, BHandLYP (HF exchange = 50.0 %) and M062X (HF exchange = 54.0 %), and long-range corrected hybrid functionals, CAM-B3LYP (HF exchange = 19.0 % short-range and 65% long-range), and ωB97X-D (HF exchange = 22.0% short-range and 100% long-range). The B3LYP functional has the lowest spin-contamination among all the hybrid density functional considered. Other functionals give a large spin-contamination that lead to an increase in the diradical character or even unphysical polyradical character, not observed in BBT-based materials. Also, both the $\gamma_0$ and spin contamination increased as HF exchange is increased in the hybrid functionals. The pure functional BLYP predicts the dimer ($N = 2$) of CPDT-BBT polymer has a closed-shell configuration, indicating a large repeat unit is necessary to display considerable open-shell character. Interestingly, both the BLYP and ωB97X-D predicts the same $\Delta E_{ST}$ energy gap; however, due to a large spin-contamination, the diradical index is large with $\omega B97X-D$ functional. A similar trend in $\Delta E_{ST}$ and $\gamma_0$ is observed with B3LYP and M062X; however, a large spin-contamination increased the $\gamma_0$ for the latter one. In addition, our study on large polymeric system indicate (U)B3LYP functional combined with 6-31G(d,p) basis set accurately predicted the experimental electrochemical band gap.

To see the effect of density functional of these systems, we have also performed calculations with optimally tuned range-separated hybrid functional (OT-RSH) for the smaller oligomers of these conjugated polymers. The tuned parameter, $\omega$ is determined based on LC-ωPBE functional. As representative molecules, we have considered the dimer and tetramer of CPDS-BBT (open-shell) and CPDS-iso-BBT (closed-shell) and computed the $\Delta E_{ST}$, diradical index, and spin densities. We have also investigated the performance using the screened version of RSH (OT-SRSH) at $\epsilon = 3.0$ (typical dielectric constant for organic materials) to account for the electronic polarization. The range-separated parameter ($\alpha$) using LC-ωPBE is determined by the ionization potential (IP)-scheme. In case of OT-SRSH, the tunable parameters, $\alpha$ is set to 0.2 and $\beta$ is evaluated by $1/\epsilon - \alpha$. The electronic properties calculated with (U)B3LYP, OT-RSH, and OT-SRSH methods are in agreement with (U)B3LYP functional. Therefore, we have performed all the calculations and analysis with (U)B3LYP functional and 6-31G(d,p) basis set.

Broken-symmetry (BS) calculation

The geometry optimization is initialized with a restricted wave function, and a broken-symmetry (BS) wave function is used to characterize the open-shell singlet state. A stability test on the wave function showed restricted-to-unrestricted instability for oligomers from monomers ($N = 1$) of the BBT-based polymers. However, no such instability is found in the case of the iso-BBT-based polymers. The triplet state is optimized with an unrestricted wave function. Also, the expectation value ($\langle S^2 \rangle$) can be used as an indication of spin-contamination in the ground-state, where a value of 1 and 2 indicate no spin-contamination in the pure singlet and triplet states using the BS method, respectively. After spin annihilation, triplet states indicate $\langle S^2 \rangle$ value close to 2; however, in the case of singlet state, $\langle S^2 \rangle$ value found to be higher than 1, indicating spin-contamination of triplet spin multiplicities in the singlet ground-state. No spin-projection method is used to remove spin-contamination in this work.

Diradical and tetraradical characters

The presence of unpaired electrons in an open-shell molecule is quantitatively defined by the multi-radical indexes ($\gamma_i$), where the indexes ranges from $0 \leq \gamma_i \leq 1$ ($i = 0 \rightarrow 1$), defining a pure open-shell molecule at $\gamma_i = 1$ and a closed-shell at $\gamma_i = 0$. The upper end value of the $\gamma_i$ dictates a bond dissociation limit with a high degree of localization of the unpaired electrons, whereas, the lower end defines a higher electron–electron coupling and Coulomb repulsion. The diradical ($\gamma_0$) and tetraradical ($\gamma_1$) indexes are obtained from population analysis of natural orbitals as the occupation number of the lowest unoccupied natural orbitals (LUNOs).

