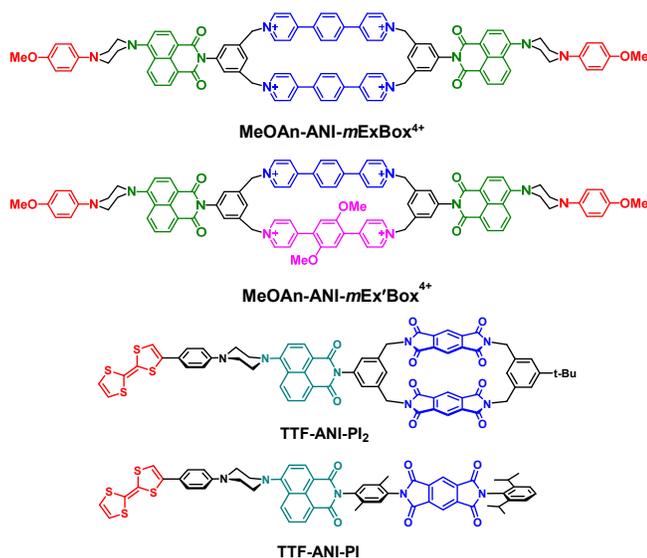


Radical Pairs as Spin Qubit Pairs: Observing and Preserving Spin Coherences

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Ultrafast photo-driven electron transfer reactions starting from an excited singlet state in a covalent organic donor-acceptor molecule generate a radical pair (RP) in which the two spins are initially entangled and, in principle, can serve as a two-qubit pair in quantum information science (QIS) protocols. Here we describe the effects of electron transfer between two equivalent sites comprising the reduced acceptor of the RP on spin coherence and the observation of zero- and double-quantum coherences in such systems. In one system, a covalent electron donor-acceptor molecule including a *p*-methoxyaniline (MeOAn) donor, a 4-aminonaphthalene-1,8-imide (ANI) chromophoric primary acceptor, and a *m*-xylene bridged cyclophane having two equivalent phenyl-extended viologens (*mExBox*⁴⁺) as a secondary acceptor (MeOAn-ANI-*mExBox*⁴⁺) was synthesized along with the analogous molecule having one phenyl-extended viologen acceptor and a second, more difficult to reduce 2,5-dimethoxyphenyl-extended viologen (MeOAn-ANI-*mEx'Box*⁴⁺).



Photoexcitation of ANI within each molecule results in sub-nanosecond formation of MeOAn^{•+}-ANI-*mExBox*^{3•+} and MeOAn^{•+}-ANI-*mEx'Box*^{3•+}, whose spin dynamics were characterized by time-resolved EPR spectroscopy and magnetic field effects on the RP yield. The data show that rapid electron hopping within *mExBox*^{3•+} promotes spin decoherence in MeOAn^{•+}-ANI-*mExBox*^{3•+} relative to MeOAn^{•+}-ANI-*mEx'Box*^{3•+} in which no hopping occurs. A second related system uses a tetrathiafulvalene (TTF) donor, an ANI chromophoric primary acceptor, and a *m*-xylene bridged cyclophane having two equivalent pyromellitimides (*PI*₂), TTF-ANI-*PI*₂, as a secondary acceptor. This molecule was compared to the analogous molecule having one *PI* acceptor, TTF-ANI-*PI*. Photoexcitation of ANI within each molecule results in sub-nanosecond formation of TTF^{•+}-ANI-*PI*[•] and TTF^{•+}-ANI-*PI*₂[•]. The effect of reducing electron-nuclear hyperfine interactions in TTF^{•+}-ANI-*PI*₂[•] relative to TTF^{•+}-ANI-*PI*[•] on decoherence was measured by pulse-EPR spectroscopy. The theoretical prediction of the contribution from an ensemble of hyperfine interactions to decoherence in these RPs is shown to be less than the full width at half maximum of the quantum beat frequencies measured experimentally. Pulse bandwidth and off-resonance excitation by square microwave pulses are proposed as larger contributors to decoherence in these molecules than the hyperfine interactions. These observations provide important information for designing and understanding novel molecular assemblies of spin qubits with long coherence times for QIS applications.