Tuning Electron Transfer Coupling and Exchange Interaction in Bis-triarylamine Radical Cations and Dications by Bridge Electron Density

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To explore the influence of the electron density of the bridge connecting two redox centres on both the hole transfer and magnetic superexchange, a series of 2,7-fluorene bridged bistriarylamine mono- and di-cations with varying bridge electron density was synthesized. By analysis of the intervalence charge-transfer bands of the mono-cations using the *Generalized Mulliken Hush* theory and VT-EPR spectroscopy of the di-cations the exchange and magnetic couplings were determined and analyzed. This series of molecules allows to correlate both forms of electronic communication with the energy of the optically accessible bridge state, suggesting a design guideline for both electronically and magnetically coupled organic compounds.



Figure 1: Model-systems **1** to **4**, a) electronic coupling *V* of the radical cations vs. inverse bridge state energy \tilde{v}_{b}^{-1} , b) magnetic exchange coupling 2*J* vs. inverse squared bridge state energy \tilde{v}_{b}^{-2} .