Prediction of the unpaired spins locations and orbital overlap ($\langle S^0B \rangle$)

NBO6 program package is used to predict the unpaired spins locations from the natural spin densities of Kohn-Sham molecular orbital (MO). The overlap between different spin orbitals ($\langle S^0B \rangle$) is computed with the Multiwfn program package, where $\langle S^0B \rangle = 1.0$ indicates a complete overlap between two spin orbitals.

Prediction of aromatic character

To predict the aromatic/quinoidal nature of the individual rings on each polymer, isotropic nucleus independent chemical shift

\[ \frac{\langle S^0B \rangle}{\epsilon} \]
Fig. 2 Resonance structures of the CPDT-BBT dimer \((N = 2)\) showing open-shell and closed-shell conformations. In the closed-shell form \((a)\), the central benzenoid ring of the BBT acceptor and thiophene units in the CPDT donor have aromatic character (in blue), leaving both thiadiazole units of the BBT acceptor with hypervalent sulfur. For the open-shell diradical forms, the thiadiazole units recover aromatic stabilization energy with either \((b)\) the sulfur-containing five-member rings in the terminal donor have an aromatic character or \((c)\) both donors have quinoidal forms. In the open-shell tetraradical form \((d)\), both the donors and thiadiazole units of the acceptors recover aromatic stabilization energy.

\[
\text{NICS}_{\text{iso}}(1) = \text{computed using the gauge-independent atomic orbital (GIAO)} \]

method wherein a single point energy calculation is carried out with a ghost atom placed at 1 Å perpendicularly above the plane of the ring to account for only the \(\pi\)-electron contribution. A large negative \(\text{NICS}_{\text{iso}}(1)\) value indicates the corresponding ring is aromatic. Ring currents are analyzed with anisotropy of the induced current density (ACID) method at CSGT-UB3LYP/6-31G(d,p) level of theory and rendering is performed with a locally developed code. The 2D-ICSS (2D-isochronal shielding surface) maps are generated by the method developed by Klod et al. The harmonic oscillator model of aromaticity (HOMA) is calculated with the following equation:

\[
\text{HOMA} = 1 - \frac{98.89}{n} \sum_{i=1}^{n} (R_i - 1.397)^2
\]

where, \(n\) is the number of bonds considered in a particular ring, \(R_i\) is the optimized bond length at the equilibrium geometry. HOMA = 1 indicates a complete aromatic structure.

**Results and discussion**

**Selection of the donor and acceptor units**

We choose the donors and acceptors with extensive screening of different electron-rich and electron-deficient units based on the diradical character and \(\Delta E_{\text{ST}}\) (see Fig. S1–S2). We have selected C-bridged CPDT and CPDS donors as they promote a planar molecular backbone and offer flexibility in using molecular topology to modulate electronic properties. They also have an elevated HOMO leading to a smaller band gap and a substantial \(\pi\)-conjugation along the molecular backbone. The substitution of S in CPDT with Se can increase the quinoidal character, leading to a higher diradical character. The BBT acceptor, when conjugated with CPDT donor, develops an open-shell diradical character and displays a smaller \(\Delta E_{\text{ST}}\) than the other acceptors for the monomer unit (see Fig. S1). The hypervalent sulfur in the BBT unit can transform from high energy \(-N=S=N-\) structure to a lower energy \(-N-S-N-\) stable configuration in the open-shell resonance form, recovering aromatic stabilization energy in the ground-state; therefore, increasing diradical character. However, the iso-BBT acceptor has a higher LUMO level than the BBT unit, which increases the HOMO–LUMO energy gap, leading to a closed-shell configuration. Therefore, the selection of these two acceptors along with CPDT and CPDS donors can display two different regimes in the diradical character scale, which can provide insights into different spin distribution along the backbone of the polymer. Furthermore, an important observation from various acceptors with thiadiazole end-cap...
units (P8–P12, Fig. S1) is that the head-to-head fusion of the thiadiazole unit with the six-member ring reduces the $\Delta E_{ST}$ and develop a small open-shell character ($\gamma_0 = 0.040$) (Fig. S1). Therefore, designing new acceptors with head-to-head conjugation of thiadiazole units in a six-member core is an efficient technique to achieve diradical character in smaller oligomers.

