About OMICS Group

OMICS Group International is an amalgamation of Open Access publications and worldwide international science conferences and events. Established in the year 2007 with the sole aim of making the information on Sciences and technology 'Open Access', OMICS Group publishes 400 online open access scholarly journals in all aspects of Science, Engineering, Management and Technology journals. OMICS Group has been instrumental in taking the knowledge on Science & technology to the doorsteps of ordinary men and women. Research Scholars, Students, Libraries, Educational Institutions, Research centers and the industry are main stakeholders that benefitted greatly from this knowledge dissemination. OMICS Group also organizes 300 International conferences annually across the globe, where knowledge transfer takes place through debates, round table discussions, poster presentations, workshops, symposia and exhibitions.

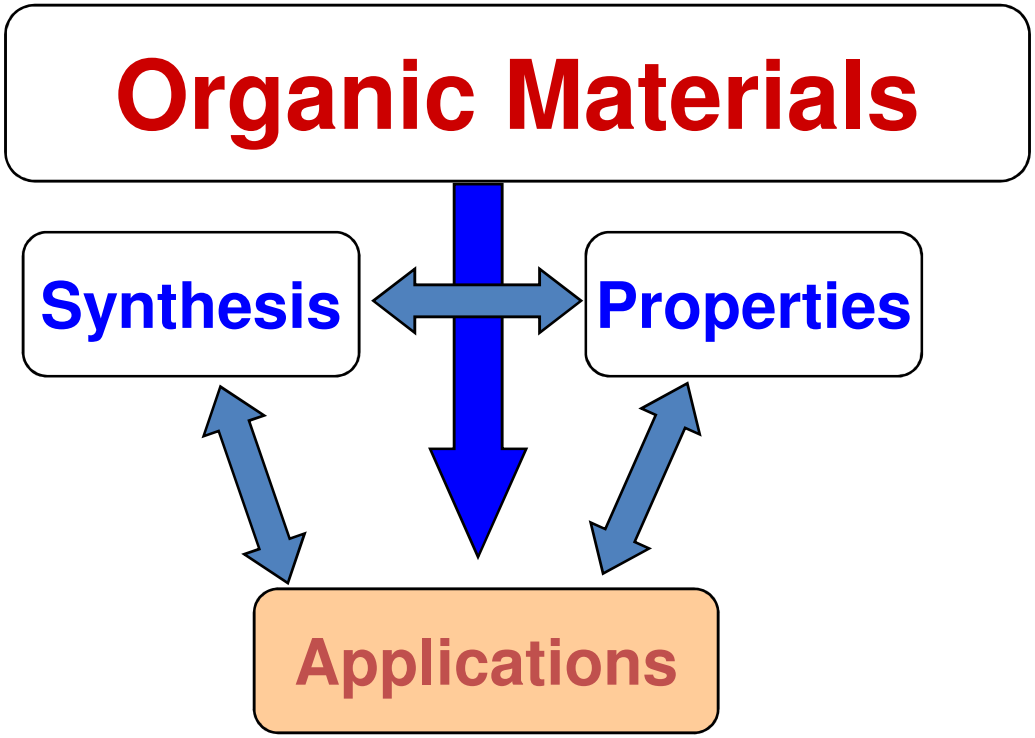
About OMICS Group Conferences

OMICS Group International is a pioneer and leading science event organizer, which publishes around 400 open access journals and conducts over 300 Medical, Clinical, Engineering, Life Sciences, Phrama scientific conferences all over the globe annually with the support of more than 1000 scientific associations and 30,000 editorial board members and 3.5 million followers to its credit.

OMICS Group has organized 500 conferences, workshops and national symposiums across the major cities including San Francisco, Las Vegas, San Antonio, Omaha, Orlando, Raleigh, Santa Clara, Chicago, Philadelphia, Baltimore, United Kingdom, Valencia, Dubai, Beijing, Hyderabad, Bengaluru and Mumbai.

Dimension Controlled Self-Assembly Of Perylene Based Molecules

RICE



Arshad Sayyad

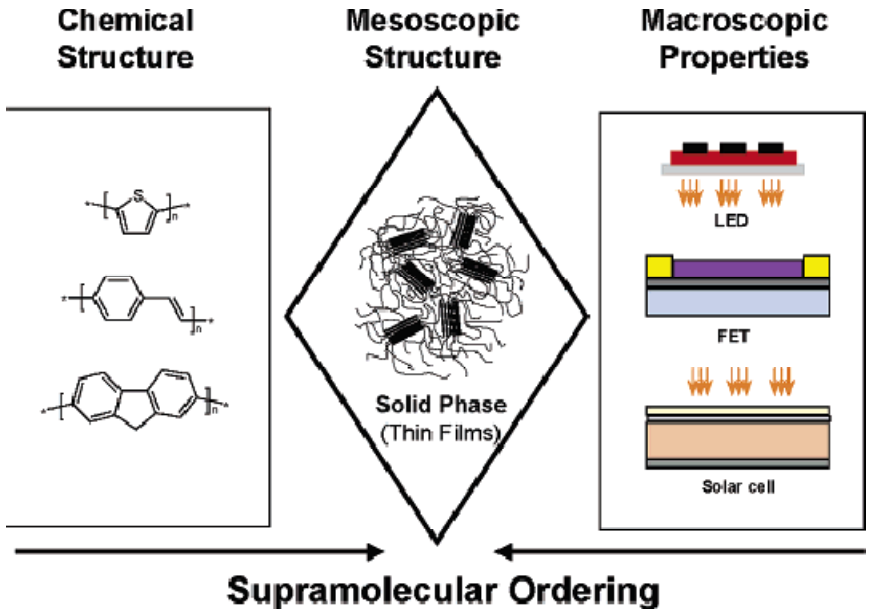
10/06/2014

3rd International Conference and Exhibition on Materials Science & Engineering

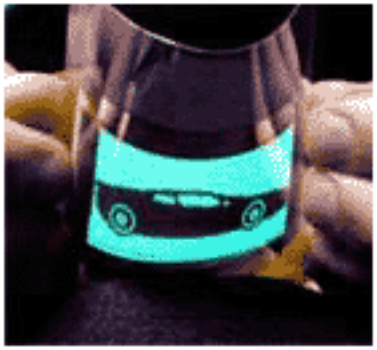
Organic semiconductors

π- conjugated materials : Active materials for electronic devices

Field Effect Transistors (FET),
Photovoltaic cells (PV),
Light emitting diodes (LED)
(85 % of current patents exist)

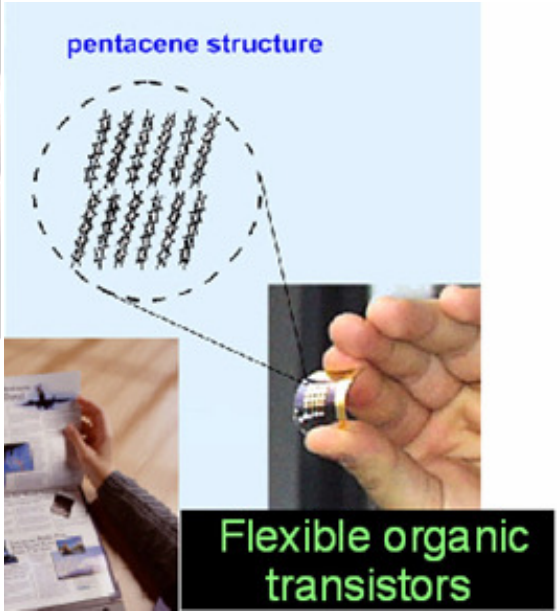


Flexible display



OLED Display Screen (from Universal Display Corp)

Electronic paper



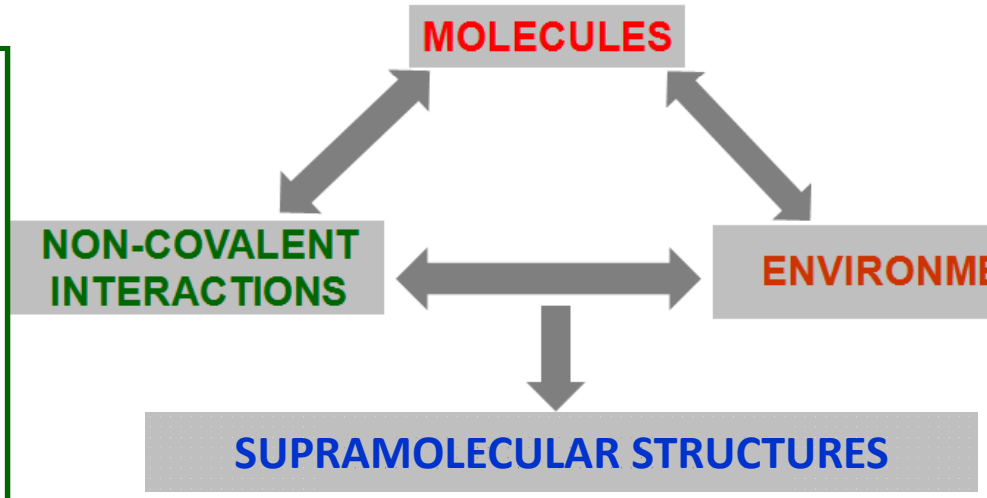
Charge transport efficiency
Intrinsic electronic properties
Ordering in the molecules

Supramolecular Chemistry

ATOMS → Covalent Interactions → **MOLECULES**

MOLECULES → Non-covalent Interactions → **SUPRAMOLECULES**

Molecules: Synthesized (functional)



Non-covalent interactions: Columbic, hydrophobic, van der Waals, π- stacking and H-bonds

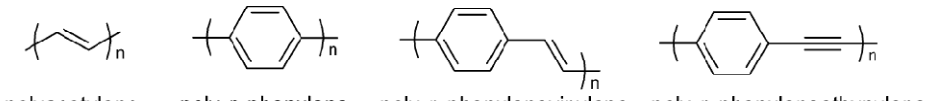
Environment: Solution or solid state

- Offer a pathway to generate structures larger than molecules.
- Control over the properties because of organization.

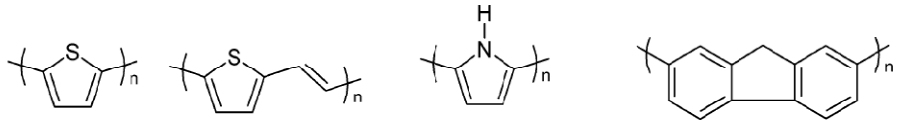
Whitesides, Science, 2002, p2418

Organic Semiconductor - Choice

Polymers:

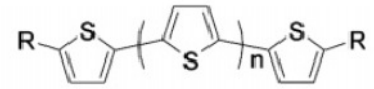


polyacetylene | poly-*p*-phenylene | poly-*p*-phenylenevinylene | poly-*p*-phenyleneethynylene

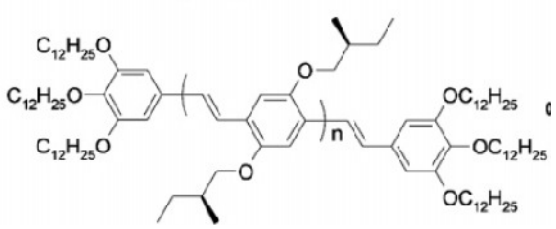


polythiophene | polythienylenevinylene | polypyrrole | polyfluorene

Oligomers:

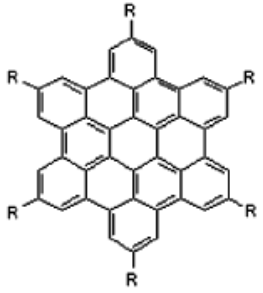


Oligothiophenes

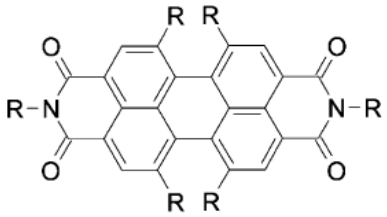


Oligophenylenevinylenes

Small Molecules:



HBC



PTCDI

Highlight

Side-chain effect

- Allows increased solubility.
- Offer pathways to control organization in solution. (Self-Assembly)
- π-conjugated materials offer possibilities to conduct self-assembly using the π-stacking interactions.
- Inherent π-stacking may lead to 1D nanostructures. (Efficient Charge Transport)

Dimension Controlled Self-Assembly

Appropriately designed Perylene based precursor:

Perylene Di-imides

Perylene Mono-imides

Salts of Perylene Tetracarboxylic Acid

Component

non-covalent interactions

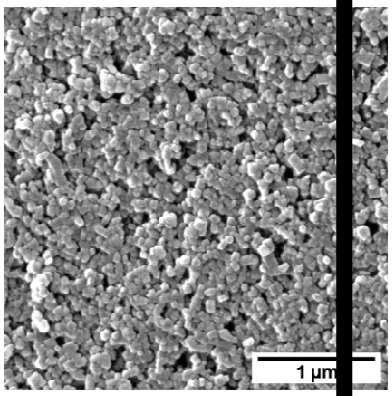
Environment

π–π, hydrophobic, Solvent cation, Hydrogen Bonding Interactions

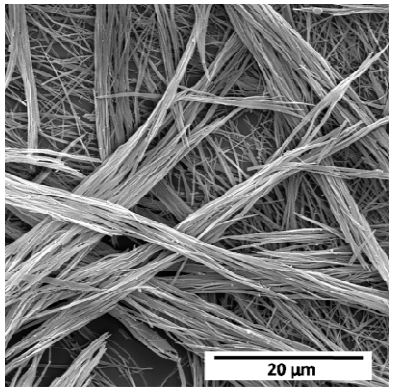
Solvents: THF, n-Propanol, Methanol, Ethanol

Temperature: RT, HT

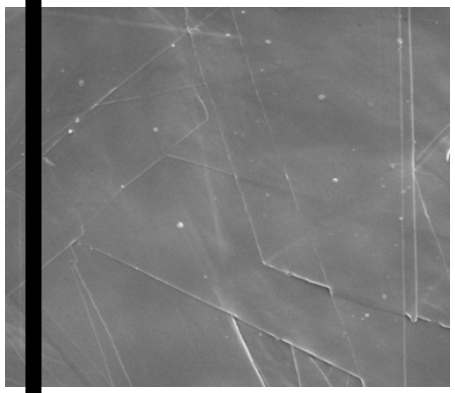
Processing: Slow/Fast Addn, Sequence of addition, Chemical reaction,



