

Ferrocene: an Exciting Building Block for Designing Supramolecular Assemblies

Nihar Sahu,¹ Mohammad Umer Lone,² Chandrakanta Guchhait,¹ Suriyaa V.,¹ Sovik Dey Sarkar,¹ Raj Kumar Roy² and *Bimalendu Adhikari¹

¹ National Institute of Technology Rourkela, Rourkela, Odisha 769008, India.

² Indian Institute of Science Education and Research (IISER) Mohali, Knowledge City, Sector 81, S. A. S. Nagar, Manauli PO, Punjab 140306, India

***Corresponding Author: Bimalendu Adhikari, adhikarib@nitrkl.ac.in**

Abstract:

Ferrocene (Fc) possesses interesting molecular and electronic attributes, like shape, size, hydrophobicity, rotational flexibility, and redox responsiveness, rendering it a promising building block in developing various supramolecular architectures, including supramolecular polymers (SPs).¹ SPs are one-dimensional molecular assemblies with a high degree of internal order formed through non-covalent interactions and are gaining prominence as functional soft materials. In SP formation, the design principle is pivotal, ensuring precise directionality and strength for the non-covalent interactions between monomers. Herein, molecules with Fc as the core component are used to leverage Fc's distinctive "molecular ball-bearing" properties for optimal molecular conformation and robust intermolecular interaction through enhanced enthalpy gain.² Molecule **1a**-[Fc(CONH-Azo-TDP)₂] featuring 1,n'-disubstituted ferrocene, with azobenzene and long alkyl chains was designed and synthesized, with the higher likelihood of forming SPs. We have also designed three reference molecules, **1b**-[Fc(CONH-Azo-TDP)], **1c**-[Ad(CONH-Azo-TDP)₂], and **1d**-[Bz(CONH-Azo-TDP)₂], to investigate and compare Fc's role in SP formation. **1a** formed a super gel, while **1b** and **1c** did not show gelation or ordered SPs. Surprisingly, despite Fc's non- π -stackable nature, **1a** displayed efficient gelation than **1d**, having a larger π surface. **1a** showed stronger π - π stacking and intermolecular H-bonding than the reference compounds investigated by UV-Vis spectroscopy and NMR. This hinted at Fc's conformational flexibility for assisting in efficient SP formation. Additionally, azobenzene was exploited for creating photo-responsive soft material. Based on these findings, possibility of syn vs. anti-conformation toward forming SP is under investigation by introduction of amide bonds at strategic positions.

Keywords: Supramolecular Polymer, Ferrocene, Redox responsive, Soft Materials, Organogel

Reference:

1. N. Sahu et al. *Ferrocene: an exotic building block for supramolecular assemblies* Chem. Commun., 2023, 59, 14482.
2. N. Sahu et al. *Introduction of Ferrocene as a Facilitator for the Construction of Supramolecular Polymers*, Chem. Eur. J., 2023, 29, e202202711.

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Raj Kumar Roy² and *Bimalendu Adhikari¹

¹National Institute of Technology Rourkela, Rourkela, Odisha 769008, India.

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Introduction

Supramolecular Polymers (SPs) are one dimensional aggregates of the monomers formed using non-covalent interactions. They are dynamic in nature and show stimuli responsiveness.

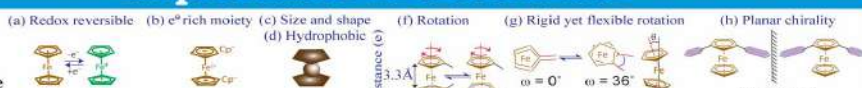


- Recent focus has been on specific strategies that can lead to the designing of monomers which will non covalently polymerize to SP.
- Proper design of monomer can strengthen the non-covalent interaction to form efficient SP.
- We planned to utilize the restricted rotation flexibility of Ferrocene (Fc) along the axis for SP formation.



Importance of Ferrocene

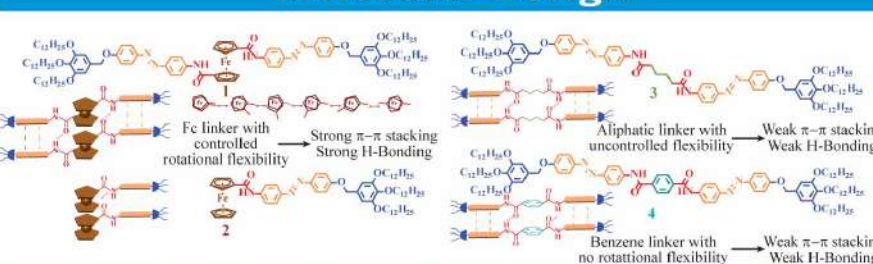
Molecular Features of Ferrocene



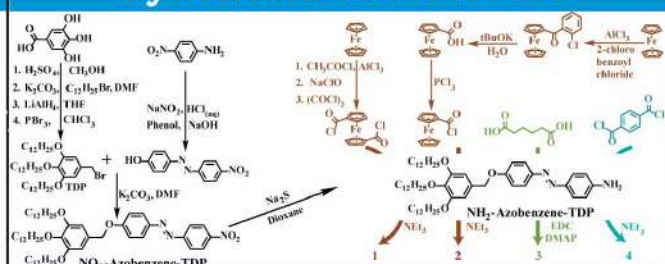
Ferrocene assisted noncovalent interactions



