

## Quantitative Formation of *m*-Phenyleneimine Macrocycle from Linear Oligomers Based on $\pi$ -Stacking and DCC

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### Introduction

Highly shape-persistent macrocycles are attractive in the fields of supermolecular chemistry and material science because of their potential applications and novel properties. A variety of supramolecular assembly, including porous organic solids, discotic liquid crystals, three dimensional nanostructures, extended tubular channels, host-guest complexes have been realized from these building blocks.[1] However, it is common for the preparation to involve a large number of synthetic steps, to require dilute conditions (< 1mM), and to afford low overall yields. The efficient preparation of functionalized macrocycles has been a challenging task. We will present the quantitative synthesis of *m*-phenyleneimine macrocycles using  $\pi$ -stacked precipitation of the macrocycle and the formation-scission reversibility of imine linkage (Dynamic Covalent Chemistry).

### Result and Discussion

Fully aromatic polyimines are expected to exhibit excellent properties such as light-emitting property, however they are often precipitated even at the initial stage of the polymerization due to their rigid-rod chain structures. We have attempted to prepare the high molecular-weight polyphenyleneimine from an AB-type monomer *via* soluble precursor polymer.[2] Polycondensation of *m*-aminobenzaldehyde diethylacetal in THF containing water gave white precipitates two week later. In the TOF-MS spectrum of polymerization solution, a strong peak at 618 amu corresponding to a macrocycle (Cm6) appeared.[3] The single crystal X-ray analysis revealed that Cm6 molecule adopted an outer N-type chair conformation as predicted by the DFT calculation (Figure 1). The Cm6 macrocycles form  $\pi$ -stacked columnar aggregates having a tubular channel. It is of interest that one molecule THF and a cluster of six molecule water are intercalated randomly between macrocycles in disorder state. The WAXD pattern of powdery Cm6 showed that the columns aggregated with hexagonally closest-packed structure. These results are supported by the SEM and TEM images. The electron diffraction pattern of Cm6 powder revealed that the nearly planar macrocycles are stacked in the long axis direction of the crystal with an interplanar spacing of 0.38 nm (Figure 2).

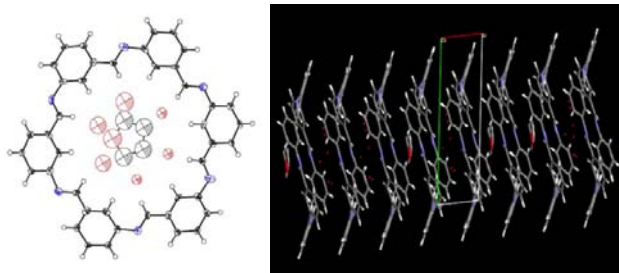
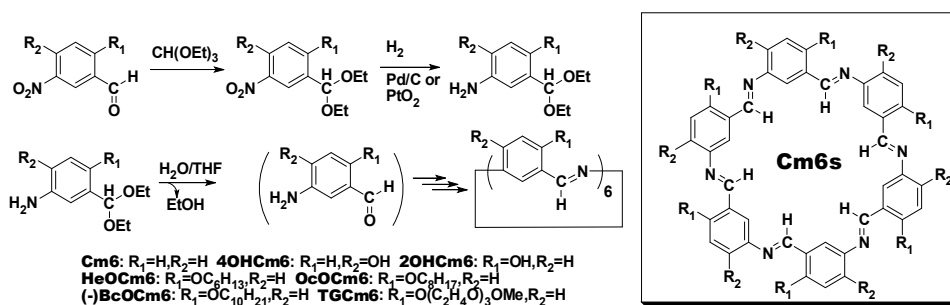


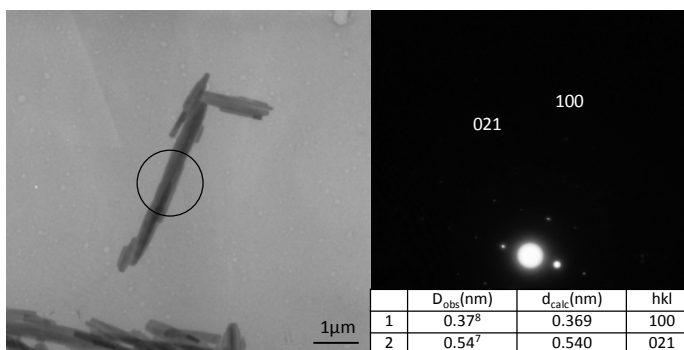
Figure 1. Single crystal X-ray analysis of macrocycle Cm6

The synthetic route to many kinds of *hexakis(m-phenyleneimine)* macrocycles Cm6s is illustrated in Scheme 1. The isolated yields of Cm6s were over 70% and quantitative in some cases. In a range of the monomer concentration from 1.28 to 0.05 molar, the time until precipitates appeared became shorter at the higher monomer concentration. The yields tended to increase with an increase in the monomer concentration. When the polymerization solution of 0.51 molar was refluxed for 8 hours at first, the Cm6 precipitates appeared after three days. The polymerization solvents other than THF such as dioxane and ethanol were effective for the Cm6s synthesis, and one molar acetic acid had an effect on the synthesis as an initiator.