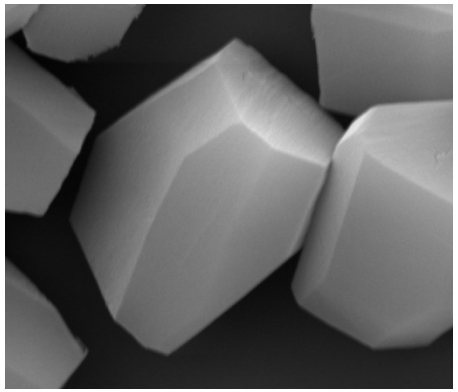
0-D Seeds



1-D Fibers

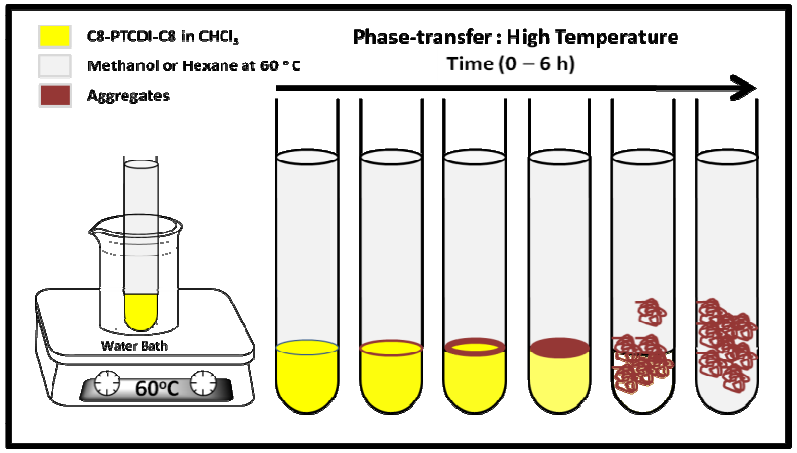


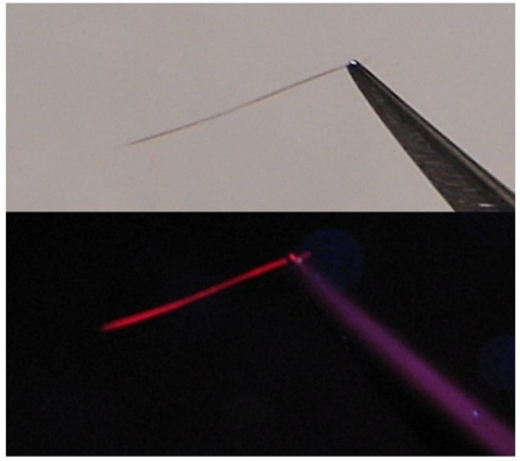
2-D Crystals

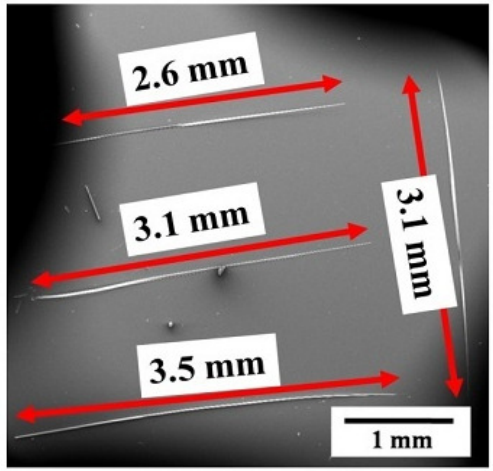


3-D Crystals

Overview

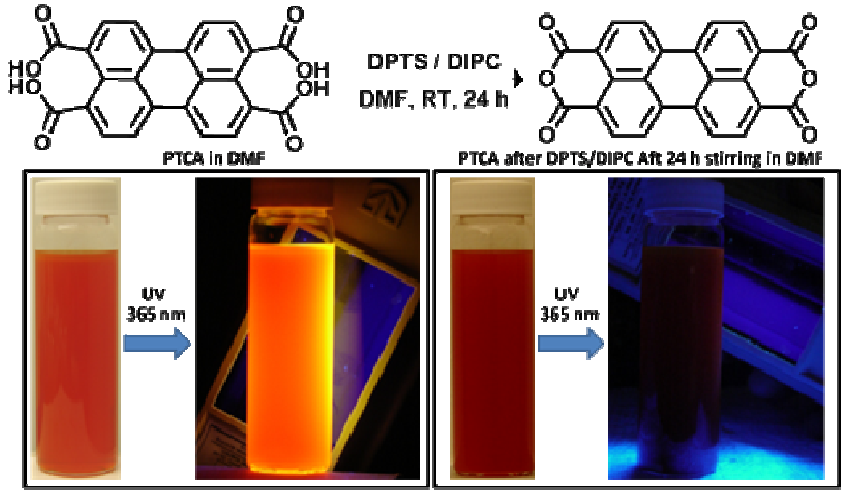


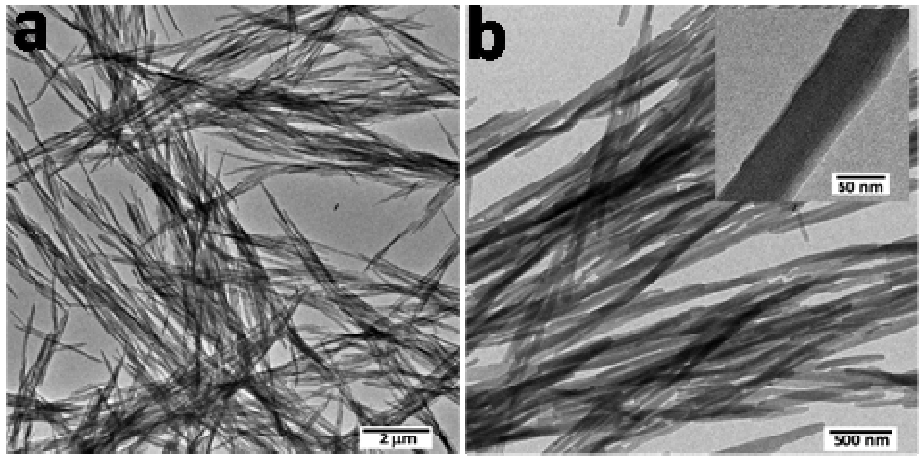




Extremely long fluorescent WIRES of PTCDI by 2L-HT method

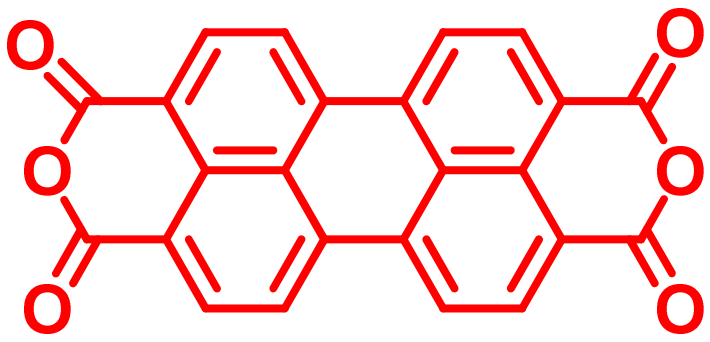
Chemical reaction mediated self-assembly of highly insoluble PTCDA



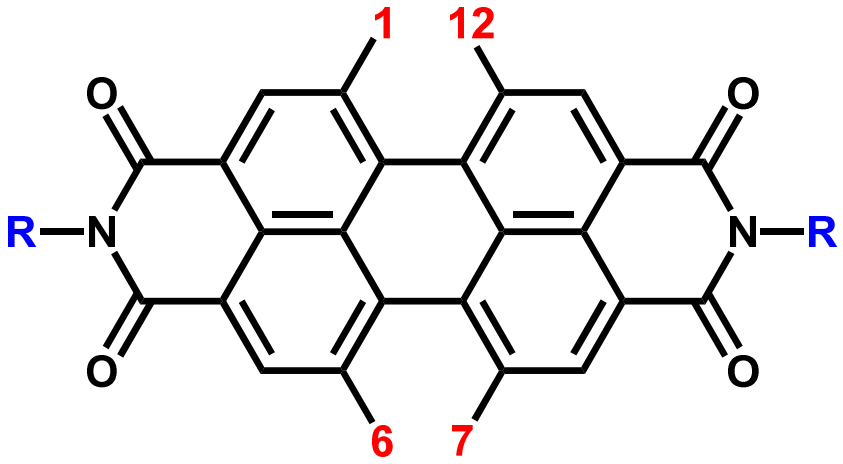


1D fibers without any side chains

Perylene tetracarboxylic diimides (PTCDI)



Perylene tetracarboxylic acid dianhydride
(PTCDA) - INSOLUBLE

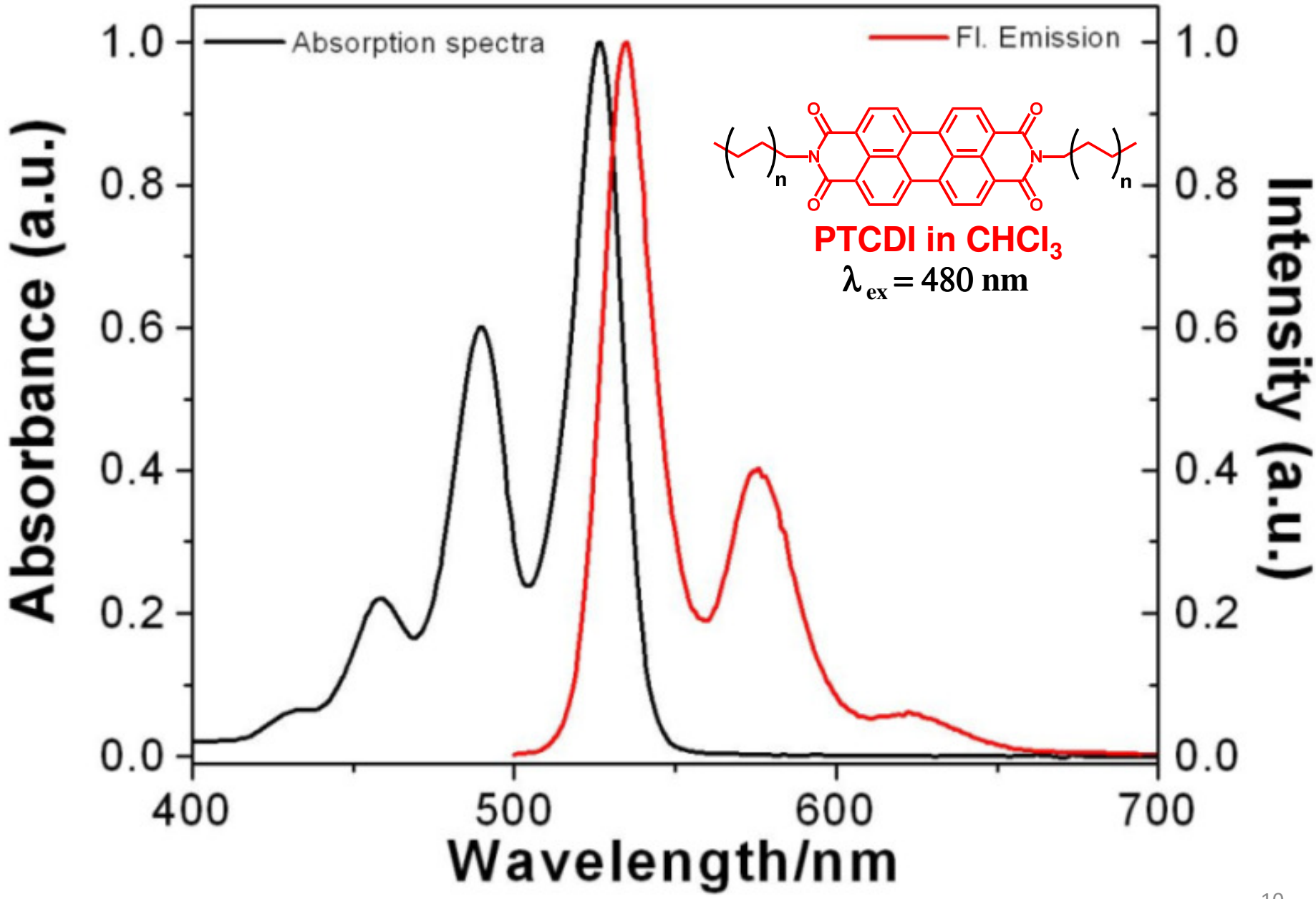


Perylene tetracarboxylic diimides
(PTCDI) - SOLUBLE

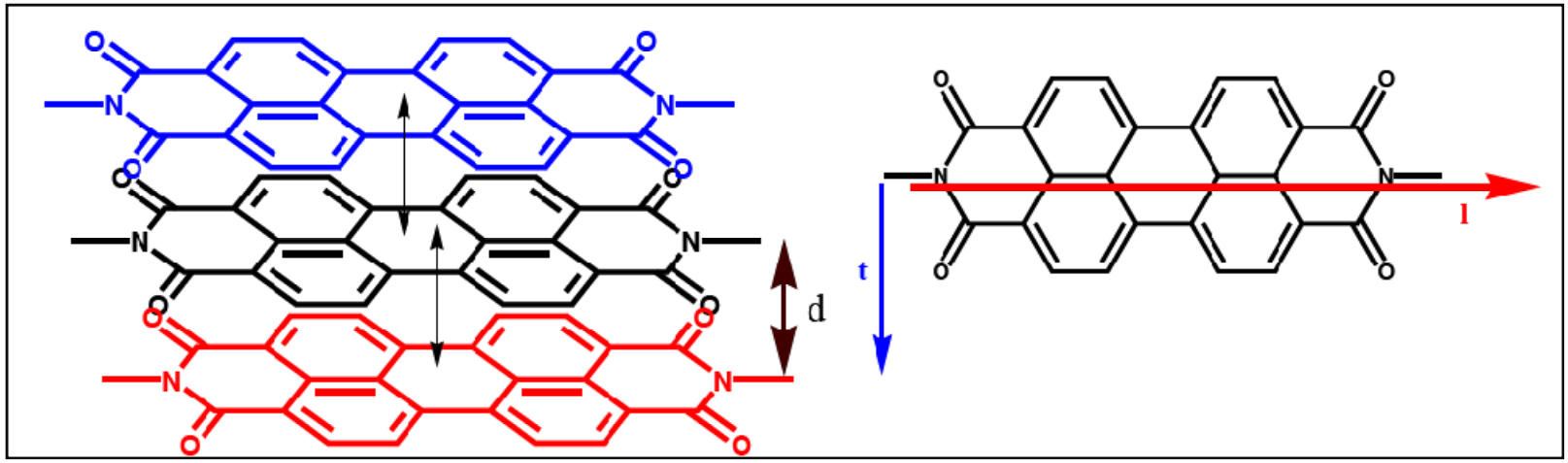
PROPERTIES

- Pigment in coloring industry
- High thermal, chemical and photochemical stability
- High electron affinity : n-type semiconductor
- High Fluorescence yields
- Strong tendency to aggregate via π-π stacking between the perylene core
- Applications in electronics and opto-electronic devices

Optical properties in homogeneous solution



PTCDI π-stacking



Efficient π-stacking

π-stacking distance (d)

0.335 (graphite) – 0.43 (distorted) nm

Generally, most π-interactions result in d-spacing around 0.38 nm

Offsets:

Longitudinal

Transverse

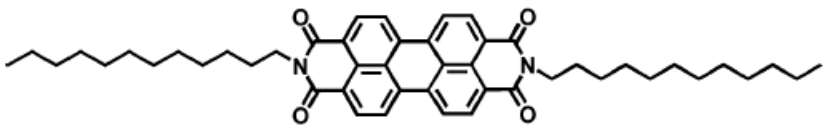
Rotational

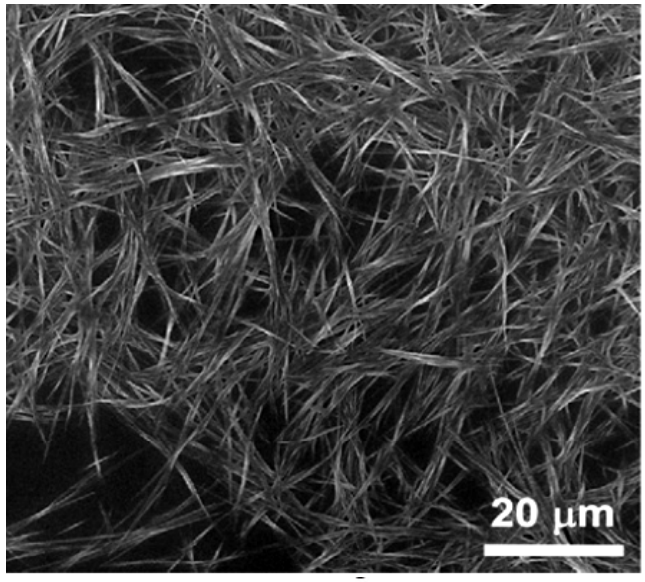
Electrical conductivity : π-π stacking direction

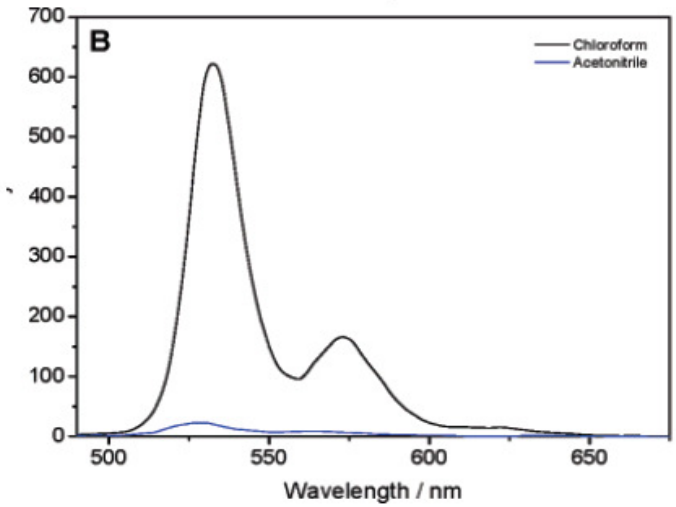
Generating ordered structures using these π–π interactions from appropriately designed perylene molecules is critical

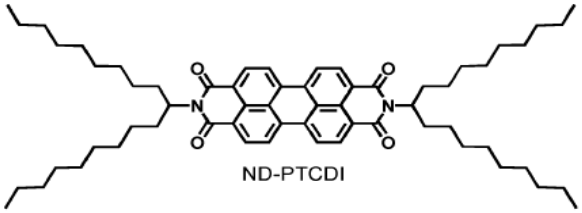
Hadicke, Acta Cryst. 1986, C42, 189; 195
Klebe, Acta Cryst. 1989, B45, 69.
Wurthner, Chem. Eur. J. 2007, 13, 450 – 465