Molecular Design

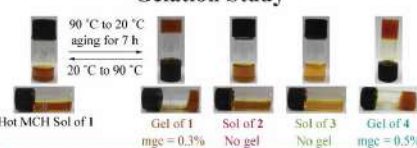


Synthesis of Molecule



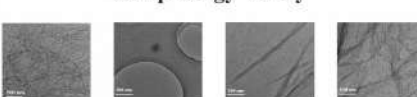
SP Synthesis

Gelation Study



- mge of 1 < mge of 4 was unexpected as 4 has a larger π surface.
- Probably due to the better orientation provided by ferrocene owing to its rotational flexibility.

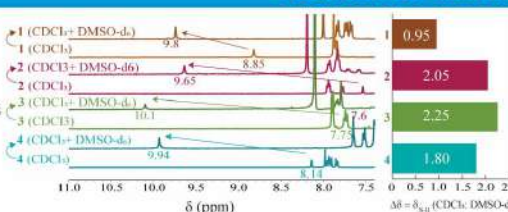
Morphology Study



- Ordered molecular nanofiber with comparable width to that of extended molecular length for 1.

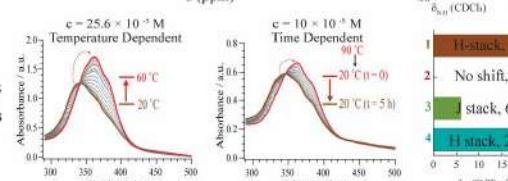
Results and Discussion

NMR Studies



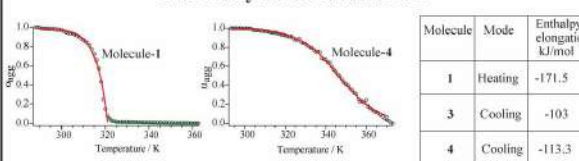
- Inter-molecular H bonding from NMR.
- Highest deshield in CDCl₃ and lowest shifting upon addition of DMSO-d₆ suggest strongest inter-molecular H-bonding in 1.
- Arising due to stronger H-bonding supported by better directionality provided by ferrocene.

UV-Vis Studies

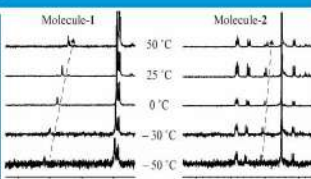


- Rotational flexibility of ferrocene provides better orientation for the azobenzene arms, which leads to stronger π - π stacking in 1 than 4 with a larger planar π surface.

Thermodynamic Parameters



Molecule	Mode	Enthalpy of elongation kJ/mol	Elongation Temperature °C
1	Heating	-171.5	47.9
3	Cooling	-103	60.1
4	Cooling	-113.3	73.1



Molecular Packing

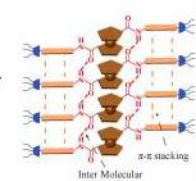
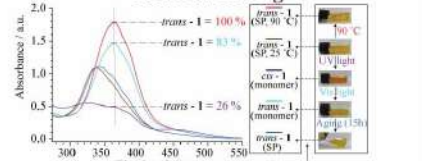


Photo Switching



Conclusion

Ferrocene through various properties shows different noncovalent interactions

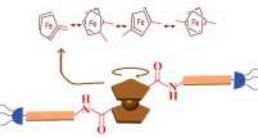
Molecular ball-bearing of ferrocene

Restricted rotational flexibility of ferrocene

Supports enthalpy driven SP with larger enthalpy gain

Efficient supramolecular polymerization in proper designed SP

Presence of ferrocene and azobenzene can be exploited as responsive soft materials



References

1. Lone, M. U.; Sahu, N.; Roy, R. K.; Adhikari, B.; *Chem. Eur. J.*, **2022**, 29, e20220711.
2. Guchhait, C.; Suriyaa, V.; Sahu, N.; Sarkar, S. D.; Adhikari, B.; *Chem. Commun.*, **2023**, 59, 14482.

Keywords

Supramolecular Polymer, Ferrocene, Azobenzene, Light responsive, Soft Materials

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