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Redox-Mediated Supramolecular Radical Gel

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Abstract : In biology, supramolecular systems require the use of chemical fuels to stay in sustained nonequilibrium steady states termed dissipative self-assembly in contrast to synthetic self-assembly. Biomimicking these natural dynamic systems, some studies have demonstrated artificial self-assembly under nonequilibrium utilizing various forms of energies (fuel) such as chemical, redox, and pH. Naphthalene diimides (NDIs) are well-known organic molecules in supramolecular architectures with high electron affinity and have applications in controlled electron transfer (ET) reactions, etc. Herein, we report the endergonic ET from tetraphenylborate to highly electron-deficient phosphonium $NDI^{2}+$ dication to generate NDI•+ radical. The formation of radicals was confirmed by UV-Vis-NIR absorption spectroscopy. Electron-donor and electron-acceptor energy levels were calculated from experimental electrochemistry and theoretical DFT analysis. The HOMO of the electron donor locates below the LUMO of the electro-acceptor. This indicates that electron transfer is endergonic (ΔE°ET = negative). The endergonic ET from $NaBPh_4$ to $NDI^{2}+$ dication was achieved thermodynamically by the formation of coupled biphenyl product confirmed by GC-MS analysis. NDI molecule bearing octyl phosphonium at the core and H-bond forming imide moieties at the axial position forms a gel. The rheological properties of purified radical ion NDI▯+ gels were evaluated. The atomic force microscopy studies reveal the formation of large branching-type networks with a maximum height of 70-80 nm. The endergonic ET from $NaBPh_4$ to $NDI^{2}+$ dication was used to design the assembly and disassembly redox reaction cycle using reducing ($NaBPh_4$) and oxidizing agents (Br_2) as chemical fuels. A part of $NaBPh_4$ is used to drive assembly, while a fraction of the $NaBPh_4$ is dissipated by forming a useful product. The system goes back to the disassembled $NDI^{2}+$ dication state with the addition of Br_2. We think bioinspired dissipative self-assembly is the best approach to developing future lifelike materials with autonomous behavior.

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