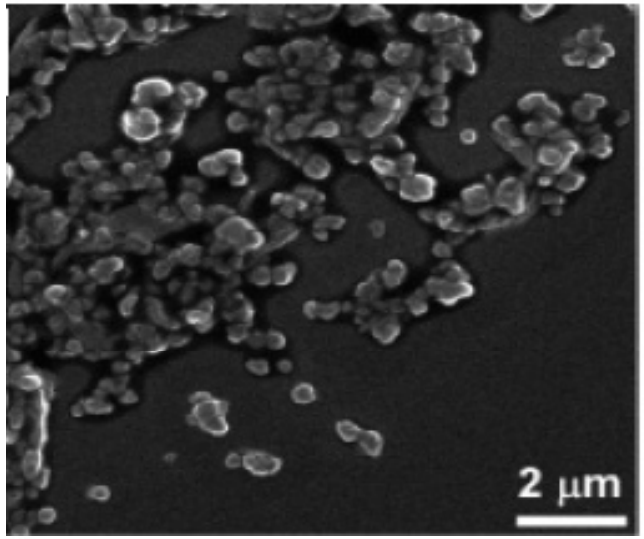
Self-assembly by π-π and hydrophobic interactions

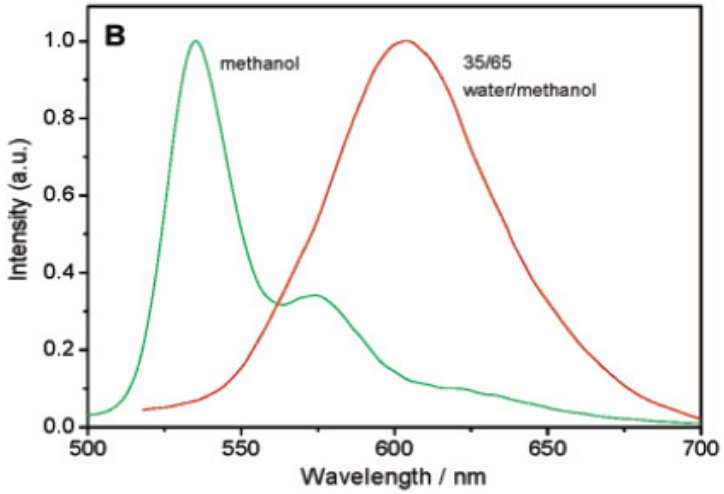








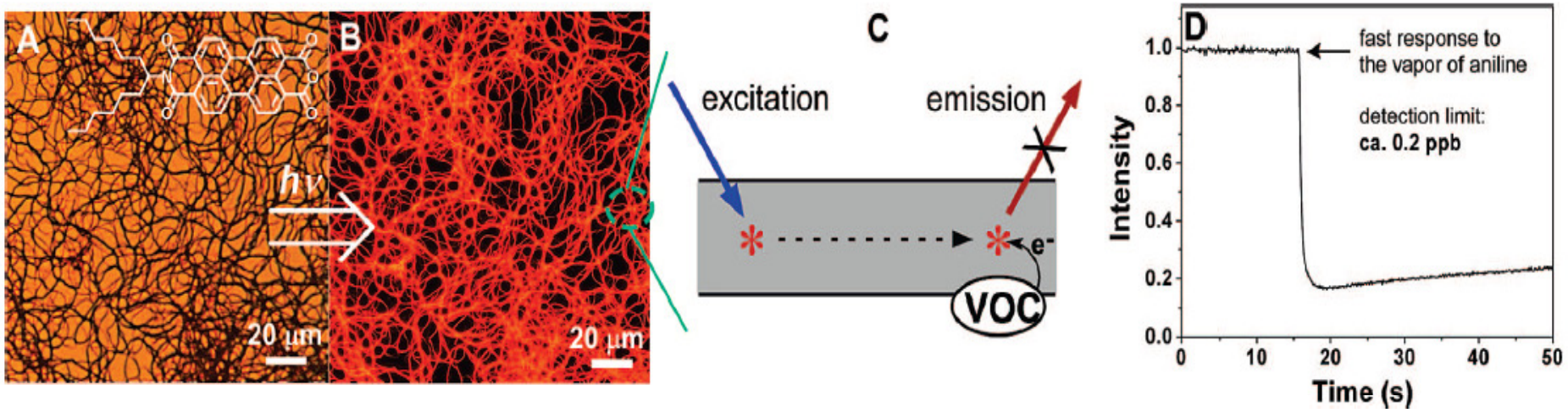




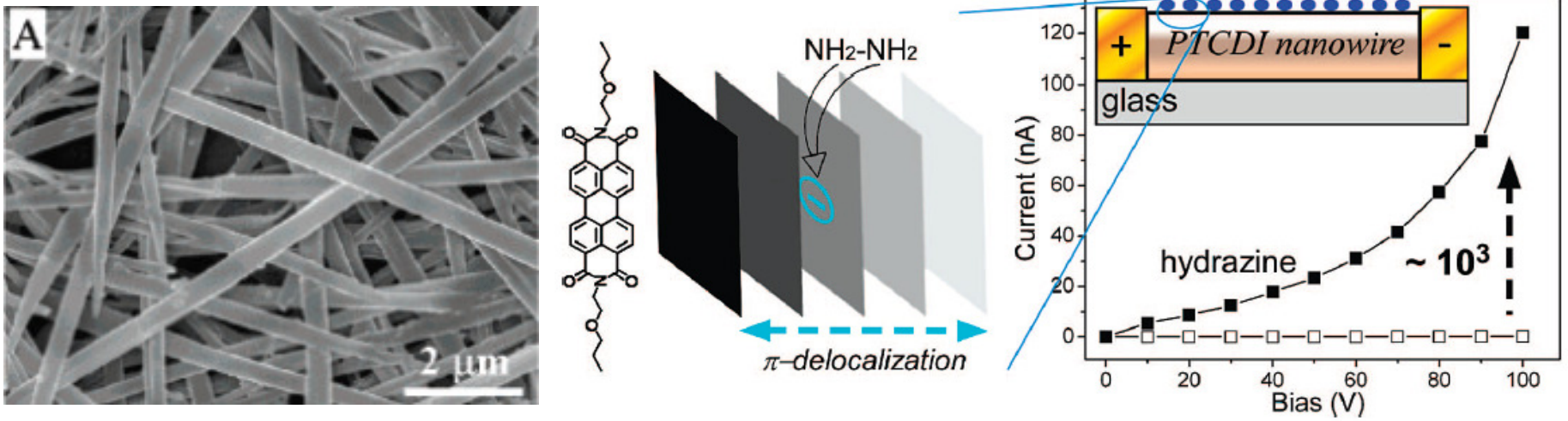
Balakrishnan et al. *JACS* 2006

Applications of ordered structures based on perylene

Sensory applications : Detection of organic amines

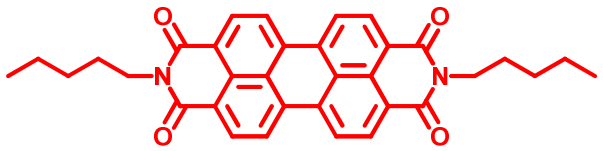


Electronic applications

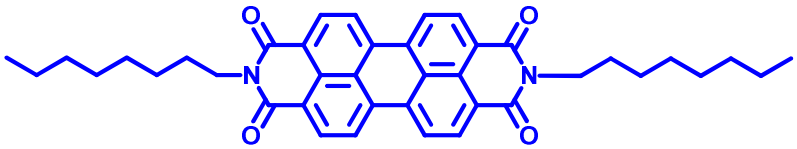


Zang et al., *Acc. Chem. Res.* 2008, *41*, 1596-1608.

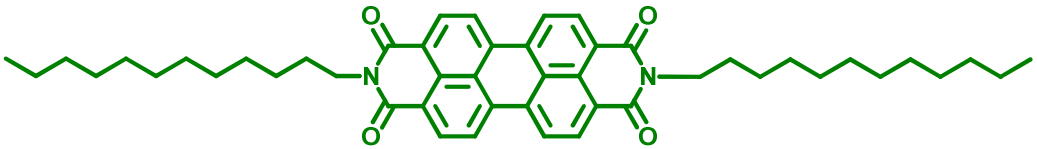
Self-assembly of linear Di-PTCDI molecules



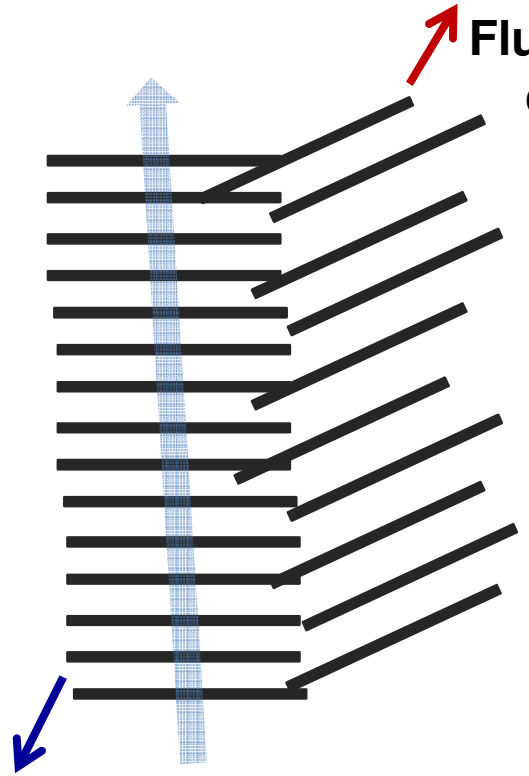
Di-C5-PTCDI



Di-C8-PTCDI



Di-C12-PTCDI

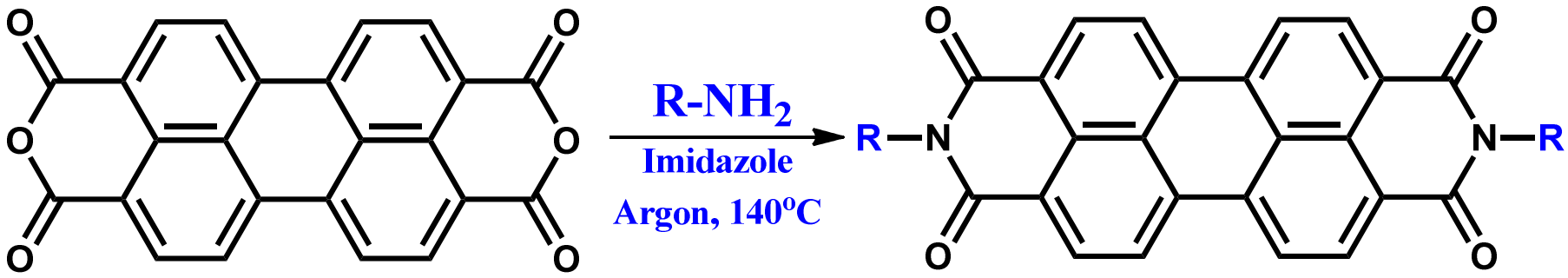


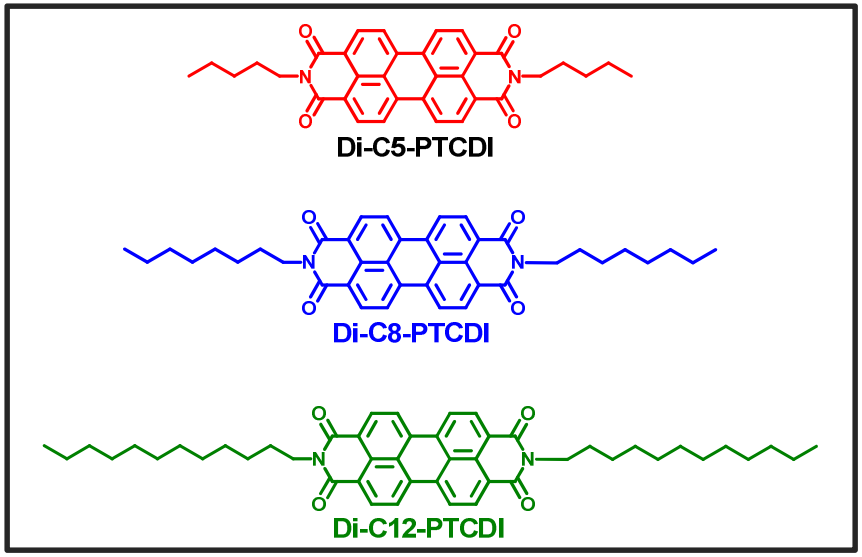
Increased electronic conductivity

Can these two sets of packing exist in same structure?

Is it possible to grow extremely long wires by solution processing?

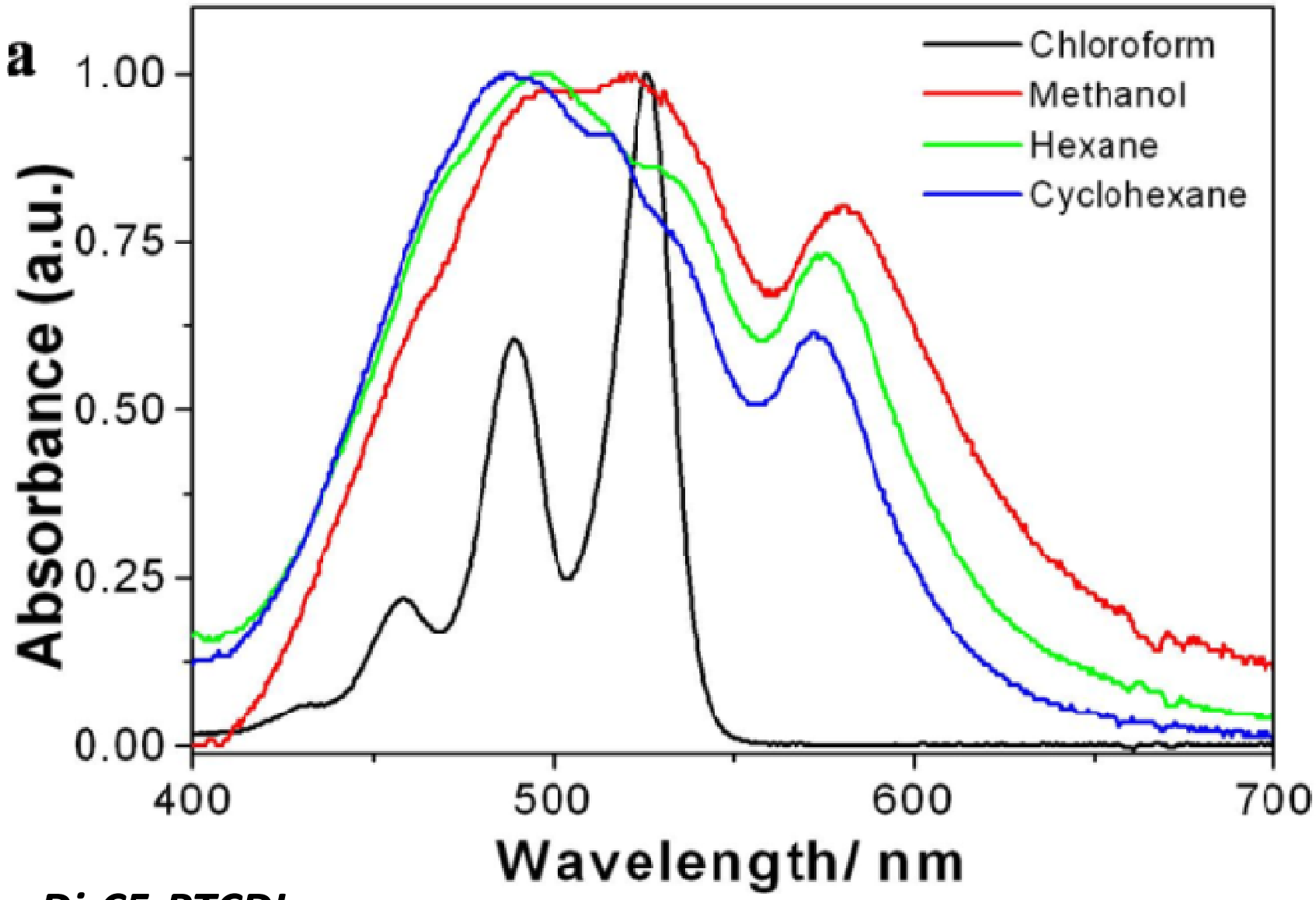
Synthesis of Di-PTCDI molecules





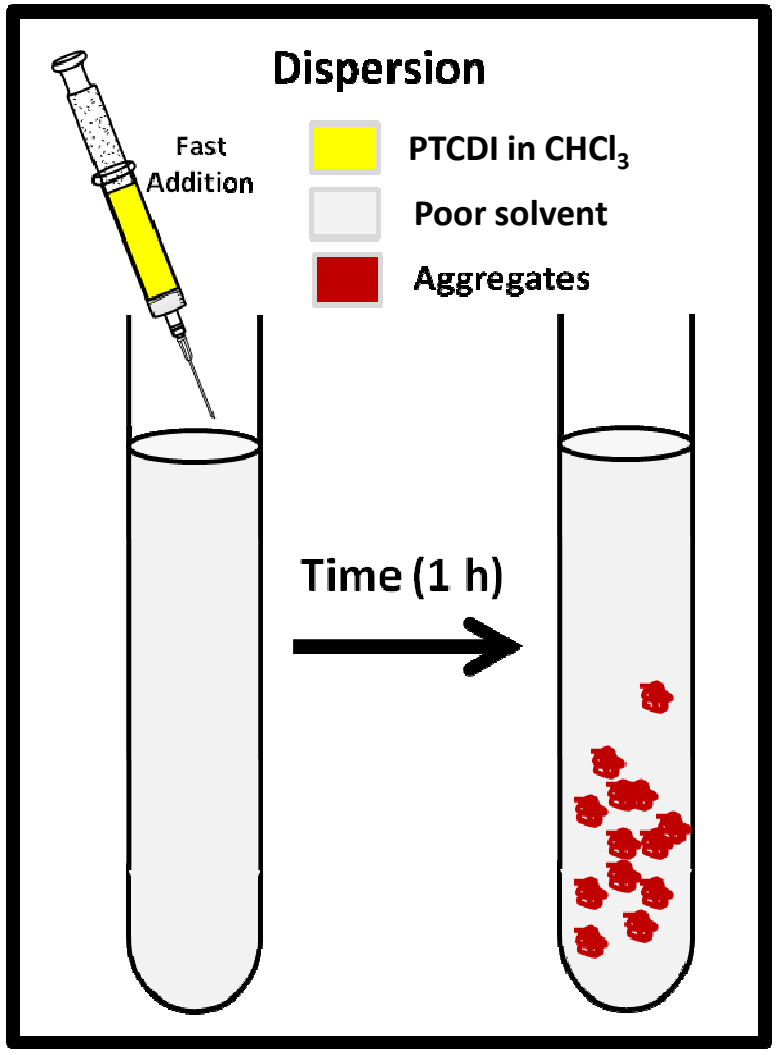
Characterization : Nuclear Magnetic Resonance (NMR) Spectroscopy