Closed-shell and open-shell resonance structures

The four canonical forms of the CPDT-BBT dimer ($N = 2$) representing closed-shell, open-shell diradical, and open-shell tetraradical character are given in Fig. 2, which describes the role of the thiadiazole and benzenoid units of the BBT acceptor, and the CPDT donor in obtaining open-shell configuration. In moving from high energy closed-shell (Fig. 2a) to stable open-shell diradical configurations (Fig. 2b–c), the four thiadiazole rings recover aromatic stabilization energy at the expense of the aromatic character of the two/four thiophene units of the CPDT donor and two benzenoid rings of the BBT acceptor, leading to a quinoidal character in the CPDT donor. However, in the tetraradical canonical form (Fig. 2d), although the same four thiadiazole rings get an aromatic character, only two benzenoid rings loose aromaticity in the BBT unit, while keeping the thiophene units of the CPDT donor aromatic as in the closed-shell form (Fig. 2a). Therefore, the tetraradical canonical form does not favor in the BBT-based polymers, indicating the open-shell diradical form is the predominant configuration in the BBT-based materials.\[22,52,53\] Also, the conjugation between the CPDT donor and BBT acceptor favor the formation of quinoidal character in the CPDT donor, which facilitates the separation of the unpaired spins towards the polymer ends, increasing the open-shell diradical character and reducing singlet–triplet energy gap. However, non-aromatic donors (such as, pentadiene and [10]annulene) (Fig. S3) greatly reduces the quinoidal character in the polymer backbone, significantly reducing the open-shell character and increasing the singlet–triplet energy gap.

Evolution of open-shell character and high-spin ground-state

The open-shell character and energy difference between the lowest singlet and the triplet state ($\Delta E_{ST}$) correlate with one another.\[15\] The key electronic properties of the polymers considered in this study are presented in Table 1 (see also Table S3 and S4). We have also included the data for CPDT-TQ polymer, which has a high-spin ground-state as quantified through experimental characterization and validated with theoretical calculation at (U)B3LYP functional and 6-31G(d,p) basis set.\[16\] The increase in oligomer length is associated with a gradual decrease in $\Delta E_{ST}$ for BBT and iso-BBT-based polymers (Table 1 and S4). However, the rate of decrease is faster for the BBT-based polymers than the iso-BBT-based polymers. At $N = 5$, the $\Delta E_{ST}$ plateaus for the iso-BBT-based polymers (Table S4); however, an opposite trend is observed for the BBT-based polymers, where addition of repeat units reduces the $\Delta E_{ST}$, while increasing diradical character ($\gamma_0$) (Table 1 S4).

The narrowing of the $\Delta E_{ST}$ indicates more stabilization of the open-shell form than the closed-shell configuration (Fig. S4). For instance, in tetramer ($N = 4$), the energy of the closed-shell is significantly increased (10.56 kcal/mol and 12.37 kcal/mol for CPDT-BBT and CPDS-BBT, respectively) compared to the open-shell state, and the triplet state lies only 0.08 kcal/mol in CPDT-BBT (0.02 kcal/mol in CPDS-BBT) above the singlet (Fig. S4). Also, the $\Delta E_{ST}$ of the CPDT-BBT octamer reaches well below the thermal energy ($kT$) at room temperature, indicating a very high population (74.99 %) of the triplet state at the ambient conditions, whereas singlet and triplet states of the CPDS-BBT ($N = 7–8$) are degenerate, showing 75.0 % population of triplet state at room conditions (Table 1 S4). The diradical character also reaches the limit ($\gamma_0 = 1.0$), signifying the lack of covalency between the unpaired electrons. To examine the effect of non-aromatic donors, we replaced the CPDT with pentadiene and [10]annulene (Fig. S3). The diradical character reduces significantly ($\gamma_0 = 0.105$ and 0.00 at $N = 4$, for pentadiene and [10]annulene, respectively) and a large increase in the $\Delta E_{ST}$ is observed (0.41 eV and 0.46 eV at $N = 4$, for pentadiene and [10]annulene, respectively), which indicates the important role of CPDT donor in realizing high-spin polymers than other non-aromatic donors.

