

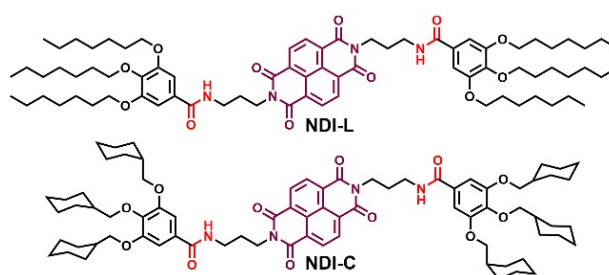
Direct Engagement of Solvent Molecules in Supramolecular Polymerization

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ABSTRACT: Despite many reports suggesting the importance of solvent-solute relationship in supramolecular assemblies, specific engagement of solvent molecules in the structure formation of abiotic self-assembled systems is not well understood yet. Recently we and others have reported¹⁻³ strong effect of the shape (linear or cyclic) of the hydrocarbon solvent on the supramolecular polymerization of π -conjugated building blocks, attached with peripheral linear hydrocarbons. To develop a deeper and unambiguous understanding on this important fundamental aspect, we have now studied two building blocks NDI-L and NDI-C (Scheme 1), having linear or cyclic peripheral hydrocarbons, respectively.⁴ They differ only by the peripheral hydrocarbon wedges, consisting of linear C7 chains or cyclic methylcyclohexane rings, respectively. UV/Vis and FT-IR spectroscopy studies reveal distinct internal order and H-bonding pattern for NDI-L and NDI-C aggregates irrespective of the solvent system. However, NDI-L produces a significantly stronger gel in Heptane (Hep) compared to methylcyclohexane (MCH), as evident from their rheological and thermal properties. In contrast, NDI-C exhibits a clear preference for MCH, producing gel with moderate strength but in Hep it fails to produce 1D morphology or gelation. Such clear-cut shape-matching effect (between the

peripheral hydrocarbon wedge and the solvent system) unambiguously support a direct participation of the solvent molecules during supramolecular polymerization and presence of a closely-adhered solvent shell around the supramolecular polymers, similar to the first layer of water molecules around the protein surface.



Scheme 1: Structure of NDI-L and NDI-C

Solvent induced CD experiments support this hypothesis as the induced CD band was observed only from a chiral co-solvent of matching shape. This is reconfirmed by the higher de-solvation temperature of the shape-matching NDI/solvent system combination compared to the shape mismatch combination in variable temperature UV/Vis experiments, revealing transformation to a different aggregate at higher temperatures rather than disassembly to the monomer for all four combinations. This talk will highlight our recent results in this area^{1-2, 4} and a broader scope for the solvent geometry regulated predictable synthesis of functional supramolecular polymers.

KEY WORDS: Supramolecular polymer; Solvent geometry; Gel; Morphology; Chirality

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