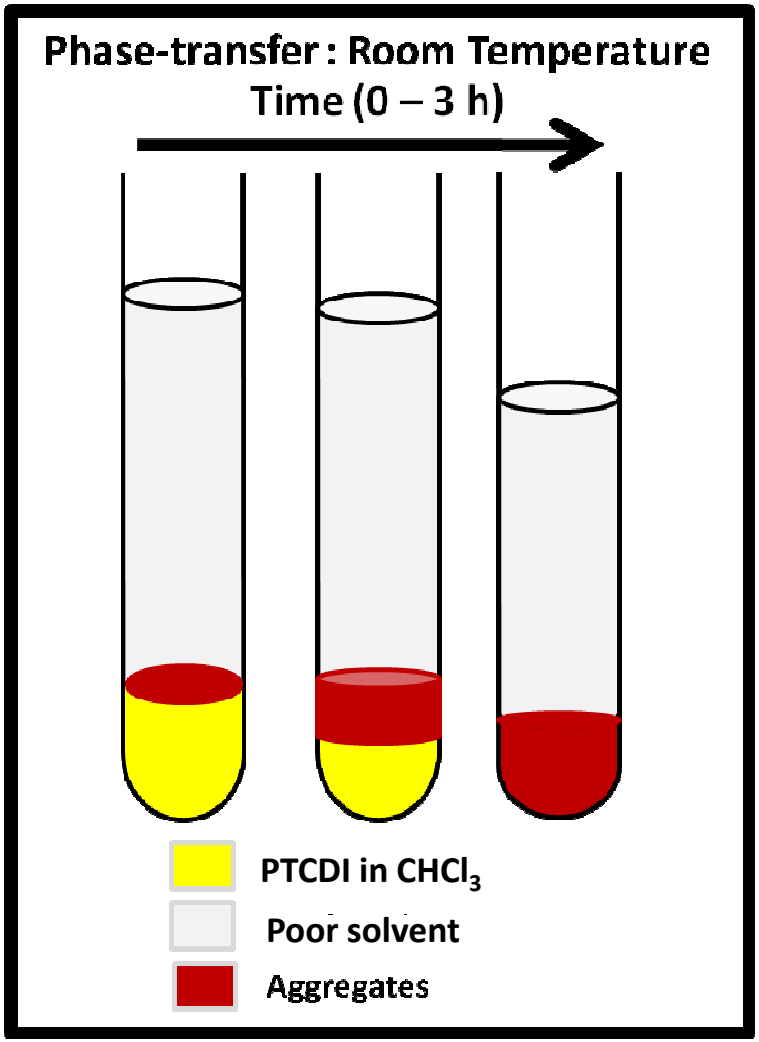
Optical Properties: Free molecules and aggregates



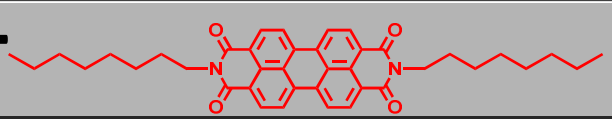
Di-C5-PTCDI

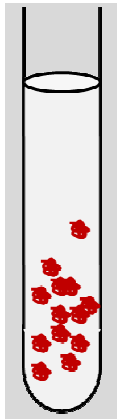
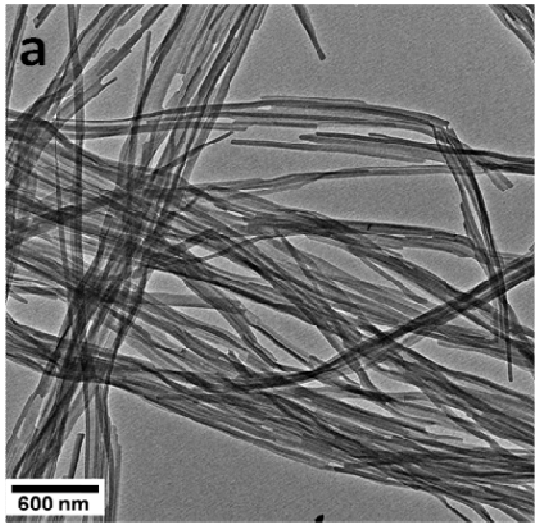
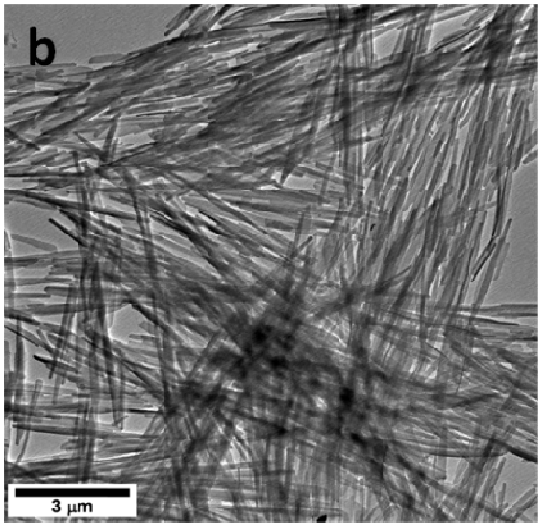
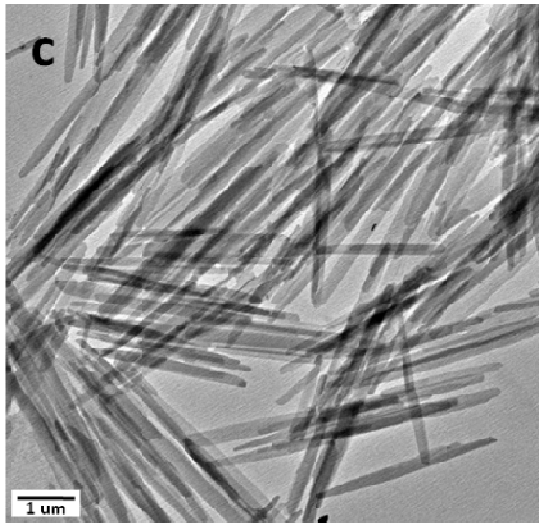
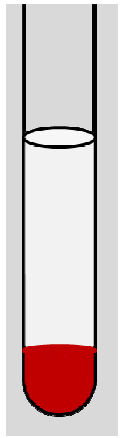
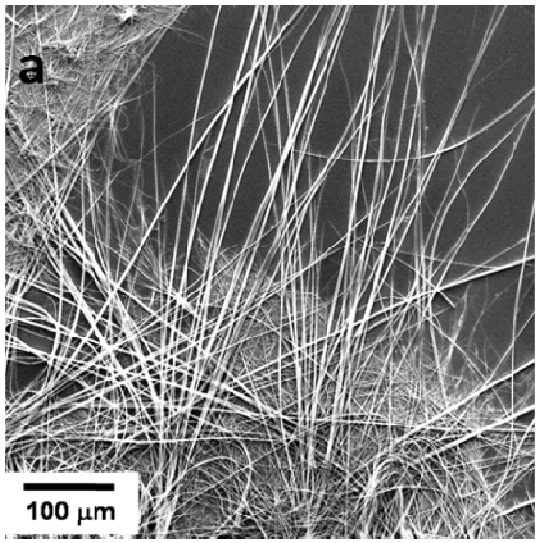
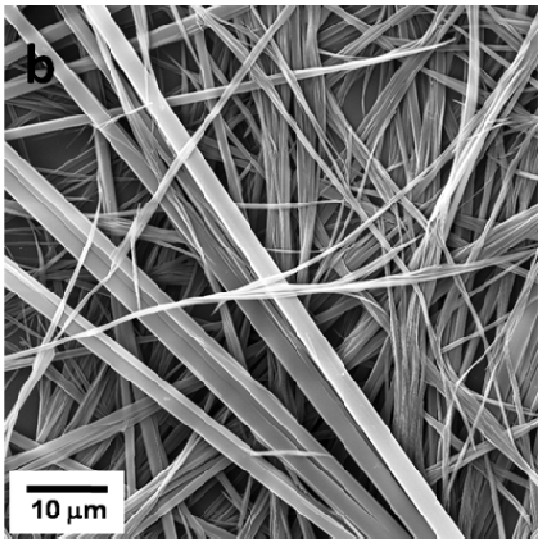
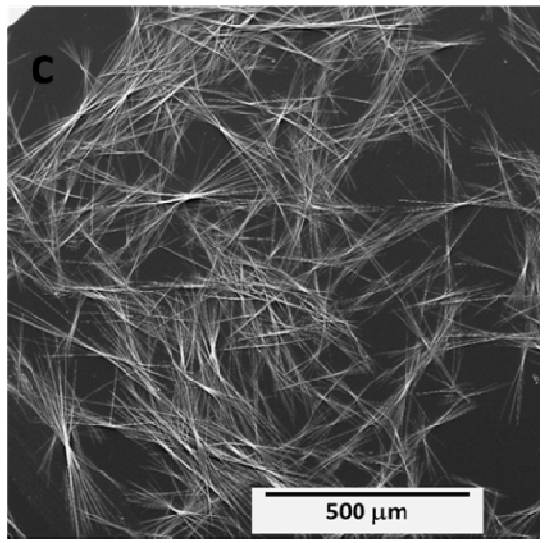
Room temperature processing conditions



