Supporting Information for

Magnetic Coupling Control in Triangulene Dimers

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Computational details

The geometries of all the systems have been optimized at the PBE0/def2-TZVP level as implemented in the Gaussian16 program. For closed-shell singlet, we have performed restricted DFT calculations, while using unrestricted DFT calculations for the triplet and quintet. For OSS, the broken-symmetry (BS)-DFT approach has been employed. The stability of the DFT wave function has been optimized and checked with keyword “stable=opt”. In order to avoid the well-known spin contamination in the calculation of OSS, we have adopted the ansatz proposed by Yamaguchi,¹ where the magnetic coupling is defined as $J = -(E_{HS} - E_{OSS})/\langle S^2 \rangle_{HS} - \langle S^2 \rangle_{LS}$, where $\langle S^2 \rangle_{HS}$ and $\langle S^2 \rangle_{LS}$ are the expectation values for the total spin of the high-spin and low-spin states, respectively. The on-site Coulomb repulsion $U$ is estimated by the spin-polarization energy as defined by $U = E_{CSS} - E_{HS}$, where $E_{HS}$ and $E_{CSS}$ represent the energy of high-spin and closed-shell singlet states. To correctly determine the relative energy of the closed-shell singlet and high-spin state in planar TAM dimer, we have utilized the domain-based local pair natural orbital coupled-cluster theory (DLPNO-CCSD(T))² with ORCA 5.0 program.³ This approach is necessary due to the poor description of electron correlation in the PBE0 functional, resulting in an incorrect $U < 0$ value. To expedite the SCF process, we have employed the “RIJCOSX” method, the auxiliary basis set def2-TZVP/C, and Coulomb fitting set def2/J for the correlated calculations.⁴ Additionally, the “TightSCF” option has been applied to tighten the convergence settings. For the TRI-series molecules, we have considered both the closed-shell singlet and quintet states, while for other diradical systems, we have considered the closed-shell singlet and triplet states. To perform a magnetic coupling profile scan of dihedrals, we have applied the "opt=(modredundant, tight)" keyword, which allows to optimize the molecular geometry while constraining only the dihedral angle. The MultiWFN program have been used for the analysis of the overlap integral of SOMO.⁵
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Figure S3. Molecular structure, spin density distribution and frontier molecular orbital of TRI(B) monomer.
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Figure S19. Relationship between magnetic coupling \((J)\) and dihedral angle \((\varphi)\) in PLY dimer.

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Figure S22. Relationship between magnetic coupling ($J$) and dihedral angle ($\varphi$) in TOT dimer.
Table S1. Comparison of TRI(N) and TRI(B) monomer with C2v and D3h symmetry.

<table>
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Table S2. Magnetic couplings of planar TRI(N) dimer calculated by PBE0, B3LYP, MN15, M06-2X and ωB97XD functionals. “-sp” indicate single point energy at PBE0 optimized geometry and “-opt” means the geometry is also re-optimized by corresponding functionals.

<table>
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References:


