Title:	Designing and modulation of long-range exchange interactions through conjugated spacers
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Abstract:	The spin-spin magnetic interactions in molecules quantified by magnetic exchange coupling constants (2J) which define the robustness for the stored information in the magnetic bits are desired to be long range in nature. To achieve this in molecular systems, organic radicals or transition metal centers which act as spin sources are coupled through a non-magnetic spacer. The π-conjugated spacers have been found to be most efficient to couple spins over long distances. However, in major cases the exponential decrease in 2J values is observed with increasing distance between the spin sources. Therefore, inducing longrange strong magnetic exchange interactions in molecules and materials is a persisting challenge. The highly π-conjugated coupler is polyacene for which the electronic and magnetic properties become quite fascinating as the number of linearly conjugated benzene rings increases. Higher-order conjugated polyacenes develop radicaloid characters due to the transition of electronic structures from closed-shell to the open-shell singlet (OSS) system. We have investigated the role of such polyacenes as the magnetic coupler when placed between the two spin sources based on nitroxy radicals. To do so, the magnetic exchange interactions (2J) are computed employing broken-symmetry (BS) approach within the density functional theory (DFT) and multi-reference complete active space self-consistent field (CASSCF) calculations within the wave function theory (WFT). In DFT based approach, various genre of exchangecorrelation (XC) functionals such as generalized gradient approximation (GGA), meta-GGA, hybrid functional, constrained spin density (i.e. CDFT) and on-site Coulomb correlation corrected GGA+U functionals are adopted. Remarkably an exponential increase in 2J values with the length of the couplers is observed. This observation has been understood in terms of increase in number of near-degenerate or quasi-degenerate molecular orbitals (MOs), reduction of HOMO-LUMO energy gap and descend of lowlying excited states as the number of fused benzene rings are increased. The increase in the length of polyacene also increases its OSS character which is computed in terms of radicaloid character (y). The intrinsic OSS characteristics of the molecular systems have already been found to influence its various physical properties like electron-hole mobility, two-photon absorptions, non-linear optical properties etc. To probe into the explicit influence of radicaloid character on magnetic exchange couplings, the spacers of same length but different radicaloid character are used to coupler spinsources. The nitroxy radical sites are coupled through a fixed length of prototypical decacene coupler. To modulate radicaloid character of the coupler, benzenoid rings are systematically added in the spin confining region of decacene. The strength of magnetic coupling between localized spin centers is found to be correlated with the radicaloid character of polyaromatic hydrocarbon (PAH) spacers. The large exchange interaction is observed for the diradical with higher radicaloid character. The understanding of long-range interactions through spacers comprising polyacenes and its PAH derivatives has given an insight into their rich electronic structures and have proven to be efficient spacers. To further realize if polyacenes are indeed universal spacers for strong magnetic exchange interactions, spin source has been changed to transition metal (TM) atoms where the unpaired electrons are localized in d-orbitals. TM porphyrin dimers are coupled through polyacene spacers and magnetic exchange interactions are studied between TM centers. Long-range magnetic exchange interactions still persist; however, they are not as strong as when the spin source were organic radicals. This is because pπ- pπ interactions which are responsible for exchange mechanism in molecular systems with organic radical spin-source are stronger as compared to dπ-pπ interactions in TM spin-source systems.
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