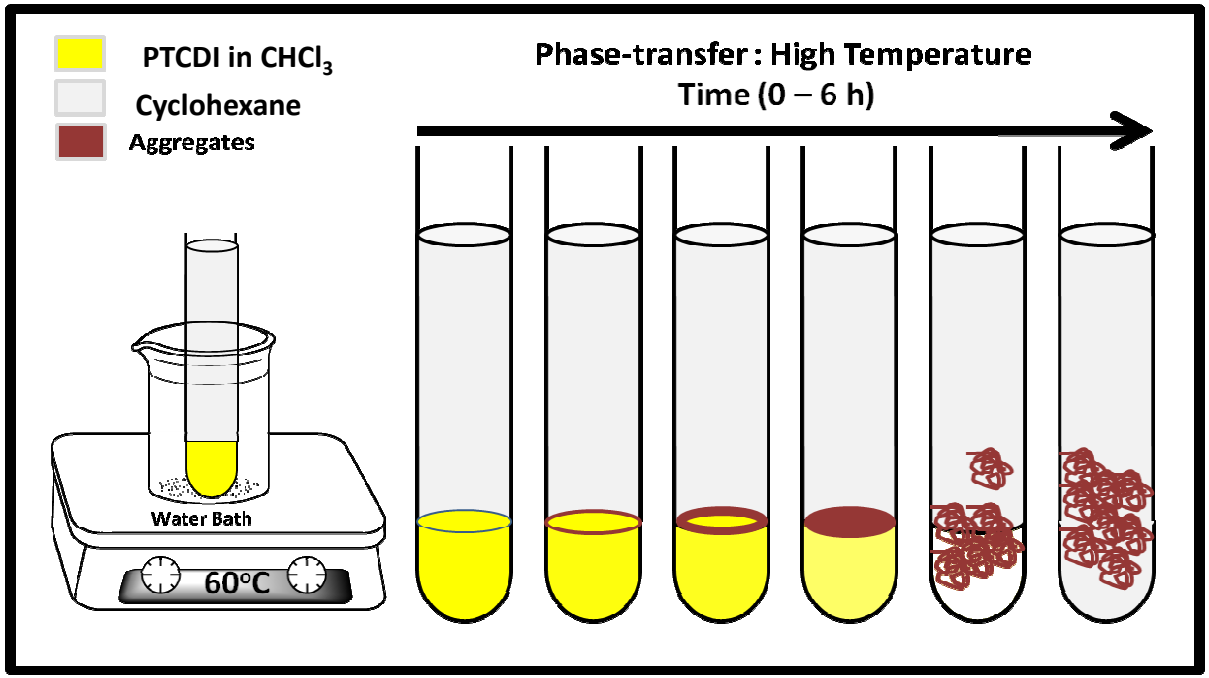


Morphology by self-assembly @ RT



	Methanol	Hexane	Cyclohexane
Dispersion				
2L-Phase Transfer				

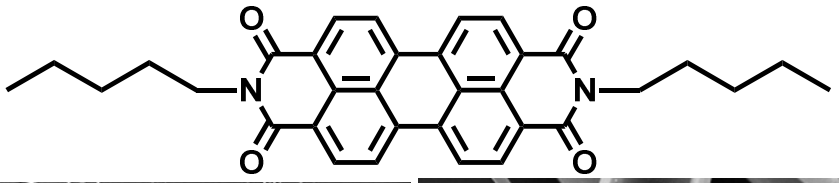
High temperature processing conditions

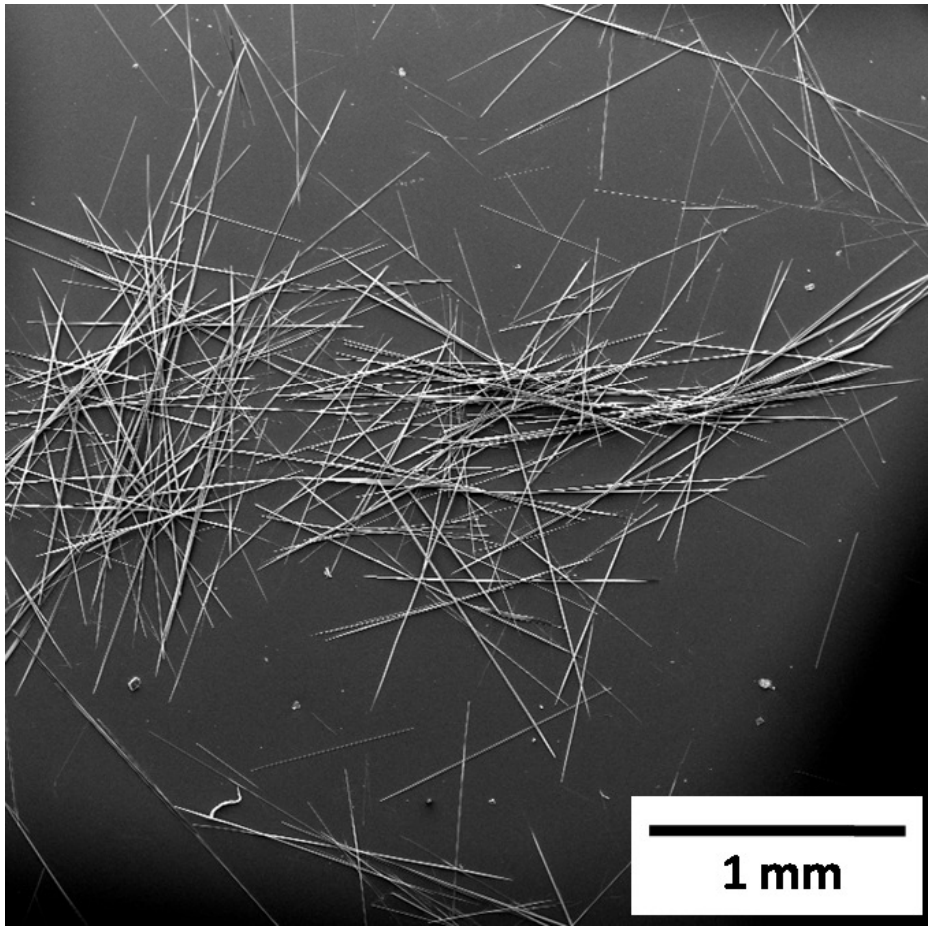


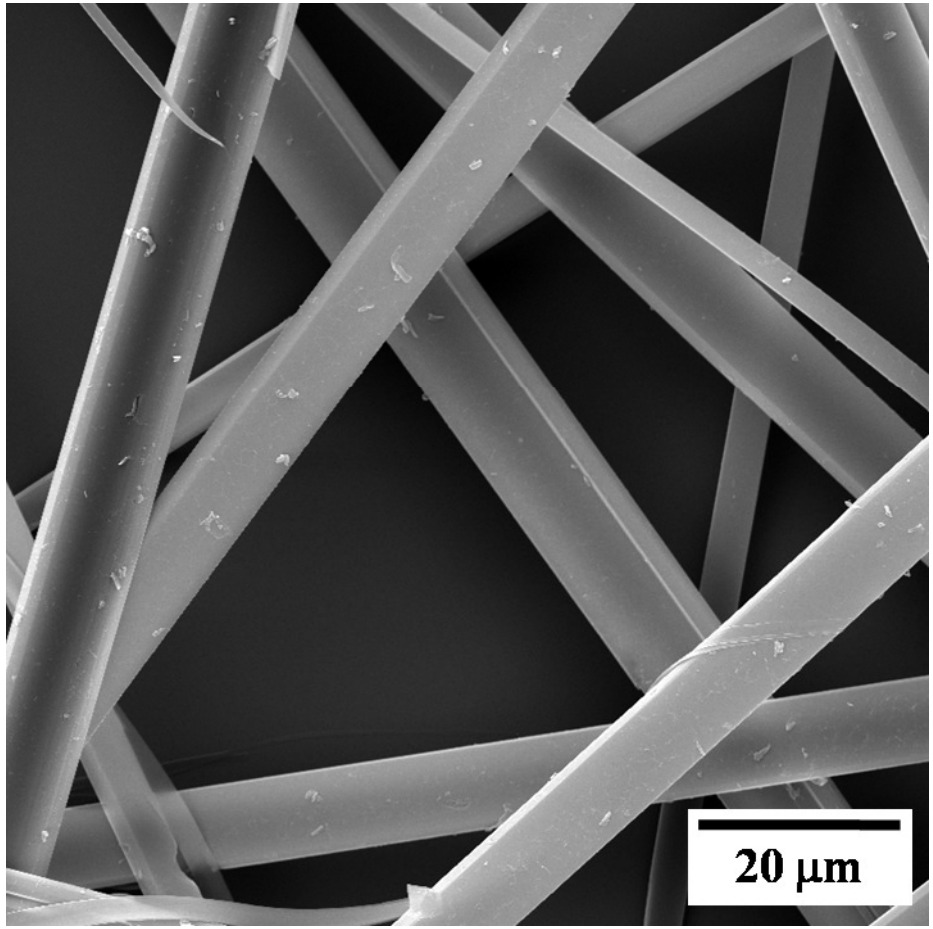
High Temperature

1. Very slow nucleation and growth
2. Less Nuclei ⇨ Growth of large 1D ordered structures
3. Incorporation of two sets of packing

Morphology by self-assembly of PTCDI @ HT (60°C)



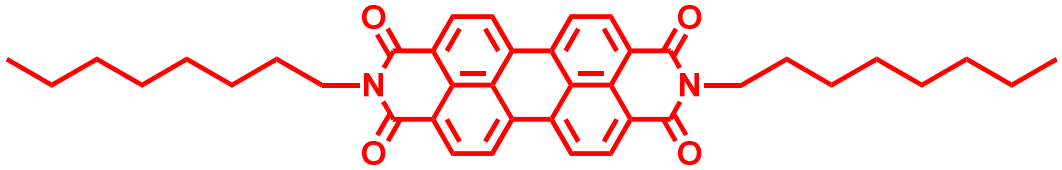


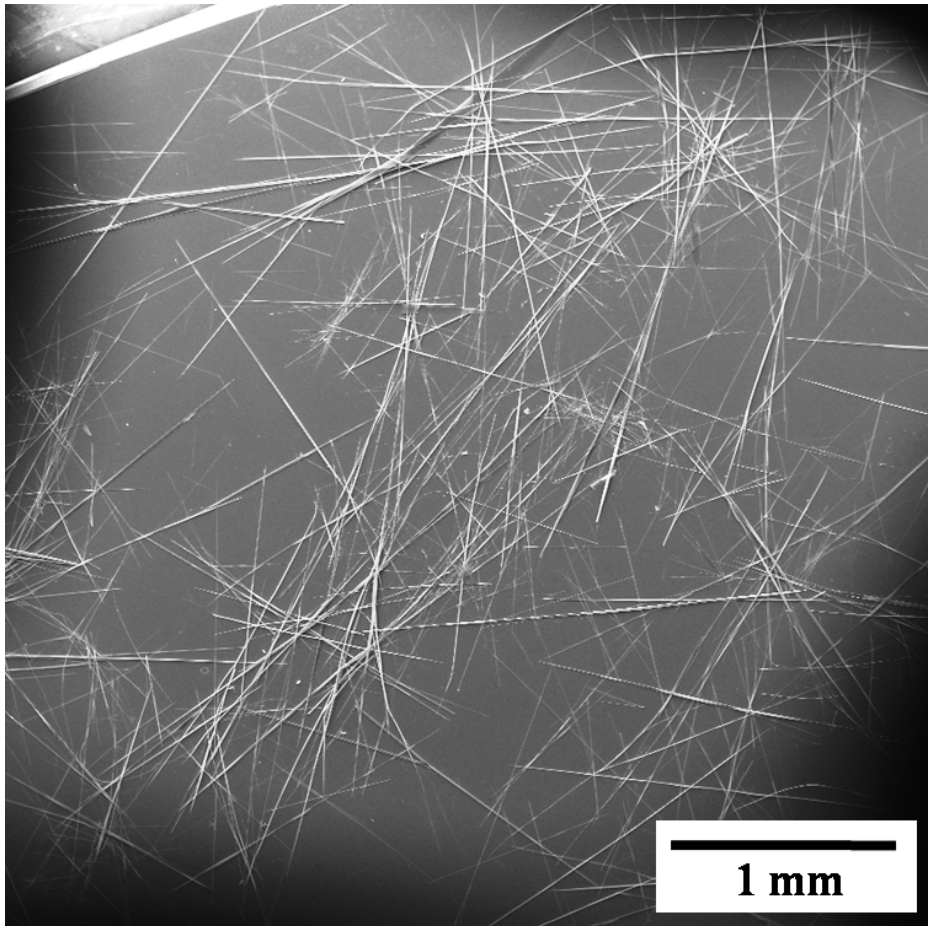


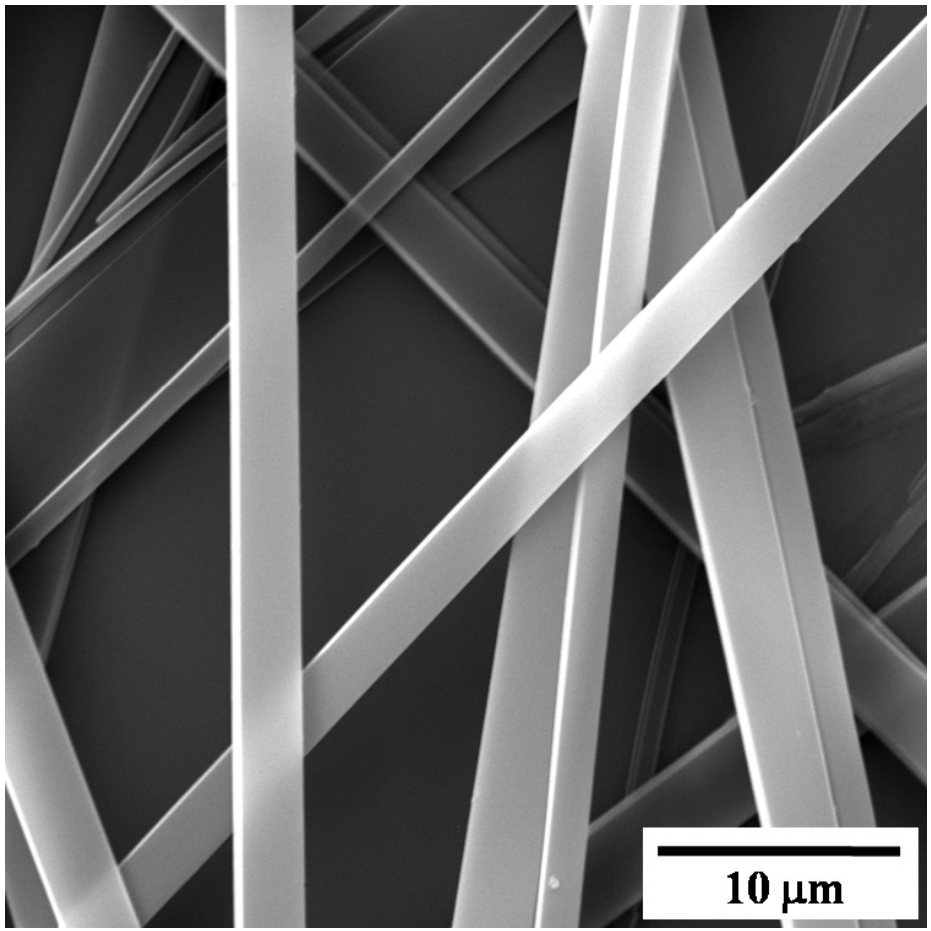
Average Width = 6.3 (± 29%) µm, Length= 1 (± 33%) mm

(x%) = relative standard deviation (calculated as standard deviation/ average *100)

Morphology by self-assembly of PTCDI @ HT (60°C)



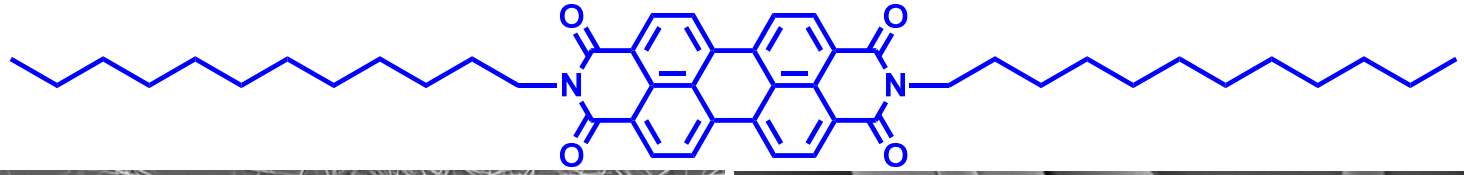


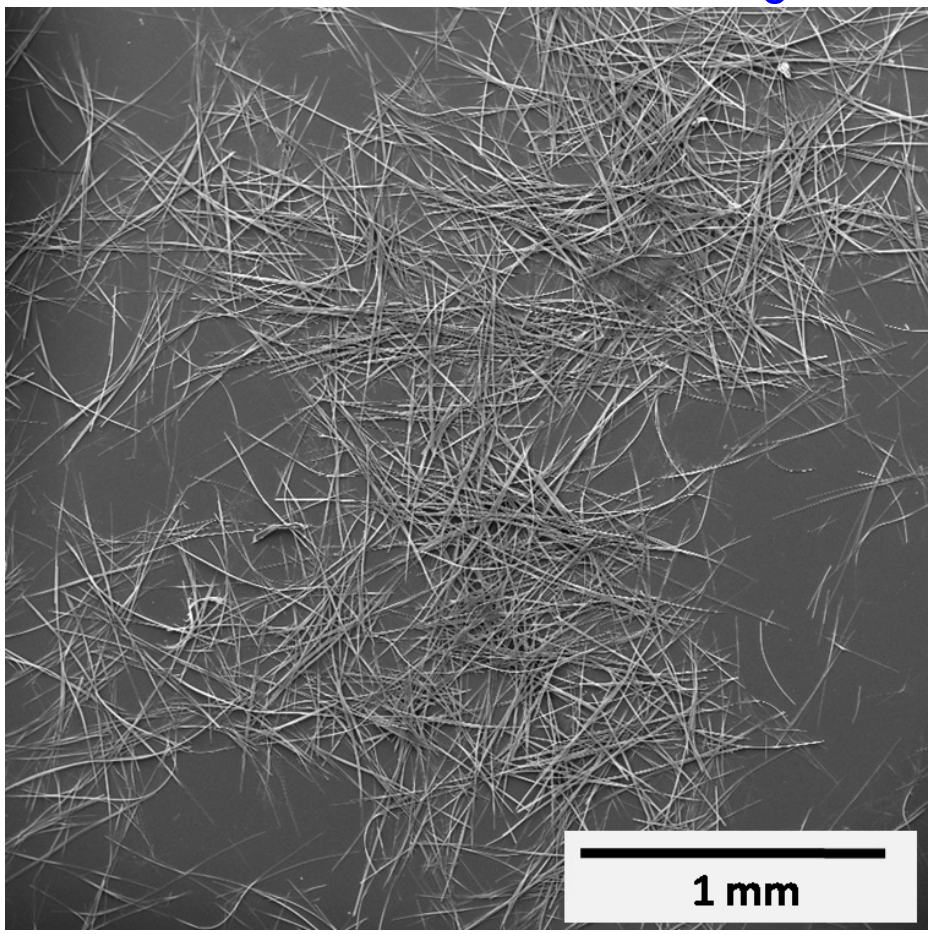


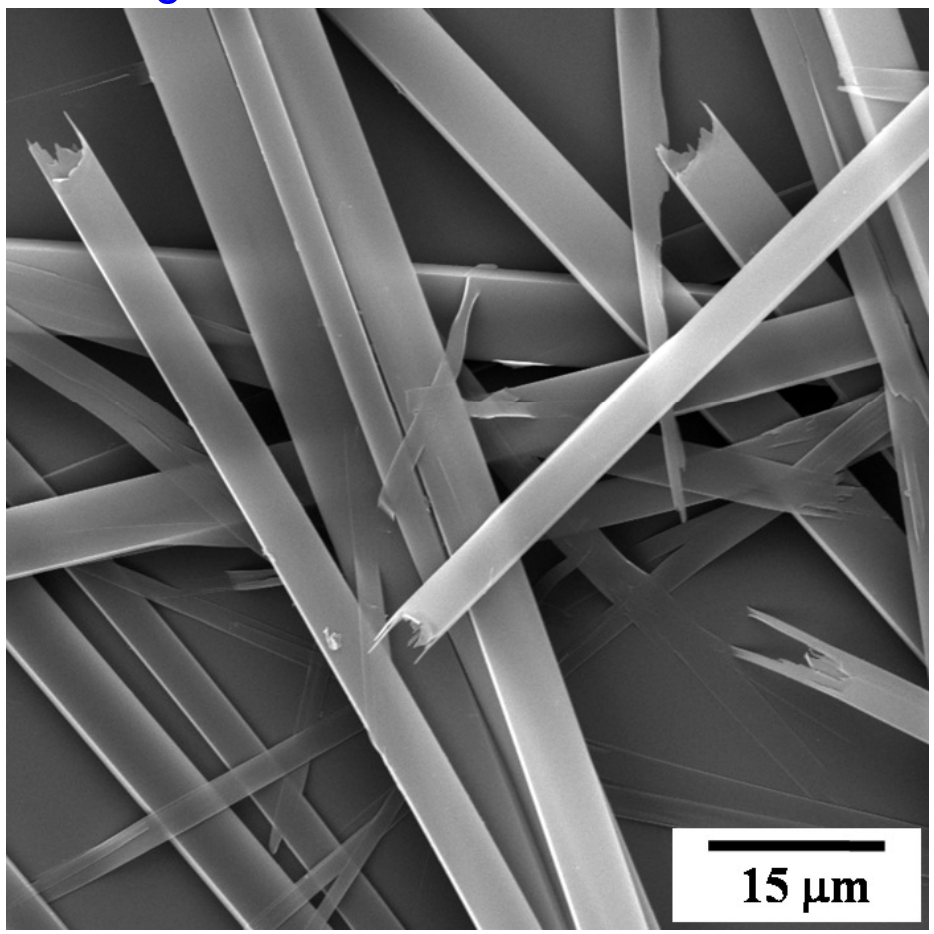
Average Width = 2.5 (± 40%) µm, Length= 1.5 (± 28%) mm

