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Autoresolution of Segregated and Mixed p-n Stacks by Stereoselective Supramolecular Polymerization in Solution

*Bhawani Narayan, Karteek K. Bejagam, Sundaram Balasubramanian, and Subi J. George**

Dedicated to Professor E. W. (Bert) Meijer on the occasion of his 60th birthday

Abstract: *A "chirality driven self-sorting" strategy is introduced for the controlled supramolecular organization of donor (D) and acceptor (A) molecules in multicomponent assemblies. The trans-1,2-bis(amido)cyclohexane (trans-BAC) has been identified as a supramolecular motif with strong homochiral recognition to direct this chirality controlled assembly process of enantiomers in solution. Stereoselective supramolecular polymerization of trans-BAC appended naphthalene diimide monomers (NDIs) has been probed in detail by spectroscopic and mechanistic investigations. This chirality-driven self-sorting design of enantiomeric components also offers to realize mixed and segregated D-A stacks by supramolecular co-assembly of the NDI acceptors with trans-BAC appended dialkoxynaphthalene (DAN) donor monomers. Such an unprecedented chirality control on D-A organization paves the way for the creation of supramolecular p-n nanostructures with controlled molecular-level organization.*

Stereoselective supramolecular polymerization[1] is the chirality-driven self-sorting of enantiomeric monomers during their self-assembly. This supramolecular autoresolution process in which the molecular components sort themselves to stereochemically pure assemblies in solution is analogous to Louis Pasteur's resolution experiments to form conglomerate crystals.[2] Although chirality driven self-sorting has been well-studied in discrete organic/coordination assemblies,[3] chiral self-recognition of monomers during extended supramolecular polymerization is seldom reported.[1,4] One of the reasons could be that majority of these supramolecular chiral systems are designed with monomers having remote chiral side chains and the absence of strong chiral mismatch and their dynamic nature leads to co-polymerization of enantiomeric monomers.[5] However, these heterochiral supramolecular systems provided mechanistic insights into asymmetric preferences in nature, such as chiral amplification.[5] Another challenge in this field is the lack of experimental techniques to probe and characterize the homochiral assemblies, in contrast to the characterization of analogous conglomerate structures in crystals. Despite these challenges, Aida and co-workers have successfully demonstrated the enantioselective supramolecular polymerization using S-shaped diketopiperazine[1a] and bowl-shaped macrocyclic chiral monomers[1b] with strong self-recognition abilities. Very recently, Meijer and co-workers have demonstrated co-operative stereoselective supramolecular polymerization of porphyrin[1c] and star-shaped monomers equipped with multiple chiral side chains at the periphery to impart them strong chiral mismatch.[1e] Herein we report for the first time the stereoselective supramolecular polymerization of self-recognizing aromatic donor (D) and acceptor (A) monomers to construct segregated (orthogonal) and mixed (alternate) p-n stacks.

Molecular level control of the organization of donor (D) and acceptor (A) molecules in multi-component D-A nanostructures is very important for achieving desired optoelectronic functions.[6] Orthogonal or segregated organization of D and A molecules leads to efficient charge separation, and hence are promising active materials for organic solar cells.[7] On the other hand, co-facial (alternate) D-A nanostructures are attractive candidates for organic ferroelectrics.[8] Various supramolecular design strategies have been employed to control the nanoscale organization of D and A molecules in these nanostructures. Segregated organization has been achieved either through structural mismatch of D and A molecules,[9] or by H-bonding[10] and amphiphilic[11] design strategies. On the other hand, foldameric[12] and non-covalent amphiphilic designs[13] have been employed for the creation of mixed stacks. However, a chirality driven self-sorting strategy has not been exploited to date for biasing the organization of such π-complementary D and A monomers in supramolecular stacks in solution.[14]

The concept of chirality driven self-sorting introduced in this communication for realizing supramolecular p-n assemblies with controlled D-A organization is shown in Scheme 1. Stereoselective supramolecular polymerization of enantiomerically pure D and A monomers with opposite chirality would result in segregated D-A stacks. On the other hand, co-assembly of D and A monomers with similar chirality would result in mixed D-A organization. In other words, chirality driven self-sorting of D and A chiral molecules would result in the segregated and mixed stacking of π-complementary aromatic units. However, the first challenge to realize this concept is the identification of self-recognizing motifs with strong chiral mismatch to functionalize the D and A chromophores. We have employed enantiomerically pure

