Dynamic Nuclear Polarization (DNP) has already transformed the scope of NMR, permitting the study of molecular and materials surfaces, in cell NMR or highly dilute metabolites that would evade the detection of conventional NMR spectroscopy. Still, the vast majority of successful DNP experiments fall into a narrow range of sample conditions of dissolved or dispersed organic S=1/2 bi-radicals in a ¹H-rich solvent glass. Even within this category, only a handful or biradical archetypes relying on bisnitroxides or nitroxide-trityl combinations yield reasonably high DNP performance, hence limiting the scope of DNP. Furthermore, the direct transfer of polarization from isolated electron spins to a surrounding nucleus is inefficient at high B₀. It is understood that utilizing coupled electron spins (e-e) can remedy this problem. Two distinct DNP mechanisms (Cross Effect (CE) and Thermal Mixing (TM)) rely on e-e couplings (1’s-100’s MHz) to induce triple-flip transitions between two coupled e spins and a hyperfine coupled nucleus. The resonance condition is satisfied when the difference of the EPR frequencies of the coupled electron spins matches the nuclear Larmor frequency. These shortcomings ask for new strategies to design paramagnetic systems that span the optimal frequency and relaxation range for DNP. I will present two novel concepts that expand the scope of DNP: (1) The rational design of TM DNP that exploits a strongly coupled electron spin network, in which the difference of the EPR frequencies of the coupled electron spins matching the ¹H Larmor frequency as generated from dipolar and exchange coupling between the coupled electron spins. High ¹H TM DNP. A strongly coupled electron spin network is generated by exploiting spin clustering. (2) The concept of utilizing narrow line radicals to extract and sensitive DNP effects from higher than S=1/2 paramagnetic systems by frequency matching.