(x%) = relative standard deviation (calculated as standard deviation/ average *100)

Morphology by self-assembly of PTCDI @ HT (60°C)







Average Width = 4.0 (± 35%) µm, Length= 0.6 (± 31%) mm

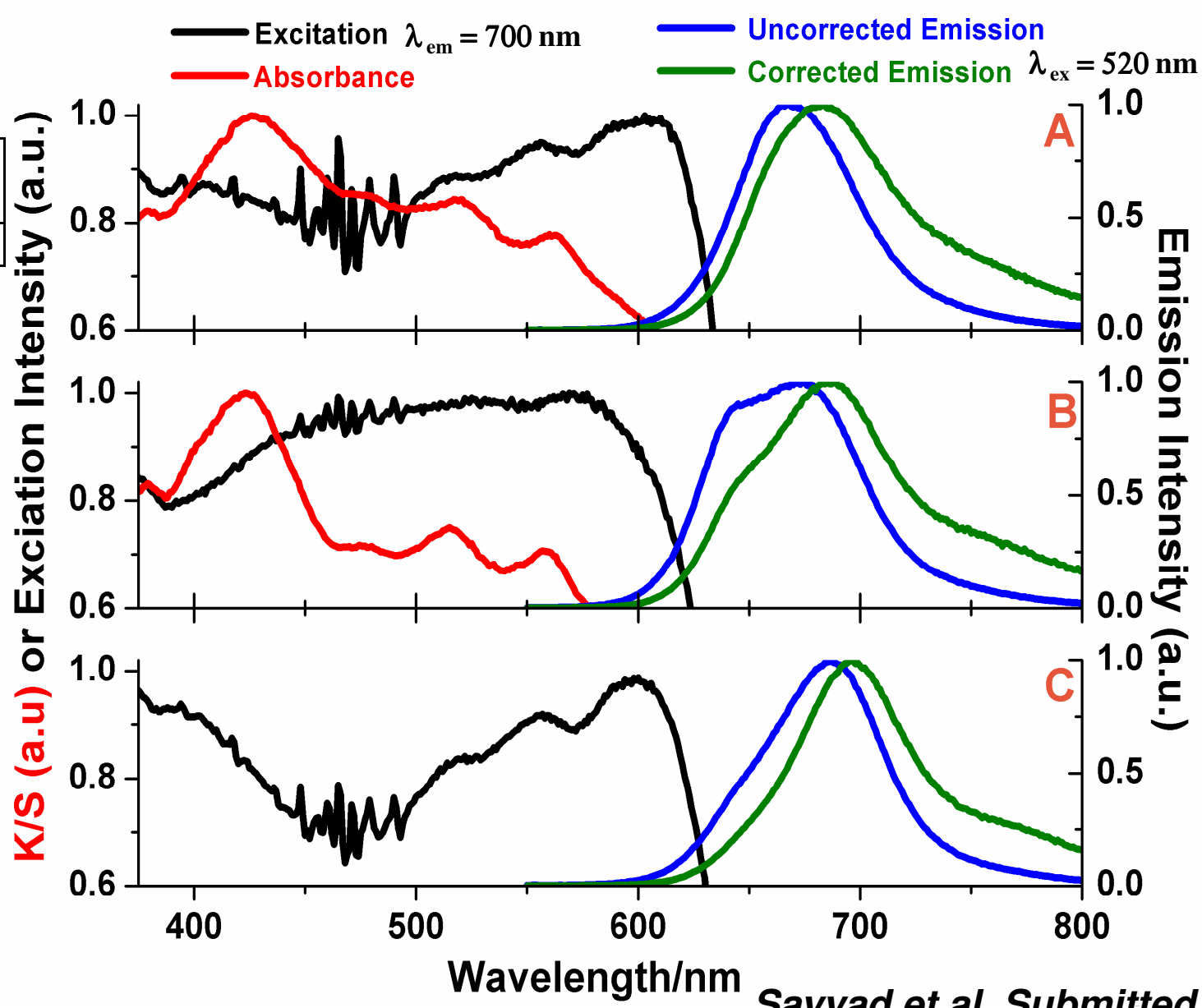
(x%) = relative standard deviation (calculated as standard deviation/ average *100)

Optical Properties

PTCDI	λ_{em} (nm)
C12-PTCDI	663

PTCDI	λ_{em} (nm)
C8-PTCDI WIRES	647, 675

PTCDI	λ_{em} (nm)
C5-PTCDI WIRES	684, 653



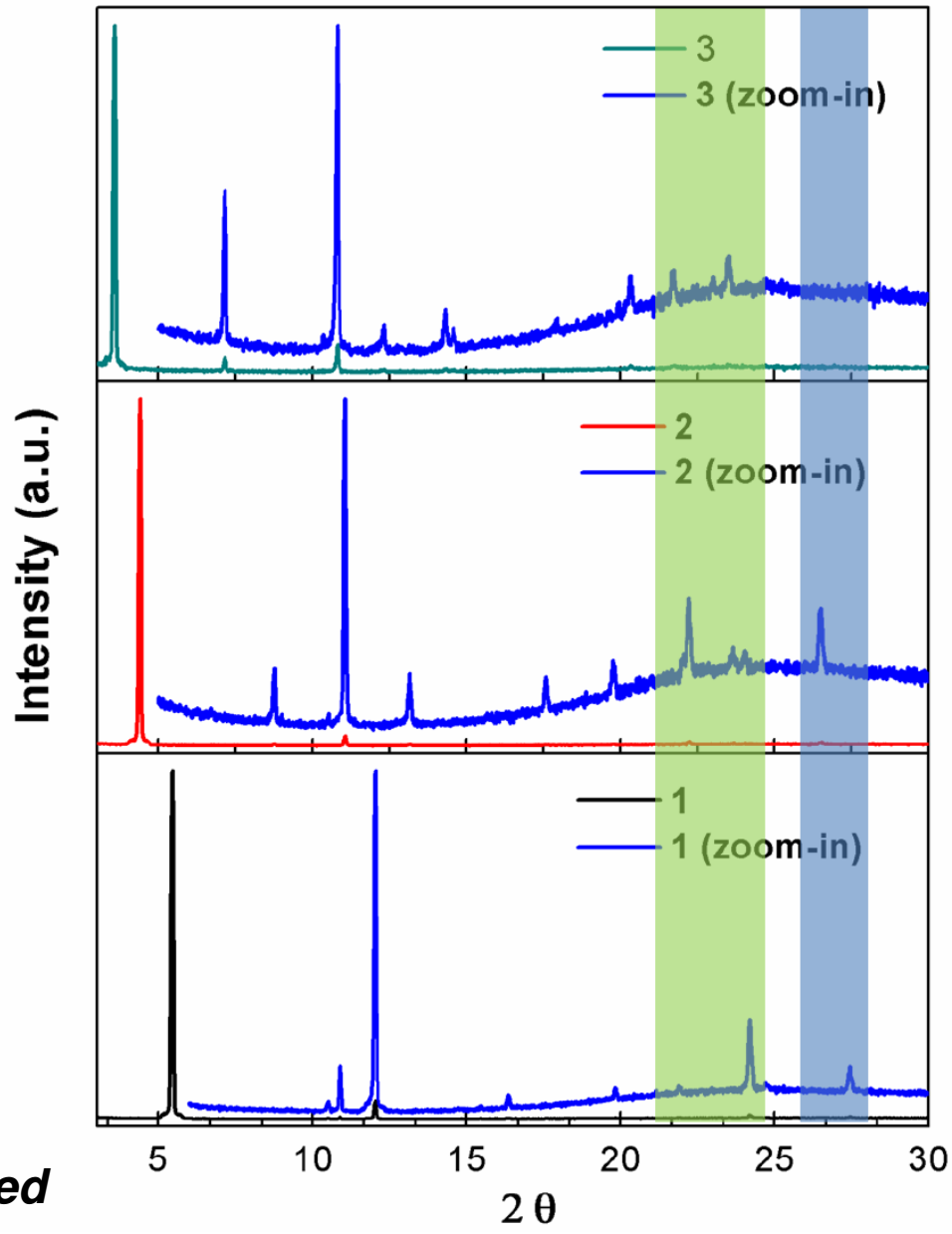
Sayyad et al. Submitted

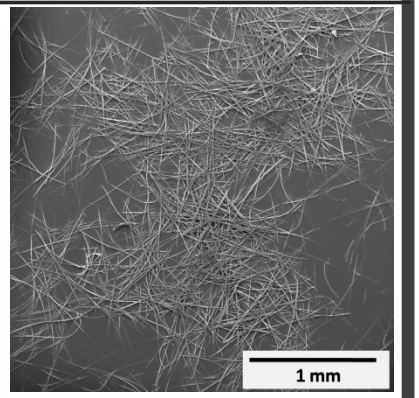
Structure property : X-ray diffraction

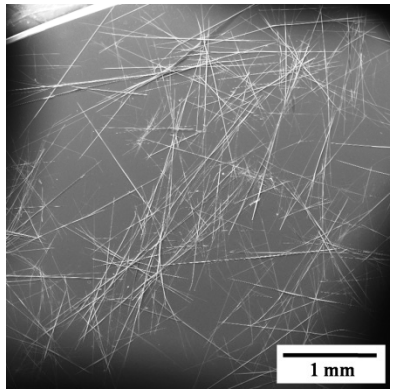
PTCDI	λ_{em} (nm)
C12-PTCDI	663

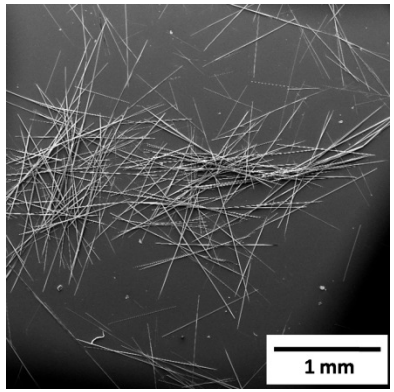
PTCDI	λ_{em} (nm)
C8-PTCDI	647, 675

PTCDI	λ_{em} (nm)
C5-PTCDI	684, 653









Sayyad et al. Submitted

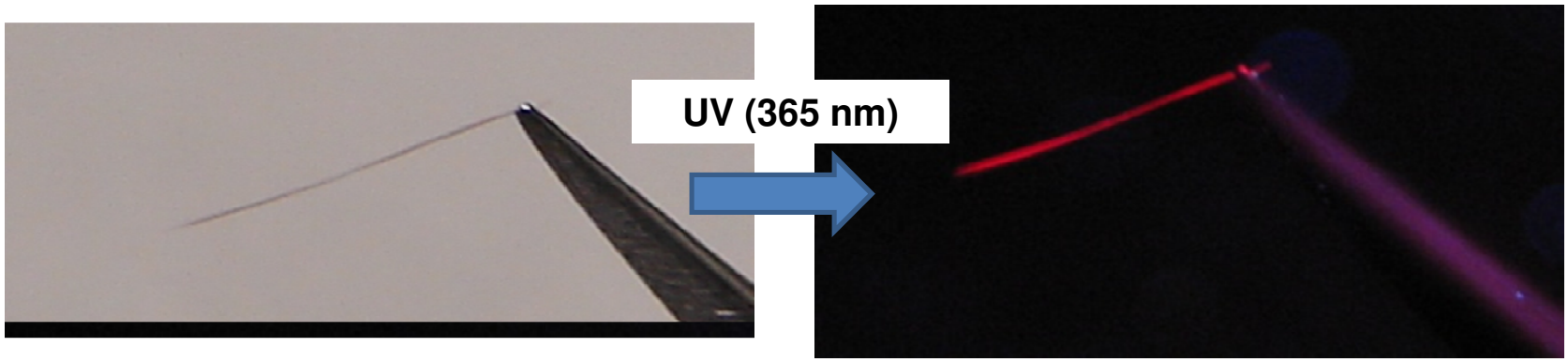
Self-assembly of PTCDI molecules by 2L-HT method

Extremely long WIRES of PTCDI – Solution processing

Intense excimeric emission

Two different sets of packing exists (close in energy levels)

Applications: Optoelectronics devices.



Advantages and disadvantages of hydrophobic side chains

Importance of Side Chains

Increase in solubility

Solid state miscibility

Structural and morphological changes

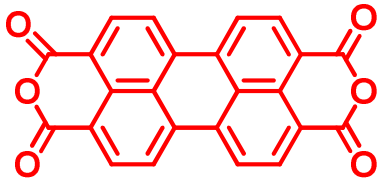
Systems in which alkyl substitutions improve charge mobility

An additional upper bound on device performance

Creation of localized, persistent, self-trapped charges with low mobilities.

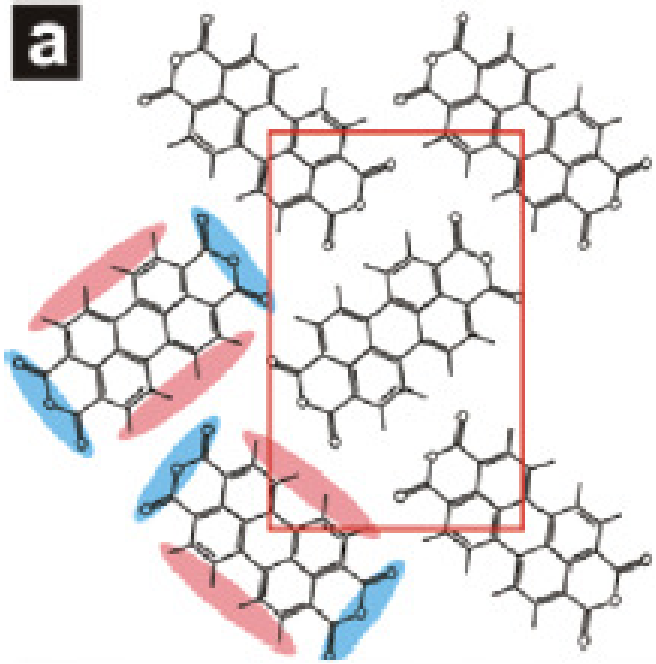
Charles et al. *JACS* ASAP, 2010

Self-assembly of PTCDA



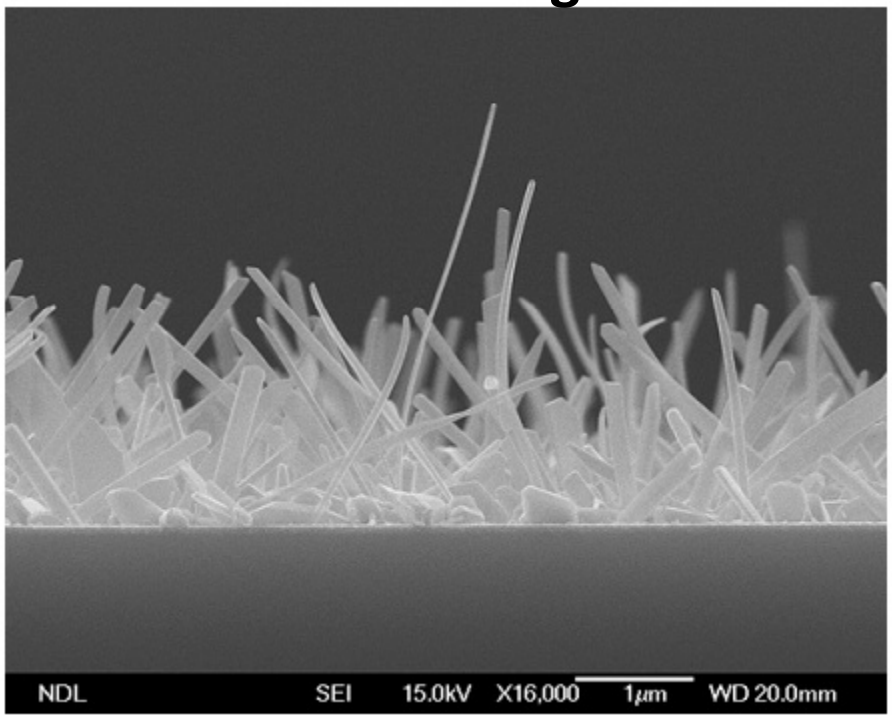
PTCDA (Extremely insoluble)

Herringbone Arrangement



Films of PTCDA
Ultra high vacuum
Vapor phase deposition methods

π-stacking



1D fibers of PTCDA
Vaccum sublimation on titanium substrate
Ti-CVD

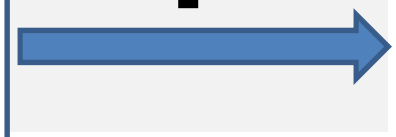
Can 1D nanostructures of PTCDA be realized by solution processing ?