The connecting bonds between the donor and adjacent acceptor units vary within 1.392–1.420 Å in BBT-based polymers and 1.447–1.455 Å in iso-BBT-based polymers (Fig. S5–S19, Table S5–S6), indicating a highly $\pi$-conjugated backbone in case of the open-shell polymers, which can increase the electronic coherence and charge-transfer along the $\pi$-conjugated backbone. On the other hand, the non-aromatic donors reduces the $\pi$-conjugation, as observed from a large connecting bonds (1.45 Å, and 1.47 Å) between the pentadiene and [10]annulene donors and BBT acceptor, respectively (Fig. S20–S21). A coplanar geometry ($\phi \approx 180^\circ$) observed in the BBT-based polymers increases the diradical character and reduces $\Delta E_{ST}$ and HOMO–LUMO gaps (Fig. S22–S23). Also, a coplanar geometry facilitates $\pi$-stacking and induces strong intermolecular interactions between the unpaired electrons as well.\[17,28\] However, the iso-BBT-based polymers are less planar (Fig. S24) due to the steric repulsion between the sulfur in iso-BBT acceptor and hydrogen atom in the donor unit, reducing the $\pi$-conjugation, which is readily visible from the large connecting bonds. Moreover, the singlet and triplet electronic states display equal bond lengths (Table S5–S6) for the larger repeat units ($N = 7–8$), signifying a (near-)degeneracy between these two electronic states, as evident from $\Delta E_{ST}$ of the BBT-based polymers (Table 1 S4, Fig. S4).

A very small $\Delta E_{ST}$ indicate a significant electronic correlation between these two states; therefore, increasing the exchange interaction in the triplet state.\[11,16\] The MO diagrams (Fig. S25–S28 and S33–S36) of the BBT-based molecules indicate with the increase in oligomer length, the $\alpha$- singly occupied MO (SOMO) and $\beta$-SOMOs are progressively localize to the opposite ends of the polymers chain. Consequently, the unpaired electrons with antiparallel spins are permitted to correlate in separate spaces, reducing the bond covalency and increasing $\gamma_0$.\[15\] These types of disjoint MOs are reported for longer acenes (Fig. 1c)\[22\] or other long $\pi$-conjugated open-shell molecules\[7,11,15\], which also has recently been demonstrated in an alternating D–A scaffold.\[15\] However, in the case of the iso-BBT-based polymers, the HOMO
Table 1 Electronic properties computed at (U)B3LYP/6-31G(d,p) level of theory and basis set for the CPDT-TQ, BBT- and iso-BBT-based polymers, provided as a function of chain length (N). The singlet–triplet energy gap (ΔE_{ST}), population (P_T) of the triplet (S = 1) state at room temperature, energy of the FMOs, energetic difference between the FMOs (E_F), and diradical character index (ν_0) of the polymers. Energy values are in eV, and ν_0 is a dimensionless quantity.

| Polymer  | N  | ΔE_{ST} | P_T | HOMO | LUMO | E_F | ν_0 |
|----------|----|---------|-----|------|------|-----|-----|
| CPDT-TQ  | 4  | -1.02 × 10^{-1} | 6.45 | -4.17 | -3.26 | 0.91 | 0.422 |
|          | 8  | -2.30 × 10^{-2}  | 56.65 | -4.07 | -3.30 | 0.77 | 0.913 |
| CPDT-BBT | 2  | -7.85 × 10^{-4}  | 14.37 | -4.61 | -3.43 | 1.18 | 0.604 |
|          | 4  | -3.37 × 10^{-3}  | 72.61 | -4.44 | -3.50 | 0.95 | 0.966 |
|          | 6  | -1.44 × 10^{-4}  | 74.90 | -4.40 | -3.51 | 0.89 | 0.997 |
|          | 8  | -5.44 × 10^{-6}  | 74.99 | -4.39 | -3.52 | 0.88 | 1.000 |
| CPDT-iso-BBT | 2  | -10.50 × 10^{-1} | 0.00 | -5.08 | -3.07 | 2.01 | 0.000 |
|          | 4  | -9.50 × 10^{-1}  | 0.00 | -4.93 | -3.24 | 1.69 | 0.000 |
|          | 6  | -9.40 × 10^{-1}  | 0.00 | -4.89 | -3.29 | 1.60 | 0.000 |
|          | 8  | -9.40 × 10^{-1}  | 0.00 | -4.88 | -3.31 | 1.57 | 0.000 |
| CPDS-BBT | 2  | -4.88 × 10^{-4}  | 33.26 | -4.61 | -3.46 | 1.16 | 0.700 |
|          | 4  | -7.51 × 10^{-4}  | 74.48 | -4.47 | -3.51 | 0.96 | 0.984 |
|          | 6  | -1.09 × 10^{-5}  | 74.99 | -4.44 | -3.52 | 0.91 | 0.999 |
|          | 8  | -0.00 × 10^{0}   | 75.00 | -4.43 | -3.53 | 0.89 | 1.000 |
| CPDS-iso-BBT | 2  | -9.20 × 10^{-1}  | 0.00 | -5.00 | -3.17 | 1.83 | 0.000 |
|          | 4  | -3.90 × 10^{-1}  | 0.00 | -4.84 | -3.36 | 1.48 | 0.000 |
|          | 6  | -7.80 × 10^{-1}  | 0.00 | -4.79 | -3.41 | 1.38 | 0.000 |
|          | 8  | -7.80 × 10^{-1}  | 0.00 | -4.77 | -3.44 | 1.33 | 0.000 |