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[*] B. Narayan, Prof. S. J. George
Supramolecular Chemistry Laboratory, New Chemistry Unit,
Jawaharlal Nehru Centre for
Advanced Scientific Research (JNCASR)
Jakkur P.O., Bangalore 560064 (India)
E-mail: george@jncasr.ac.in

K. K. Bejagam, Prof. S. Balasubramanian
Chemistry and Physics of Materials Unit, JNCASR
Jakkur, Bangalore 560064 (India)

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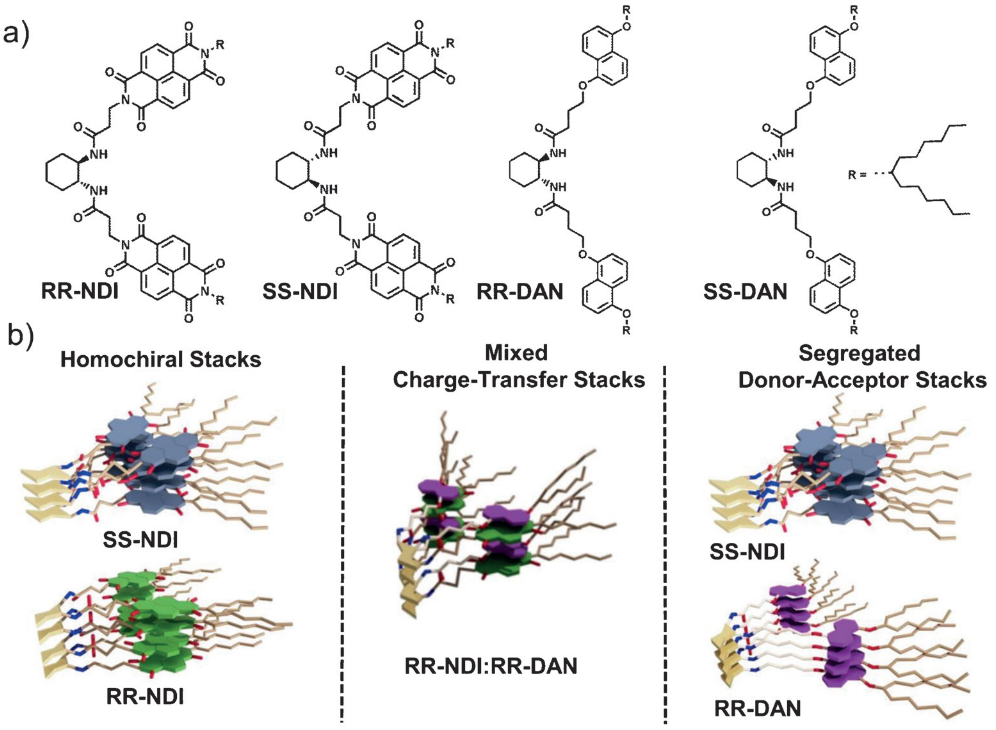

Scheme 1. a) Molecular structures of enantiomeric naphthalene diimide (NDI) acceptors (**RR-NDI**, **SS-NDI**) and dialkoxy naphthalene (DAN) donors (**RR-DAN**, **SS-DAN**) used in the present study. b) Representation of the possible supramolecular structures that can be formed by the chiral self-sorting of D and A monomers.

trans-1,2-bis(amido)-cyclohexane with two stereogenic centers as the self-assembling chiral group in our molecular design.[15] The core-to-core H-bonding interactions between the bis(amido)cyclohexane moieties are expected to provide significant energy differences between homochiral and heterochiral stacking of the enantiomeric molecules during their supramolecular polymerization process. To investigate the chirality driven control on D-A organization, we have chosen the well-studied naphthalene diimide (NDI) and 1,5-dialkoxy naphthalene (DAN) derivatives as A and D chromophores, respectively. The structures of the bischromophoric molecules,[16] **RR-NDI**, **SS-NDI, RR-DAN** and **SS-DAN** used in the present study are shown in Scheme 1 a.[17]