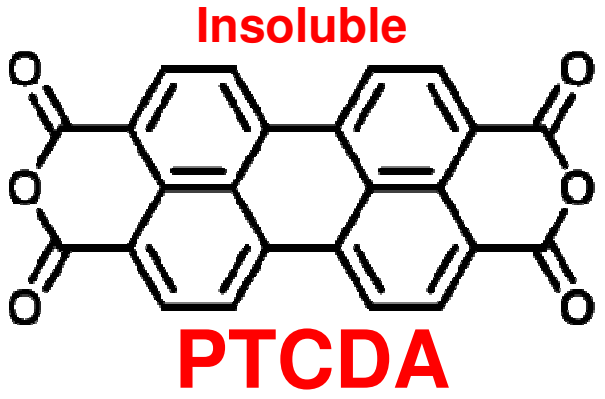
Forrest et al. Chemical Reviews, 1997, 97,6,1793-1896

Dai et al. Organic Electronics 8 (2007) 505–512

Choice of precursor and chemical reaction

Appropriate Soluble Precursor





PTCA is miscible in DMF (0.5 mg/ml)

Carbodiimide chemistry : Acid anhydrides

Rate of reaction : Higher in DMF

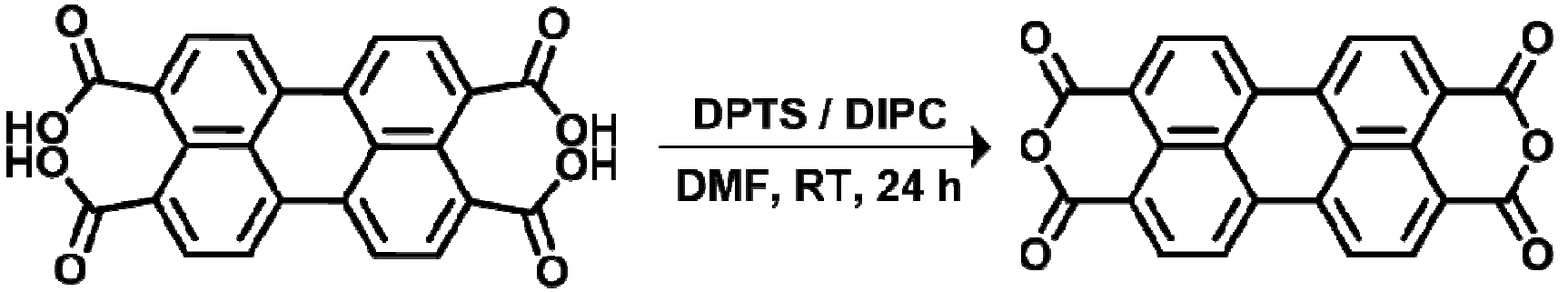
Dicarboxylic acid (separated by 3 -CH_2 groups) → **Cyclic anhydride (Intramolecular reaction)**

PTCA : Intramolecular cyclization : No polymerization is expected

28

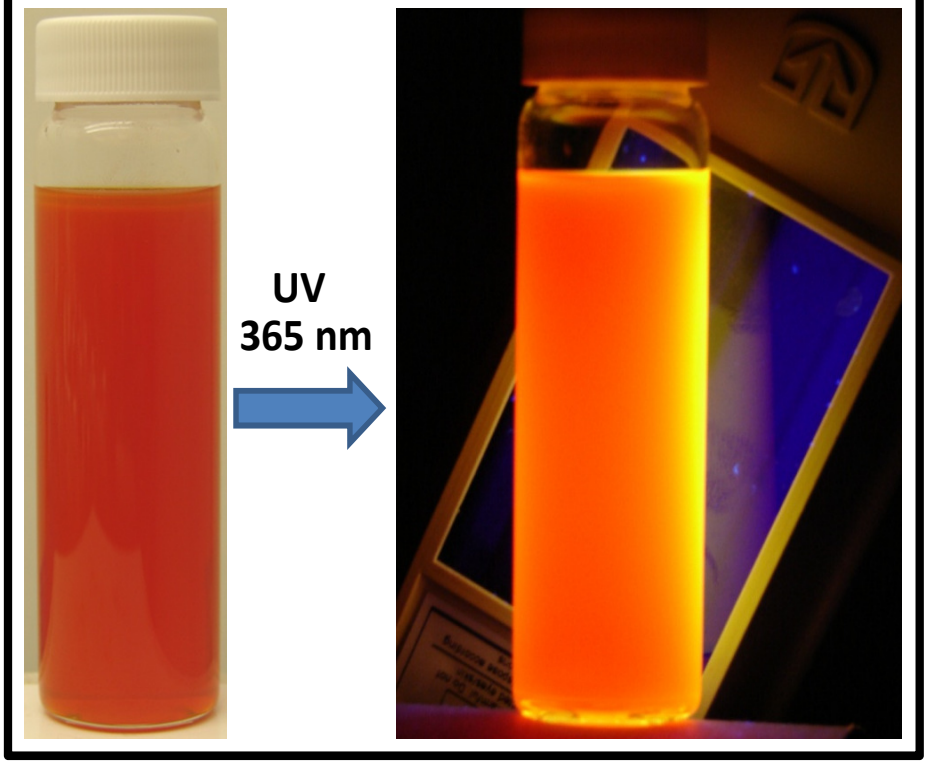
Chemical reaction mediated self-assembly

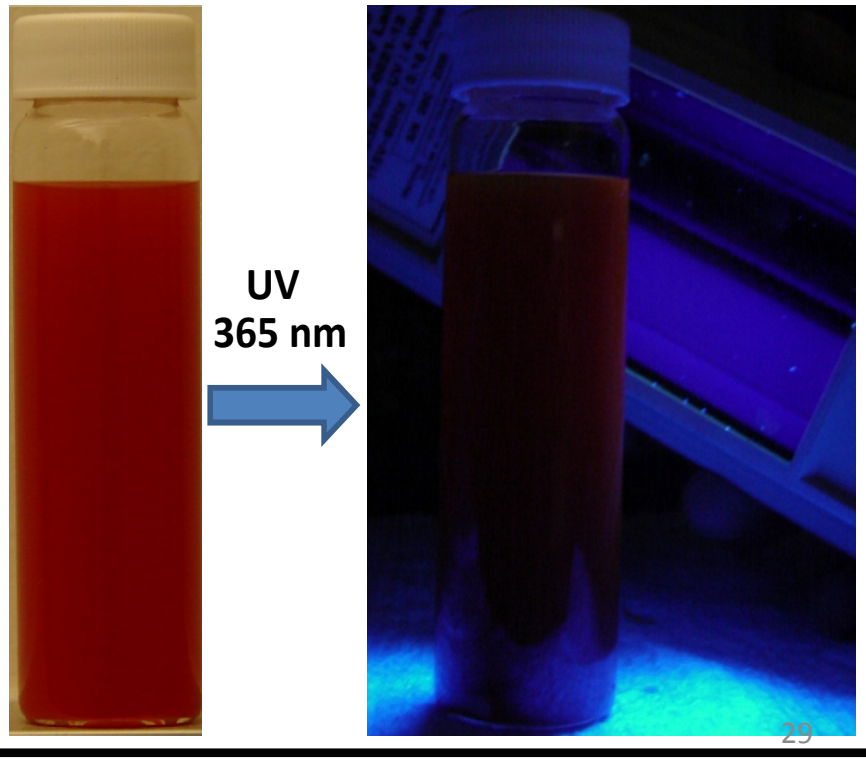
Carbodiimide Chemistry :