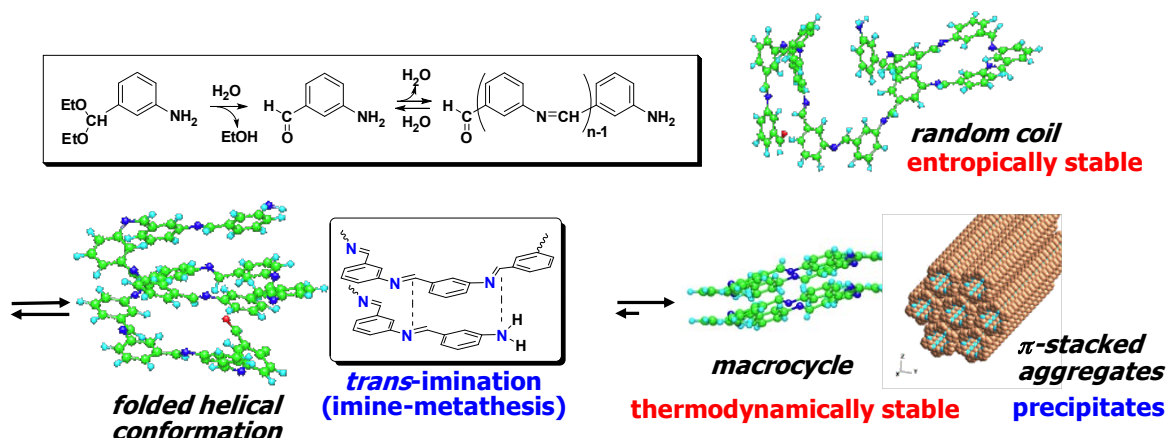


Scheme 1. Synthetic route to *hexakis(m-phenyleneimine)* macrocycles Cm6s from *m*-nitrobenzaldehydes.

**Figure 3** shows schematic illustration of macrocyclization based on MALDI-TOF and NMR analysis. The monomer was deprotected slowly with water as a weak acid, which supplied a condensable aldehyde-amino monomer in the polymerization system with a low concentration. The monomers are polycondensated to give linear imine oligomers in an equilibrium state. A random-coil oligomer forms a folded helical conformation with a strong intermolecular association of hexameric macrocycles having the same backbone structure. A *trans*-imination occurs between two imine linkages or between an amino group and neighboring imine linkage to give a macrocycle. Shape-anisotropic, nearly planar, and persistent macrocycles are known to aggregate into columnar assembly in polar solvents driven by the aromatic  $\pi$ -stacking. Macrocycle is stabilized by the free energy gained from the intermolecular, noncovalent interactions upon aggregation and that the aggregates therefore became the thermodynamically most stable species and precipitated.[4] The *trans*-imination equilibrium was shifted in favor of cyclization and the macrocycle was afforded as the predominant product. The reversible nature of imine linkage has played an important role in the quantitative formation. When the aggregates is heated in the solvent containing water, the macrocycle is converted to random coil which is entropically stable. This is an example of dynamic covalent chemistry, which is concerned with chemical reactions that are carried out reversibly under equilibration conditions.



**Figure 2.** TEM image and electron diffraction pattern of Cm6.



**Figure 3.** Possible mechanism for quantitative formation of macrocycles based on  $\pi$ -stacking and DCC.

### Conclusion

The quantitative synthesis of *hexakis(m-phenyleneimine)* macrocycle Cm6 and its analogues from *m*-aminobenzaldehyde diethylacetals has been successfully achieved. The structure of Cm6 in the solid state was determined by X-ray single crystallographic analysis, WAXD, and electron diffraction analysis. Cm6 has an outer nitrogen-type chair conformation, and forms  $\pi$ -stacked columnar aggregates and hexagonally closest-packed structure. The macrocyclization process was investigated using TOF-MS and NMR. A mechanism for the macrocyclization based on mutual conversion of linear polymers and  $\pi$ -stacked columnar aggregation is proposed. Both the nature of imine linkage and the shape-anisotropy of the macrocycle have played an important role in the quantitative formation.

### References

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