Synthesis and Properties of Cellulose Derivatives with π-Conjugated Molecules

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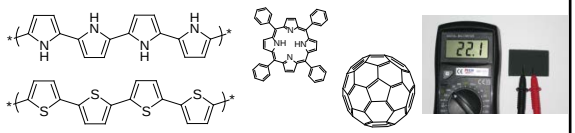
Introduction



π-Conjugated molecules

- Conductivity,Semiconductivity, Photoelectroactivity, etc.
- Chemical tunability, self-assembly via π-π interaction.
- Applications: optoelectoric devices (OTFT, OPV, etc).
- Problems: Low solubility due to aggregation, Stability, etc

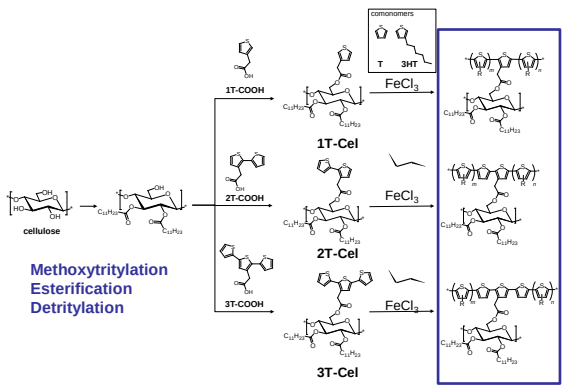
Combination with Cellulose

(1) Good physical properties
High strength, film-forming properties, stability.

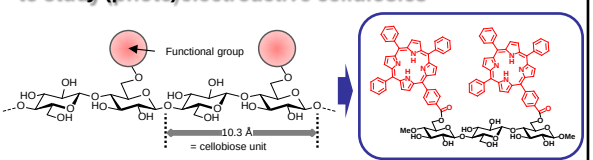
(2) Unique molecular characteristics
Linearity (rigidity), helicity, topology (substitution pattern).

Approach

1. Regioselectively thiophene-substituted cellulose derivatives as a grafting model



2. Alternatingly functionalized cellotriose as a model to study (photo)electroactive cellulosics



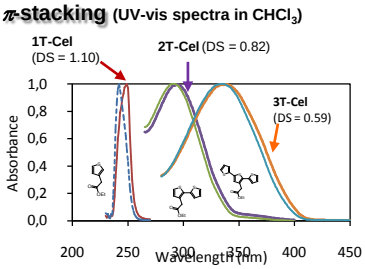
Summary

(1) A reliable protocol to synthesize (photo)electroactive polythiophene-cellulose composites, which are soluble and form flexible, readily processable materials, is demonstrated.

(2) Right-handedness derived from bisporphyrins attached to a cellotriose backbone at *O*-6 and *O"*-6 positions is revealed for the first time. This cellotriose is proposed as a model of alternatingly functionalized cellulosics, which have promising properties for applications in optoelectronics and molecular receptors owing to the chirality and rigid backbone effects.

1. Polythiophene-Cellulose Composites

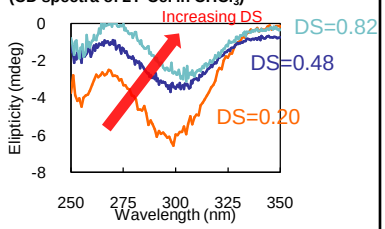
π-stacking (UV-vis spectra in $CHCl_3$)



- Slight red-shifted absorption maximum.
- π-Stacking of oligothiophene moieties (*J*-aggregation) in solution

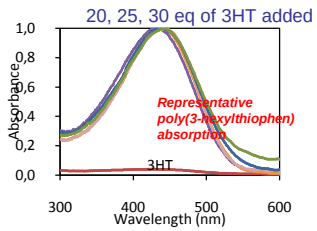
Helical arrangement

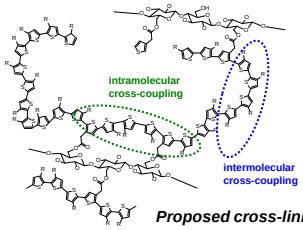
(CD spectra of 2T-Cel in $CHCl_3$)



- Negative CD band in a diluted solution
- CD intensity decreased as the DS increased ⇒ the remaining hydrogen bonds are needed for helical arrangement

Oxidative copolymerization





- Over 20 eq of 3HT yielded π-conjugated polymers.
- Around 445 nm corresponded to π-π* transition.

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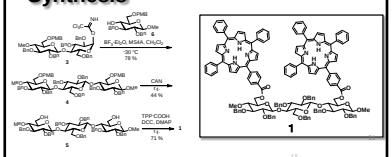
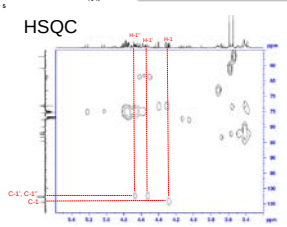
2. Alternatingly functionalized cellotriose

Synthesis

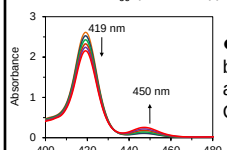


HSQC

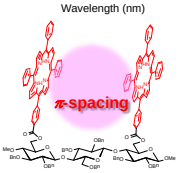


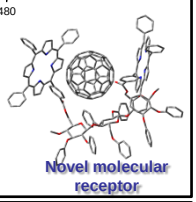
π-spacing

Addition of C_{60} (1,2,3,4 eq)

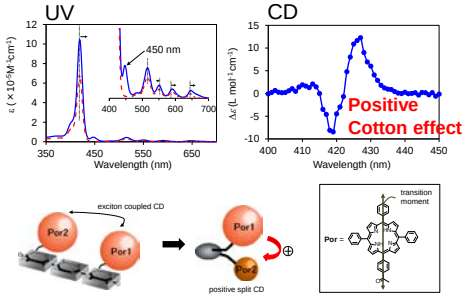


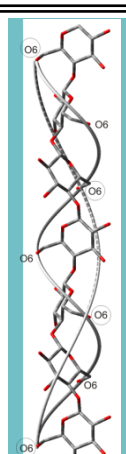
- Change of Soret band by the addition of fullerene C_{60} and C_{70}.





Helical arrangement





QM minimization

Thread connecting all of the O6 atoms ⇒ **left-handed**

Thread connecting the O5 atoms Alternatingly ⇒ **right-handed**

- Absorption at 450 nm: intramolecular electron coupling ⇒conformational restriction due to the rigid backbone
- **Right-handedness** derived from alternatingly substituted porphyrins

K. Sakakibara, F. Nakatsubo, A. D. French, T. Rosenau, *Chem. Commun.*, **2012**, *48*, 7672-7674.

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