Spin density distributions of the D–A polymers

Control and modulation of localized spins (radical centers) are necessary to realize organic magnetic and spin manipulation devices. The spin density distribution along the polymers’ backbone are shown in Fig. 3 and Fig. S47–S50 in the Supplementary Information. Increasing the oligomer length localizes the unpaired electrons at the polymer ends of the BBT-based polymers, indicating a complete polarization of the unpaired spins. We observe a greater localization in the CPDS-BBT polymer than the CPDT-BBT polymer (see Fig. 3). For the iso-BBT-based polymers, upon increasing the chain length, the spin density distribution for the S = 1 state is localized at the polymer core instead of at the ends as observed in the BBT-based polymers (Fig. 3, S47–S50), which indicates the choice of the acceptors manipulates the spin localization in these polymers. A large and dilute aromaticity in the pentadiene-based polymer delocalizes the spin density along the polymer backbone (Fig. S51).

We have also analyzed the spin density distribution of the triplet state (S = 1) for CPDT-BBT and CPDS-BBT octamers (N = 8) with a range-separated functional,ωB97X. We selected the ωB97X functional as it provided the smallest mean absolute deviation for selected polycyclic aromatic hydrocarbons when compared to QCISD spin densities. The spin density distribution predicted with ωB97X is consistent with the density distribution obtained with the UB3LYP functional (Fig. 3, S54), which indicates the localized spin topology is an intrinsic property of the BBT-based polymers.

Generally, for an open-shell system, it is observed that unpaired electrons occupy the frontier molecular orbitals (i.e., highest energy singly occupied molecular orbitals). To see if this is the case for extended (polymeric) systems, we analyze the α- and β-SOMOs for CPDT-BBT and CPDS-BBT at N = 8. We find that the α-SOMO is delocalized along the polymer backbone, while the spin density plots show localized spin density at the polymers ends. The β-SOMO (Fig. S52), however, is localized at the chain end. Upon further examination of SOMOs of CPDT-BBT (N = 8) with energies lower than the frontier SOMOs (Fig. S52,S53), we notice a significant overlap (S^{αβ} = 0.903) between the α-SOMO (E = -4.547 eV) and β-SOMO-1 (E = -4.579 eV), potentially cancelling the contribution to the total spin density of these orbitals. It turns out that the α-SOMO-1 (E = -4.631 eV) and β-SOMO (E = -4.388 eV) (S^{αβ} = 0.234) contribute to the total spin density (Fig. S52, Table S7), which is consistent with the inferences drawn from the spin density plots (Fig. 3). Furthermore, the atomic spin density calculated for the S = 0 and S = 1 states have the same positive value (0.26 and 0.38 in CPDT-BBT; 0.25 and 0.40 in CPDS-BBT, respectively) at the terminal C atoms (Fig. S44), which increases from the core to the ends of the BBT-based polymers, hence reducing the overlap between the unpaired electrons. Moreover, a large positive density is observed at the terminal nitrogen (N) atoms in the BBT acceptor, which can facil-
Fig. 3 The ground-state geometry and pictorial representations of spin density distributions for the (a) CPDT-TQ, (b) CPDT-BBT, (c) CPDT-iso-BBT, (d) CPDS-BBT, and (e) CPDS-iso-BBT ($N = 8$) polymers in their $S = 1$ states. The blue and green surfaces represent positive and negative contributions of the spin density at an isovalue = 0.0002 au. The most probable locations for the unpaired electrons with largest atomic spin density are highlighted in open circles.