First, we investigated the H-bonding-induced supramolecular polymerization of enantiomerically pure **SS-** or **RR-NDI** monomers in solution. NDI derivatives exist as monomers in 1,1,2,2-tetrachloroethane (TCE) at room temperature and in methylcyclohexane (MCH) at high temperatures (> 363.15 K), as evident from the corresponding absorption spectral features.[17] On the other hand, absorption spectra of these NDIs in MCH at room temperature showed broadening with reversal of vibronic band intensities at 360 nm and 380 nm, characteristic of H-type aggregation of NDIs.[17] Hence, the supramolecular polymerization was performed in MCH/TCE solvent mixture (99:1 (v/v)) under thermodynamic conditions by slowly cooling the solutions of NDI monomers (2.5×10^{-5} M) from 368.15 K to 298.15 K with a temperature gradient of 1 K min^{-1}. Circular dichroism (CD) spectra of resulting solutions of **SS-NDI** and **RR-NDI** showed mirror-image bisignated signal, with a zero-crossing at 383 nm, close to the absorption maximum typical of enantiomeric helical assemblies with exciton-coupled chromophores (Figure 1 a). Interestingly, enantiomeric NDI monomers in TCE also showed weakly coupled mirror-image CD spectra with a maximum at 385 nm, which is significantly different from that of the assemblies, thus indicating a different origin. To shed light on these differences, concentration-dependent CD studies were performed.[17] The g-values (anisotropy factor) in TCE monitored at 385 nm remained constant at -2.1×10^{-4} for **RR-NDI** while there was a nonlinear increase in the g-value obtained at 359 nm in MCH/TCE, 99:1 (v/v), suggesting the intra and intermonomeric interactions in TCE and MCH/TCE, 99:1 (v/v), respectively, being the origin of different CD signals. The plot of α (degree of aggregation) versus temperature obtained by

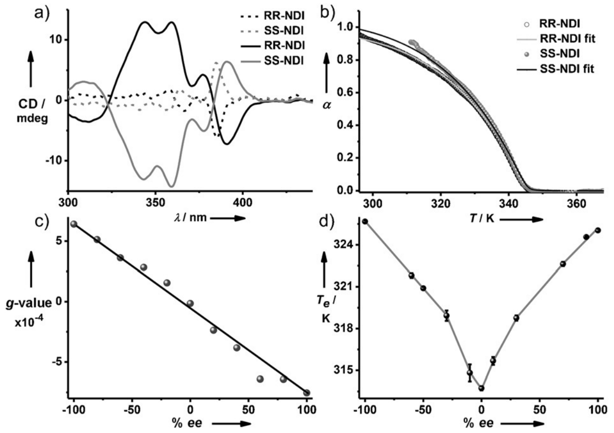

Figure 1. Stereoselective supramolecular polymerization of enantiomeric NDIs: a) CD spectra of NDIs ($c=2.5\times10^{-5}$ M) in TCE (-----) and in a MCH/TCE solvent mixture (99:1 (v/v),——); b) plot of fraction of aggregates (α) versus temperature obtained by monitoring spectral changes at 399 nm in the absorption spectra ($c=10^{-4}$ M, $-dT/dt=1$ K min^{-1}); c) g-value of the stacks constructed from various enantiomeric mixtures of NDI monomers showing its linear dependence with the *ee* value of the mixture ($c=2.5\times10^{-5}$ M, $l=10$ mm); d) plot of T_e versus % *ee* of NDIs showing a clear decrease in T_e with decreasing *ee* support self-sorting leading to homochiral NDI stacks (the error bars are obtained from the co-operative fits of corresponding cooling curves).

monitoring the absorption changes at 399 nm during the temperature-dependent studies of enantiomeric NDIs (10^{-4} M) showed non-sigmoidal curves (Figure 1 b). Fitting of these cooling curves with a temperature-dependent nucleation–elongation model yielded an elongation temperature (T_e), the temperature at which polymerization begins, of 345.35 K.[18] As expected, probing the CD spectra also revealed non-sigmoidal cooling curves for both NDIs.[17]

