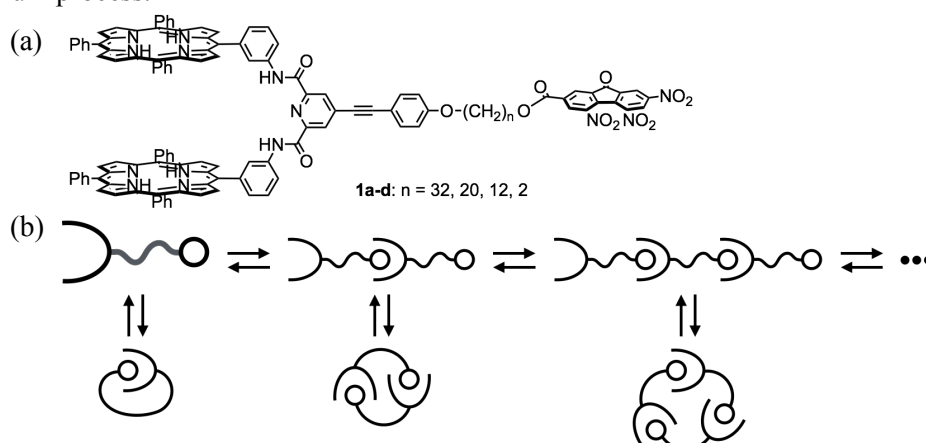


## 1B4b

## Ring-chain mechanism in supramolecular polymerization through molecular recognition of bisporphyrin cleft and trinitrofluorenone

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Supramolecular polymers have attracted considerable attention in developing of a new class of functional materials including stimuli-responsive and self-healing properties due to their reversible nature. Monomers possessing a host and a guest moiety, so-called head-to-tail monomer, polymerize via intermolecular host-guest binding. In this polymerization, there is a competition between intra- and intermolecular associations, namely ring-chain equilibrium, depending on the flexibility of the linker. However, there are limited reports presenting a quantitative thermodynamic picture describing the conformational entropy in the ring-chain equilibrium process.



**Figure 1.** (a) Molecular structures of head-to-tail monomers **1a-d**. (b) Schematic illustration of ring-chain competition in supramolecular polymerization.

We have reported the supramolecular polymerization of a monomer possessing a bisporphyrin (bisPor) cleft and a trinitrofluorenone (TNF) through charge transfer interaction.<sup>[1]</sup> In this study, we synthesized four head-to-tail monomers **1a-d** with various length of alkyl chains as linker moieties to study the supramolecular polymerization behavior. The supramolecular polymerization of **1a-d** was studied using UV/vis, <sup>1</sup>H NMR, DOSY, and viscometry. The thermodynamic parameters of the ring-chain equilibrium were determined in the initial stage of the supramolecular polymerization. The conformational entropy, relying on the chain flexibility, had a significant impact on the critical polymerization concentration.<sup>[2]</sup>

[1] T. Haino *et al.*, *Angew. Chem. Int. Ed.*, **2012**, *51*, 1473.

[2] T. Haino *et al.*, *Macromolecules*, **2019**, *52*, 6160.