To better understand different spin topologies in the BBT and iso-BBT-based polymers and to gain insights into the aromatic/quinoidal nature of the $\pi$-conjugated backbones, we analyze the bond length alternation (BLA), HOMA, and NICS$_{iso}$ (1). The C–C bond lengths of the BBT core vary between 1.405 and 1.467 Å, indicating quinoidal character. Upon increasing the chain length, the BLA is increased in the core of the BBT-based polymers indicating transition towards a high energy quinoidal structure. In contrast, the opposite ends of the polymers show a reduced BLA (Fig. 4a, S5–S7, S12–S15), indicating energetically favorable aromatic structure (Fig. 2b). In case of the CPDT-BBT octamer, the NICS$_{iso}$ (1) value of ring 1A is $-7.20$ ppm, whereas NICS$_{iso}$ (1) value of the benzenoid ring of the BBT acceptor is $-1.20$ ppm (HOMA: 0.634) at the oligomer center (4E) and $-4.90$ ppm (HOMA: 0.738) (8E) at the end (Fig. 4b, Table S11). Consequently, the charge densities are pushed from the higher energy quinoidal core to the lower energy aromatic ends to reduce Coulomb repulsion, ultimately localizing the unpaired spins.
at the ends of the BBT-based polymers (Fig. 2b). The NICS$_{\text{iso}}$(1) is higher (less negative) in the CPDS-BBT octamer, where ring 1A, 4E, and 8E show NICS$_{\text{iso}}$(1) values $-7.15$, $-1.13$ (HOMA: 0.640), and $-4.43$ (HOMA: 0.739) ppm, respectively (Table S19), which indicates a larger quinoidal contribution than the CPDT-BBT polymer. On the other hand, the iso-BBT-based polymers ($N = 8$) have large negative NICS$_{\text{iso}}$(1) values (Table S15, S23) along the backbone ($-8.28$, $-8.72$, and $-10.51$ ppm in CPDT-iso-BBT; $-7.59$, $-8.71$, and $-10.23$ ppm in CPDS-iso-BBT in the 1A, 4E, and 8E rings, respectively), with HOMA values $> 0.940$ in the benzenoid rings, indicating a more aromatic backbone, which agrees with the reduced BLA parameter as well (Fig. S8–S11, S16–S19). However, the $S = 1$ state of the iso-BBT-based polymers have increased NICS$_{\text{iso}}$(1) along the backbone (Table S15, S23), the largest value is observed at the polymer core where the unpaired electrons are localized.

**Effect of D and A units on the diradical character ($\gamma_0$)**

To explore the effect of different acceptors and substituents on the donor unit, and to quantify the localization of the unpaired electrons, we have assessed the open-shell character with the quantitative descriptor diradical index ($\gamma_0$), where the index ranges from $0 \leq \gamma_0 \leq 1$, defining a pure open-shell molecule at $\gamma_0 = 1$ and a closed-shell at $\gamma_0 = 0$. The $\gamma_0$ values depend on the acceptors used to $\pi$-conjugate with the donor units (see Table 1 and S4).

The hypervalent sulfur in the BBT unit imparts strong electron-accepting ability, as evident from the development of open-shell character even at the monomer unit, indicating the open-shell diradical form is lower in energy than the closed-shell form (Table S4, Fig. S4). The BBT acceptor has a deeper LUMO energy level than the iso-BBT, which reduces the HOMO–LUMO energy gaps ($E_g$). Adding more repeat units in the polymers chain increases HOMO and decreases LUMO energy level; therefore, fine-tuning in the corresponding energy levels occurs, resulting in a gradual decrease in the $E_g$ gap. A linear extrapolation of the $E_g$ as a function of the inverse number of the repeating units ($1/N$) to the polymer chain limit ($N \rightarrow \infty$) provides the electrochemical band gap. The band gaps obtained for the CPDT-BBT, CPDS-BBT, CPDT-iso-BBT, and CPDS-iso-BBT are 0.74, 0.76, 1.41, and 1.17 eV, respectively (Fig. S55). A similar extrapolation for the CPDT-TQ polymer gives a band gap of 0.58 eV, which is in excellent agreement with the experimental electrochemical band gap. Clearly, the BBT-based polymers have a significantly narrower band gap than the iso-BBT based polymers, which facilitates admixing of the FMOs in the ground-state, leading to a significant population in the LUNOs; therefore, developing open-shell diradical character in the CPDT-BBT and CPDS-BBT polymers.

A small band gap can enhance the ambipolar charge-transfer characteristics of these polymers as well.