To study the self-recognizing/self-discrimination behavior of **RR-NDI** and **SS-NDI** enantiomers during co-assembly, temperature-dependent supramolecular polymerization of enantiomeric mixtures (MCH/TCE, 99:1 (v/v), $c = 2.5 \times 10^{-5}$ M) with varying enantiomeric excess (*ee*) were carried out under thermodynamic conditions and the spectral characteristics of resulting assemblies were recorded at 298.15 K. Absorption spectra of the self-assembled solutions hardly showed any change, whereas the bisignated CD spectra showed a monotonic increase in their intensity with an increase in *ee*.[17] This is evident from the plot of g-value against the *ee* values (%), which showed a linear change (Figure 1 c). This suggests that the assemblies constructed from the racemic mixture of NDI monomers (zero *ee*) are either self-recognition-driven homochiral stacks (supramolecular conglomerates) or self-discrimination-driven heterochiral stacks (supramolecular racemates). Although the similarity between the absorption spectra of assemblies constructed from various enantiomeric mixtures with that of enantiomerically pure assemblies suggested the formation of homochiral stacks, it was necessary to resort to more reliable probes to confirm this observation. Interestingly, a plot of T_e of various assemblies versus corresponding *ee* values gives a V-shaped curve, with a decrease in the elongation temperature with decreasing enantiomeric excess. Minimum T_e (313.73 K) was attained when the *ee* is zero, hinting at the formation of supramolecular conglomerates (Figure 1 d).[17] Interestingly the T_e of a 1:1 mixture of **RR-NDI** and **SS-NDI** matched exactly with that of the enantiomerically pure assemblies at half the concentration, thus confirming the self-recognizing stereoselective polymerization of the present system.[17]

A better understanding of the preference for this self-recognition behavior was obtained through molecular modelling studies. Homo- and heterochiral dimers of NDI monomers (Figure 2) were considered as basic building units of an assembly. The homochiral dimer is seen to be favored over the heterochiral dimer by 15.1 kcal mol^{-1}, consistent with the spectroscopic studies. A difference in chirality leads to significant differences in molecular packing, resulting in an energy penalty for the heterodimer. Chiral mismatch penalty offered by the optimized chiral core alone (chopping off NDI) was accounted to be 5.1 kcal mol^{-1} at B3LYP/6-31g(d).[17]

Next, we sought to construct orthogonal and mixed p-n assemblies through the stereoselective supramolecular polymerization of rationally designed D and A monomers. In this regard, we have used similar chiral naphthol derivatives (**RR**- or **SS-DAN**) as donor monomers.[9b] Although, the DAN derivatives also self-assemble in MCH/TCE solvent mixtures, the UV/Vis absorption spectral changes and CD intensity are minimal upon stacking to follow the supramolecular polymerization process spectroscopically.[17] However, the bisignated CD signal in MCH/TCE solvent mixture indeed showed the presence of excitonically coupled, helically stacked DAN chromophores.[17] Transmission electron microscopy (TEM) studies further confirmed the self-assembly of these DAN derivatives into one-dimensional nanostructures.[17] To realize the p-n assemblies, multi-component supramolecular co-polymerization of enantiomeric mixtures of D and A monomers were attempted in a similar fashion to that of homo-polymerization described above (MCH/TCE, 99/1(v/v), $c = 10^{-4}$ M, $-dT/dt = 1$ K min^{-1}). Co-assembly of D and A molecules to mixed p-n assemblies can be probed spectroscopically by the appearance of a charge-transfer (CT) absorption band.

Stereoselective supramolecular co-polymerization between D and A monomer with similar chirality (**RR-NDI** and **RR-DAN**) does indeed lead to alternately organized p-n stacks, as evident from the appearance of strong CT band with a maximum at 503 nm (Figure 3). Formation of mixed CT stacks is further evident from the deep red color of the co-assembled solutions.[17] Probing the intensity of the CT band as a function of equivalents of DAN showed a saturation with 10 equivalents of DAN monomers. High-resolution mass spectrometry of the co-assembled **RR-NDI**:**RR-DAN** (10^{-4} M) solution showed a mass at 2055.2896 corresponding to the 1:1 complex, reiterating the formation of co-facial CT pairs.[17] Finally, TEM imaging of the CT solution showed the formation of micrometer-long fibrous structures.[17] In contrast, supramolecularly polymerized solutions of D and A monomers with opposite chirality (**SS-NDI**:**RR-DAN**) did not show significant CT absorption, and the resulting sol-

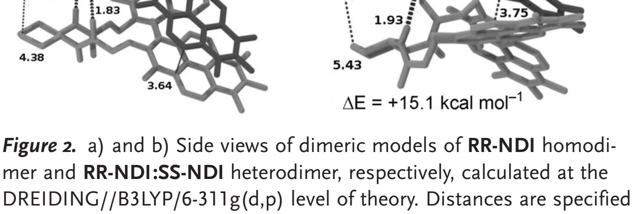

Figure 2. a) and b) Side views of dimeric models of **RR-NDI** homodimer and **RR-NDI:SS-NDI** heterodimer, respectively, calculated at the DREIDING//B3LYP/6-311g(d,p) level of theory. Distances are specified in Å. The swallow tail chains have been truncated to methyl groups to decrease the computational cost.