The calculated $\gamma_0$ values correspond well to those obtained in previous oligomer studies of BBT-based diradicaloids. The tetrasradical ($\gamma_1$) character for the octamer ($N = 8$) is found to be negligible ($\gamma_1 = 0.05$, as observed from the LUNO+1 occupancy) in both CPDT-BBT and CPDS-BBT polymers, indicating the diradical character is predominant in the CPDT-BBT and CPDS-BBT polymers (Fig. 2b–d). The non- aromatic donors pentadiene and [10]annulene induces a large aromatic character in the polymer backbone, which can be realized by a small BLA in the BBT core (Fig. S20–S21). In case of the pentadiene donor, a large negative NICS$_{\text{iso}}$(1) value ($\approx -8.91$ ppm) is observed in the benzenoid ring than the CPDT-BBT tetramer ($\approx -2.04$ ppm) (see Table S9 and S24), reducing the diradical character in the former polymer.
**Fig. 5** The resonance structures and magnetic properties of the CPDT-BBT polymer ($N = 8$) in the triplet ($S = 1$) state. (a–b) The resonance structures indicate regaining aromatic stabilization energy in the thiadiazole units (shaded in blue), (c) ACID plots, and (d) 2D-ICSS (ppm) maps. In the ACID plots, the clockwise (diatropic: aromatic) and counterclockwise (paratropic: quinoidal) ring currents are indicated by red and blue arrows, respectively. The applied magnetic field is perpendicular to the molecular backbone and pointed out through the molecule plane. ACID plots were generated with an isovalue = 0.025 a.u. (0.105 vs. 0.966 at $N = 4$). With the increase of the oligomer chain length in the CPDT-BBT and CPDS-BBT polymers, $\gamma_0$ increases rapidly and reaches to the diradical saturation limit at a larger chain length (Fig. S56); therefore, diminishing the bonding covalency between the unpaired electrons and reaches the bond dissociation limit at $N = 8$, with a vanishing effective bond order $(1 - \gamma_0)$. As a result, the unpaired electrons are completely decoupled and localized at individual sites with a higher degree of electronic coherence, where parallel alignment (either both spin-up or spin-down) is possible to reduce the electron-electron repulsion; resulting in $S = 1$ as a ground-state.  

Looking at the resonance structures of the CPDT-BBT polymer, two thiadiazole units recover aromatic stabilization energy in the open-shell form from the closed-shell configuration (Fig. 5a–b). Upon increasing the polymer chain length, the number of aromatic thiadiazole units, which recovers stabilization energy, increases (Fig. S57–S59), adding to the driving force for $\pi$ bond-breaking; therefore, increasing the $\gamma_0$, a manifestation of Clar’s aromatic sextet rule. The NICS$_{iso}(1)$ (Table S8–S11, S16–S19) obtained on the thiadiazole units of the BBT-based polymers show a considerable decrease (more negative) in the calculated value (−9.50 to −11.50 ppm), which indicates an aromatic character of the thiadiazole units, facilitating double-bond breaking. The ACID plots show two clockwise (diatropic) ring current circuits in the top and bottom of the BBT units, indicating a local aromatic character and recovery of aromatic stabilizing energy in the thiadiazole units (Fig. 5c, S57–S59). The cyclopenta rings in the CPDT donor indicates counterclockwise ring currents, while the sulfur-containing five-member rings have clear clockwise ring currents at the two ends and diminished clockwise and counterclockwise ring current contribution at the core of the polymer chain. A significant decrease in the diatropic ring current contribution in moving from the terminal thiophene to the oligomer center coincides with the accumulation of charge density at the chain ends; therefore, increasing the distance between the unpaired spins and reduces bond covalency, concomitantly, increasing $\gamma_0$ (Fig. 5c, S41–S45, S47–S49). Furthermore, the 2D-ICSS plots indicate the thiadiazole units of the BBT acceptor is magnetically shielded (negative 2D-ICSS). In contrast, the benzenoid units of the BBT acceptor and five-member rings in the donor is...
magnetically de-shielded (Fig. 5d, S57–S59), which is further supported by the large negative NICS$_{iso}$(1) values in the auxiliary rings (Table S8–S11, S16–S19) and less negative NICS$_{iso}$(1) in the donor and acceptor cores (Fig. 4b). Therefore, the one-to-one correspondence between the calculated SOMOs, spin density, NICS$_{iso}$(1), HOMA values, ACID, and 2D-ICSS plots unambiguously confirms the BBT-based polymers develop a pure diradical character due to an increased number of aromatic thiadiazole units, a small band gap which admixes HOMO and LUMO in the ground-state, and a significant quinoidal core with aromatic ends.

**Effect of different end terminations**

Besides the symmetric (−D−A−)$_N$ arrangement, we have also assessed the electronic properties with different end groups, such as placing D and A at both ends of the CPDS-BBT heptamer (N = 7) backbone, respectively. From the BLA, it is evident that when the polymers end with D units, both ends of the oligomer has increased aromaticity because the five-member rings with sulfur hetero-atom recovers aromaticity in the open-shell state, indicated by a reduced BLA in the donor units (Fig. 6b–c). Therefore, the unpaired electrons are localized at the two ends (Fig. 6d), which is in agreement with the $\alpha$- and $\beta$-SOMO distribution on the oligomer backbone (Fig. S60). However, when both ends contain BBT acceptor units, a significant quinoidal character is observed in the backbone with less localization in the $\alpha$- and $\beta$-SOMOs (Fig. S61–S62), although the spin densities are localized at the ends due to a larger contribution of the $\alpha$- and $\beta$-SOMO in the oligomer ends (Fig. S62). The substitution of the D units does not change the HOMO energy level from the unsubstituted heptamer ($\gamma_0 = 1$ in all cases), which is because the number of aromatic sextet rings is almost similar (Fig. 6a, S61). The unpaired electrons are completely localized at the terminals, reducing the bond covalency between the unpaired electrons. Therefore, $\gamma_0$ depends on the spin localization and the
number of aromatic sextet units than the energy gap between the FMOs in this case. Therefore, if a larger separation between the unpaired electrons is ensured, the diradical character will be unaffected by the change in the HOMO–LUMO energy gaps. Due to a large $\gamma_0$, a very small $\Delta E_{ST}$ gap is observed for both derivatives with significant thermal population ($>74.99\%$) of the $S=1$ state (Table S3–S4), although a small increase in the $\Delta E_{ST}$ gap is observed from the unsubstituted heptamer ($N=7$). Therefore, structural symmetry in an alternating D–A polymer is important to have a small FMO energy gap, which is necessary for a broader absorption spectrum.

Conclusions

We report donor-acceptor conjugated polymers where spin manipulation is achieved through careful selection of molecular scaffold to have a closed-shell low-spin ground-state to an open-shell high-spin ground-state in the pristine form. The monomer unit of the BBT-based polymers develop an open-shell character and achieve a pure open-shell character at $N=8$. The essential design criteria involve utilizing BBT acceptor in the polymer backbone to down-shift the LUMO energy level, where the CPDT/CPDS donors up-shift the HOMO level, reducing the HOMO–LUMO energy gap. A small electronic gap admixes the FMOs in the ground-state inducing an open-shell diradical character, whereas the aromatic stabilization energy of the thiadiazole units rapidly increases the diradical character as the number of repeat units are increased. This phenomenon, combined with the large spatial separation between the unpaired electrons, pushes the diradical character to the bond dissociation limit. Consequently, the Coulomb repulsion in the triplet state is decreased, reducing the energy gap between the singlet and triplet state, forming a degenerate state in the large chain-limit. This degeneracy will facilitate magnetic switching from a low-spin ground-state to high-spin ground-state, favoring the triplet multiplicity in the long polymer chain-limit, leading to an intramolecular ferromagnetic exchange coupling between the unpaired spins. However, the iso-BBT-based polymers have a significantly increased $\Delta E_{ST}$ and HOMO–LUMO energy gap, leading to a closed-shell configuration. This study paves the way towards molecular magnetism based on conjugated polymers without utilizing heavy inorganic elements.

Author contributions

NR and MAS conceived and designed the study. MAS performed DFT calculations and analysis. MAS wrote the first draft of the manuscript and made subsequent revisions. MMH developed codes for generating AICD and 2D-ICSS diagrams and generated all the ACID and 2D-ICSS maps and contributed to the development of the first draft. CSS performed all the OT-(S)RSH and orbital overlap calculations and contributed to the development of the first draft. NR supervised the project and revised the manuscript. All authors approved submission of the manuscript.

Conflict of interest

There is no conflict of interest to declare.

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