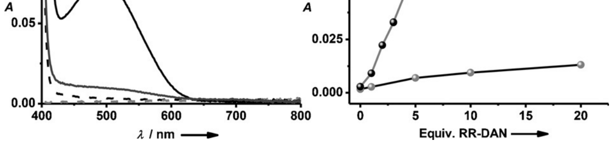

Figure 3. Stereoselective supramolecular co-polymerization of D-A monomers: a) Absorption spectra of co-assembled solutions of **RR-NDI** or **SS-NDI** with **RR-DAN**, demonstrating the formation of alternate and segregated D-A stacks, respectively. b) Plot of CT absorbance at 503 nm with increasing equivalents of RR-DAN.

utions remained colorless even in the presence of 10 equivalents of DAN monomers. This suggests the formation of segregated homochiral D and A stacks by the self-recognition of enantiomeric monomers (see below).[17] Another argument could be that **RR-NDI** and **SS-DAN** with opposite chirality indeed form mixed stacks with weak interactions, leading to a less-intense CT band. However, TD-DFT calculations performed for both these D-A pairs suggest that the extent of CT is nearly the same if they co-stack. On the other hand, molecular modelling studies of both CT pairs showed that the D-A pair with opposite chirality is less stable by 10.02 kcal mol^{-1}, suggesting that it is indeed a chirality-driven self-sorting process.[17]

Temperature-dependent spectroscopic probing provided further mechanistic insights into the supramolecular co-polymerization process. Interestingly, the formation of mixed stacks as a function of temperature can be exclusively probed at the CT band (503 nm), whereas segregated polymerization of free NDI monomers can be monitored at 399 nm corresponding to the absorption of stacked NDI chromophores. The plot of α versus temperature obtained by monitoring either at 503 nm or 399 nm of an **RR-NDI**:**RR-DAN** mixture (1:5 ratio, 10^{-4} M) exhibited a sigmoidal trend, suggesting an isodesmic mechanism of self-assembly (Figure 4 a).[17] Furthermore, the similar nature of both cooling curves also indicates that the majority of **RR-NDI** monomers are incorporated in the homochiral D-A stacks.[17] In contrast, the autoresolution of the wrong enantiomer in a D-A mixture of opposite chirality (**SS-NDI**:**RR-DAN**) was shown unambiguously from the co-operative growth of NDI (399 nm), suggesting orthogonal segregation (Figure 4 a). Chirality control over the D and A monomers is further evident from the supramolecular co-polymerization of a tri-component monomer mixture of **SS-NDI**, **RR-NDI**, and **RR-DAN**. Orthogonal self-sorting of the **SS-NDI** stacks is evident from the co-operative growth of the CD signal at 364 nm (Figure 4 b). On the other hand, the growth of CT stacks of **RR-DAN** and **RR-NDI** in the tri-component mixture is evident from the sigmoidal curve obtained by probing at 503 nm.[17]

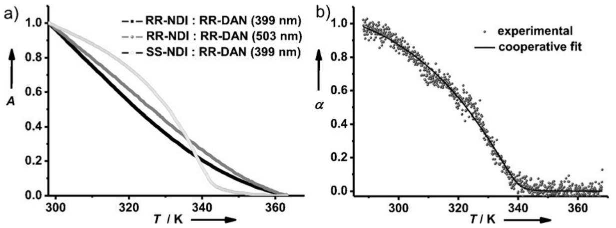

Figure 4. Mechanistic investigations of stereoselective supramolecular co-polymerization: a) Plot of absorption changes at CT (503 nm) and NDI (399 nm) absorptions in two component D-A mixtures (**RR**-/**SS-NDI**:**RR-DAN**). The NDI-DAN ratio is 1:5. b) Evolution of **SS-NDI** CD intensity at 364 nm, suggesting its segregation in a tri-component mixture consisting of equimolar mixture of bischromophoric NDIs and 5 equivalents of **RR-DAN**. (Concentrations of **RR**-/**SS-NDI** for all the experiments were 10^{-4} M).

In conclusion, we have demonstrated a novel chirality based strategy to obtain desired supramolecular organization of π-complementary donors and acceptors in multicomponent assemblies formed in solution. Detailed spectroscopic probing has provided mechanistic insights into the self-sorting and growth processes of the supramolecular stacks. These results open up a plethora of opportunities to exploit molecular chirality for the realization of multi-component nanostructures with controlled nanoscale organization.

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