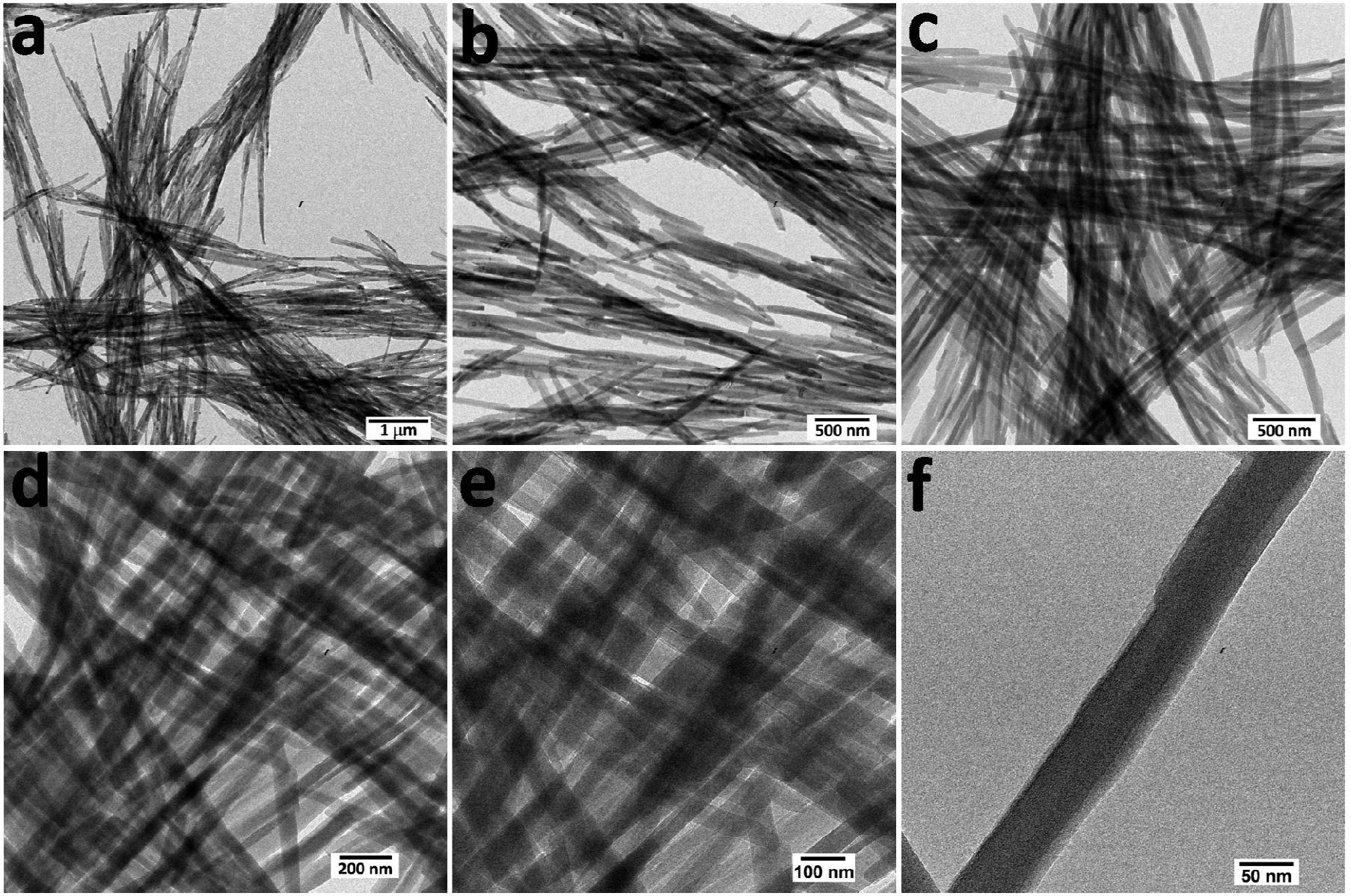
PTCA in DMF

PTCA after DPTS/DIPC Aft 24 h stirring in DMF



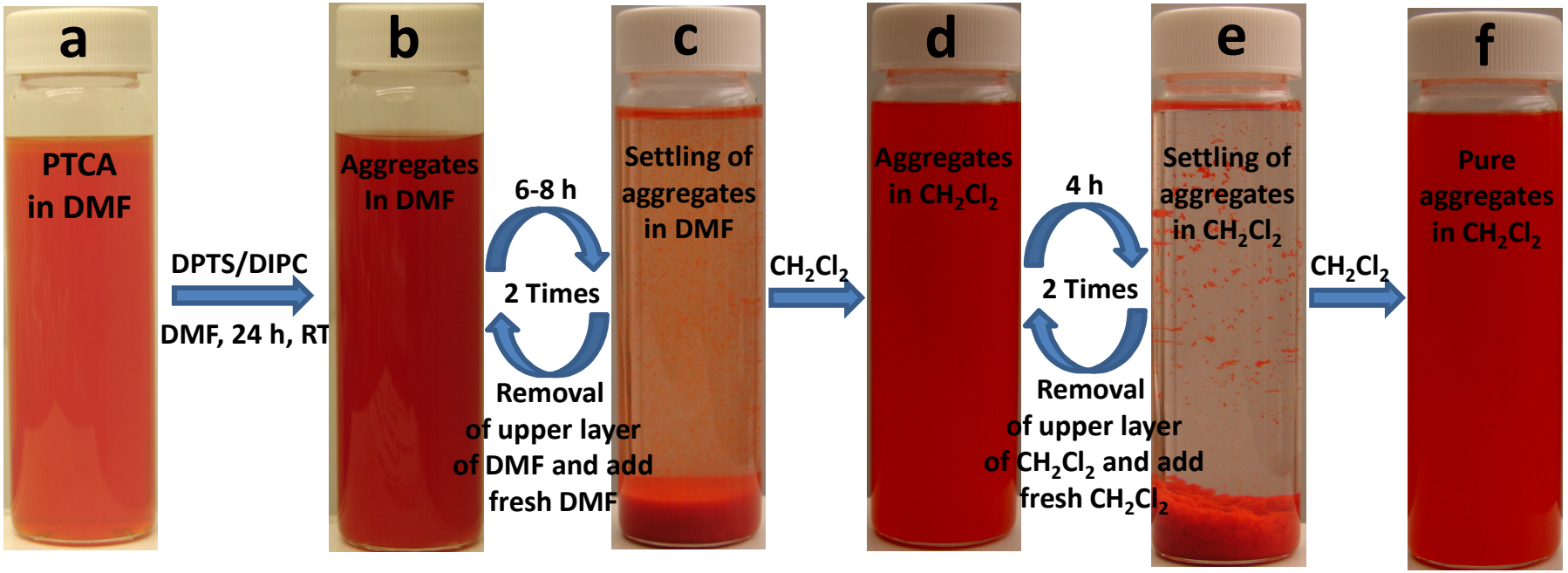


Morphology of aggregates after chemical reaction

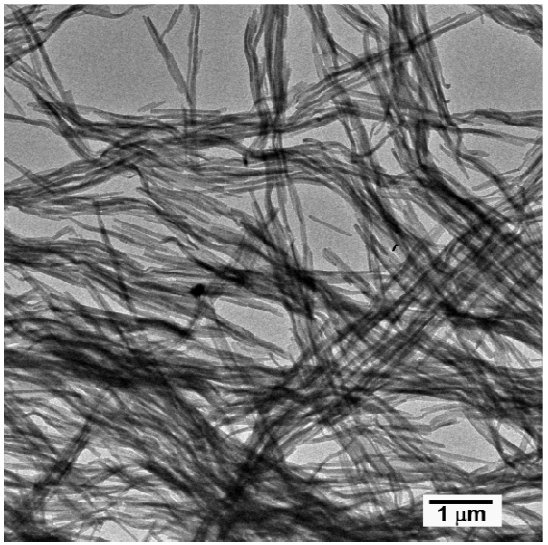


Sayyad et.al, Nanoscale, 2011,3, 3605-3608

Protocol for the chemical reaction mediated self-assembly

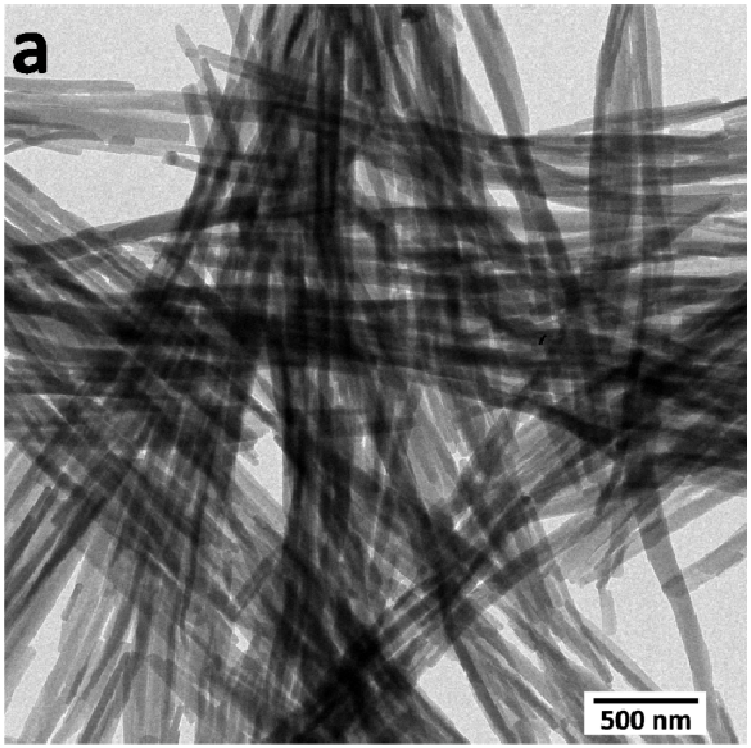


Morphology remains Same after extraction In CH_2Cl_2



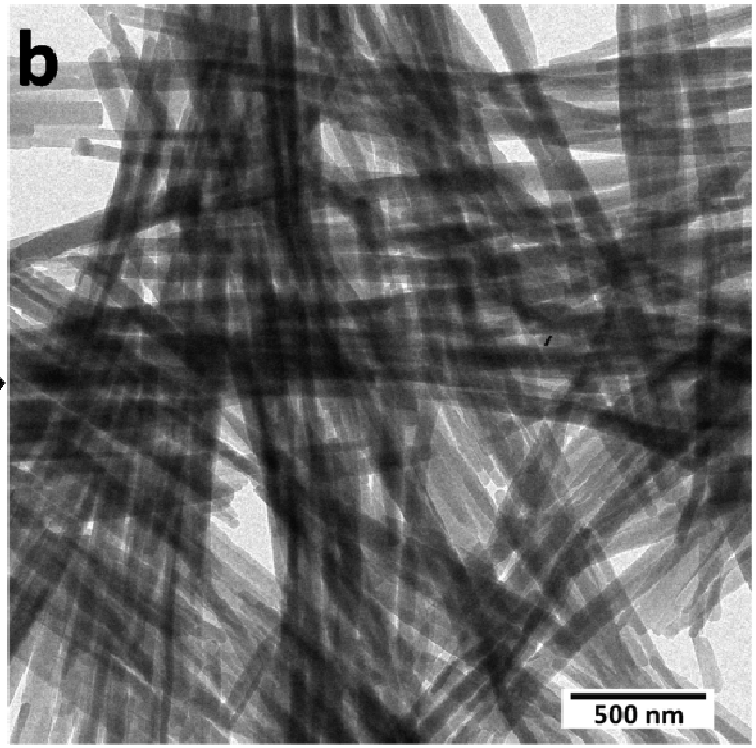
Sayyad et.al, Nanoscale, 2011,3, 3605-3608

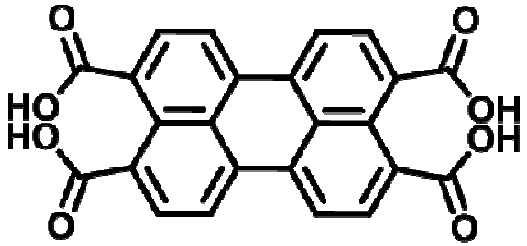
Stability of fibers towards alkali



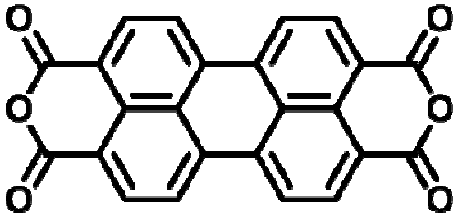
$Aq.\ K_2CO_3$

RT





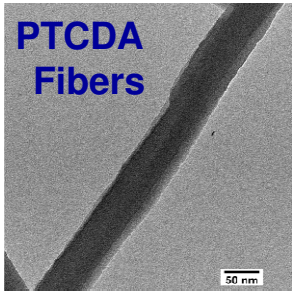
PTCA ***SOLUBLE*** in $Aq.K_2CO_3$ @ RT

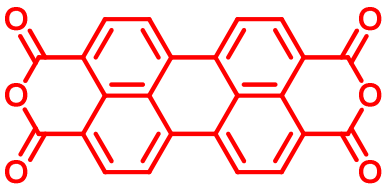


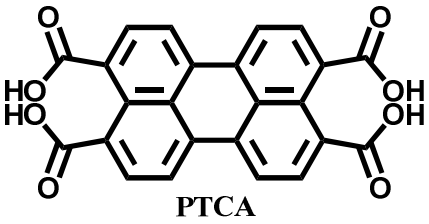
PTCDA ***INSOLUBLE*** in $Aq.K_2CO_3$ @ RT

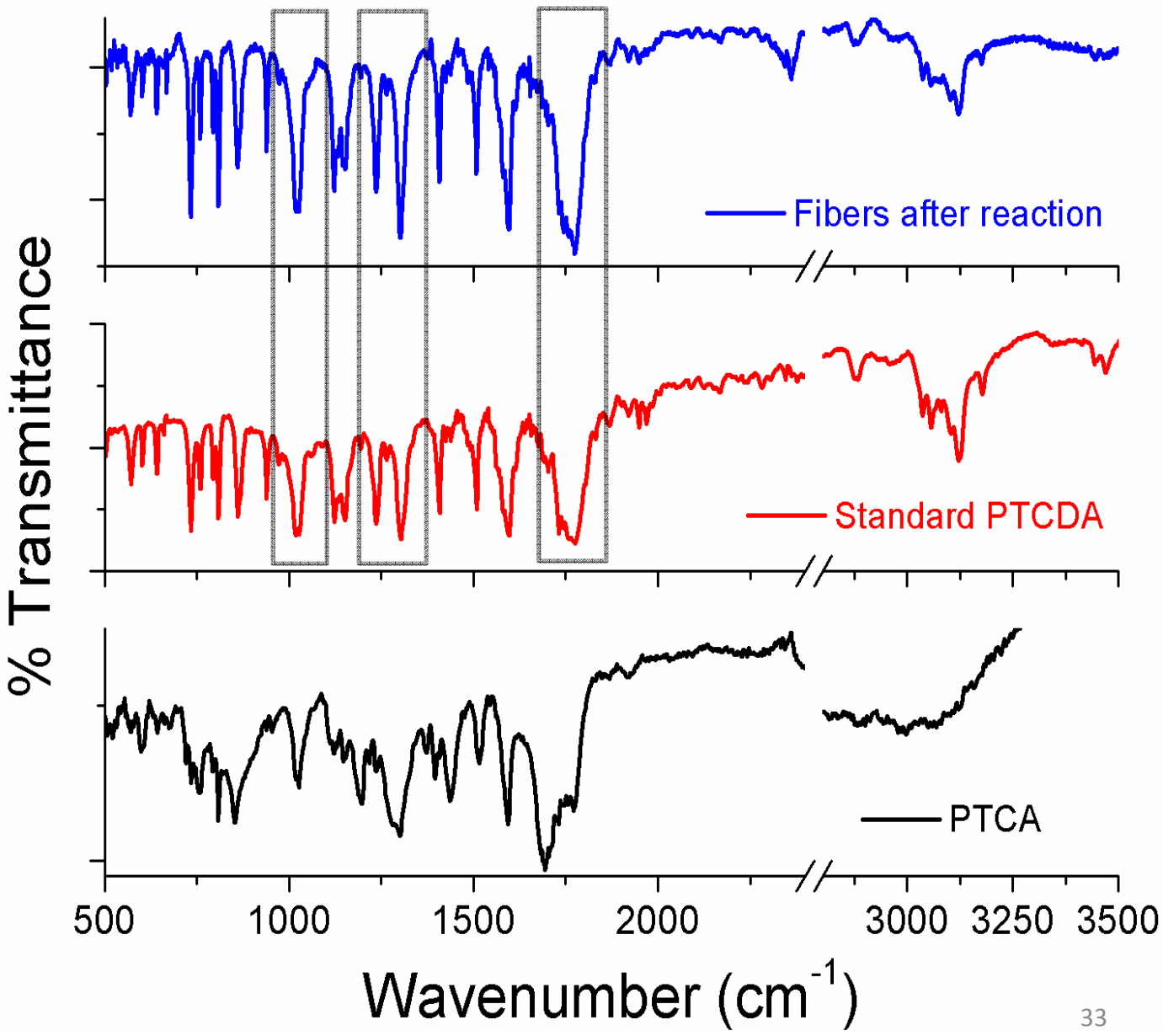
Sayyad et.al, Nanoscale, 2011,3, 3605-3608

Chemical species determination in 1D fibers (FTIR)





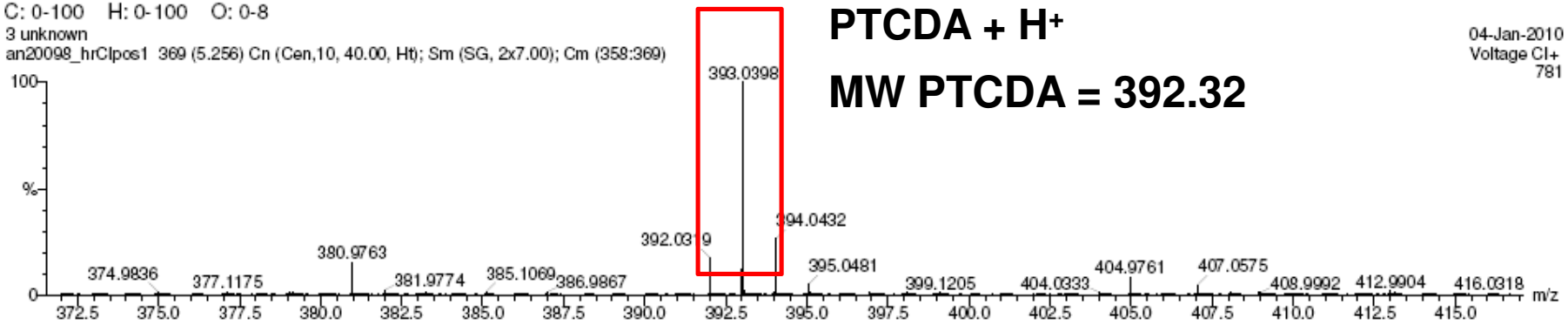




Chemical species determination in 1D fibers

Monoisotopic Mass, Odd and Even Electron Ions
43 formula(e) evaluated with 1 results within limits (all results (up to 1000) for each mass)
Elements Used:
C: 0-100 H: 0-100 O: 0-8
3 unknown
an20098_hrClpos1 369 (5.256) Cn (Cen,10, 40.00, Ht); Sm (SG, 2x7.00); Cm (358:369)

04-Jan-2010
Voltage CI+
781



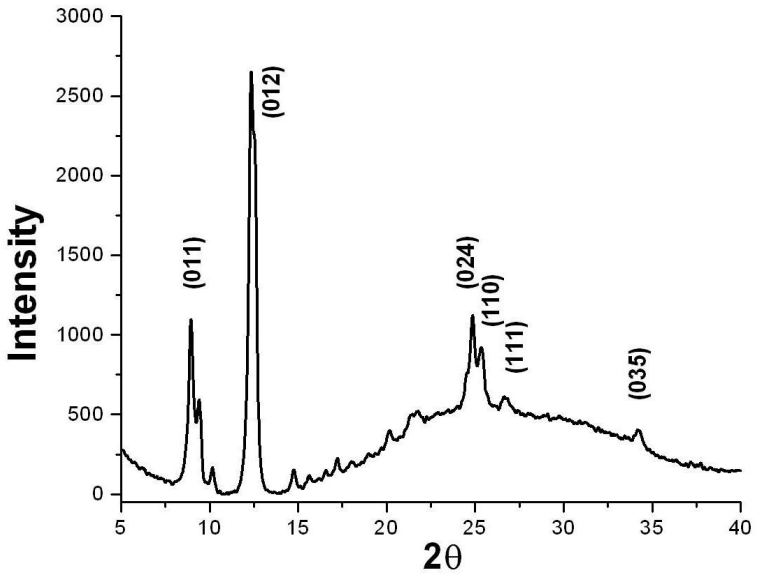
PTCDA + H⁺

MW PTCDA = 392.32

Minimum:				-1.0		
Maximum:		20.0	10.0	100.0		
Mass	Calc. Mass	mDa	PPM	DBE	i-FIT	Formula
393.0398	393.0399	-0.1	-0.3	20.5	0.1	C24 H9 O6

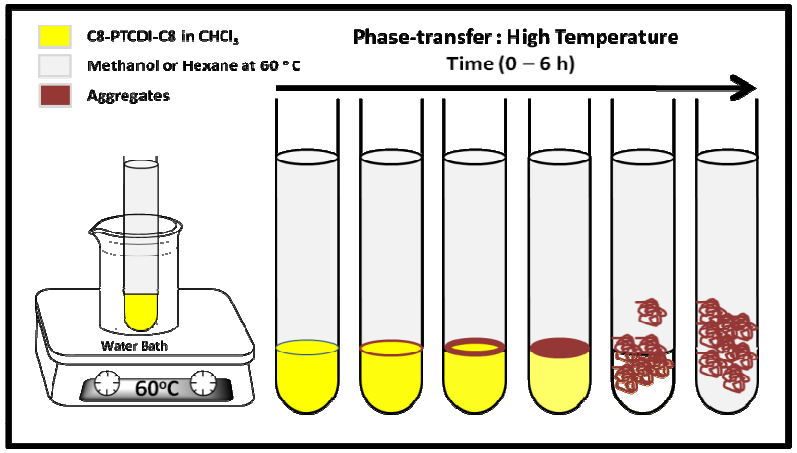
Courtesy: Dr. Kavin Keller, UT Austin

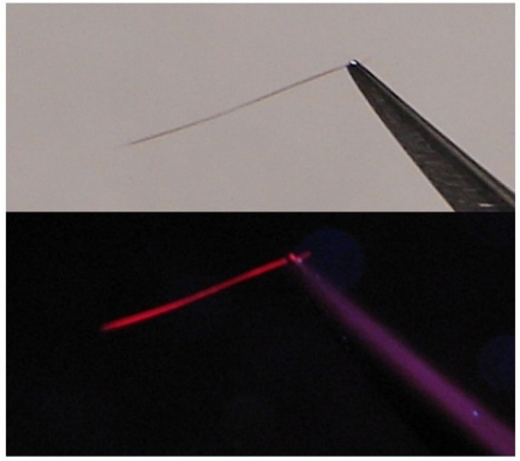
XRD

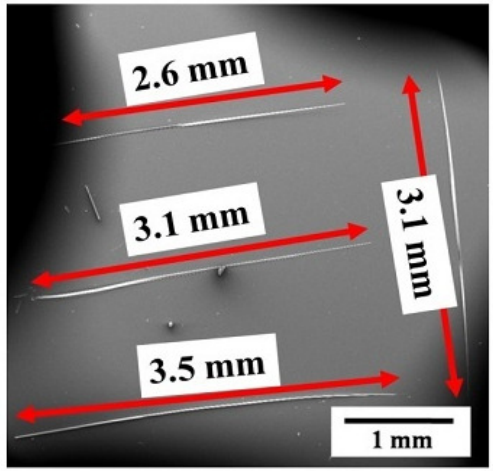


***Sayyad et.al, Nanoscale*, 2011,3, 3605-3608**

Conclusions

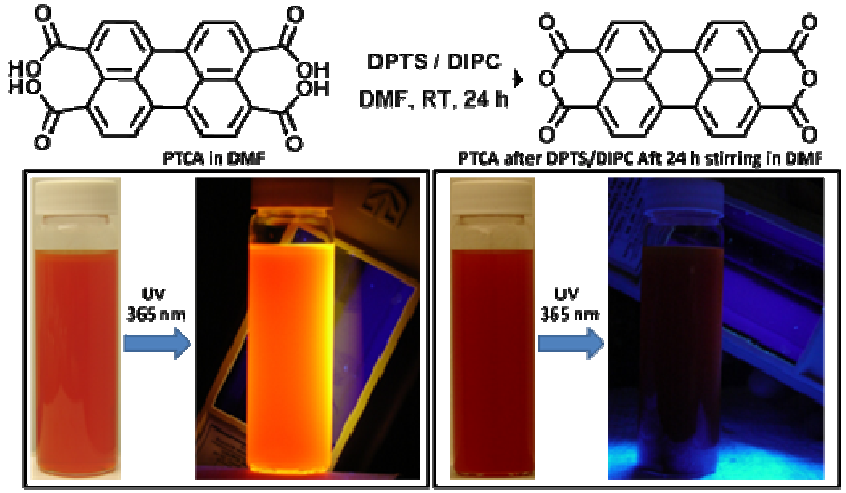


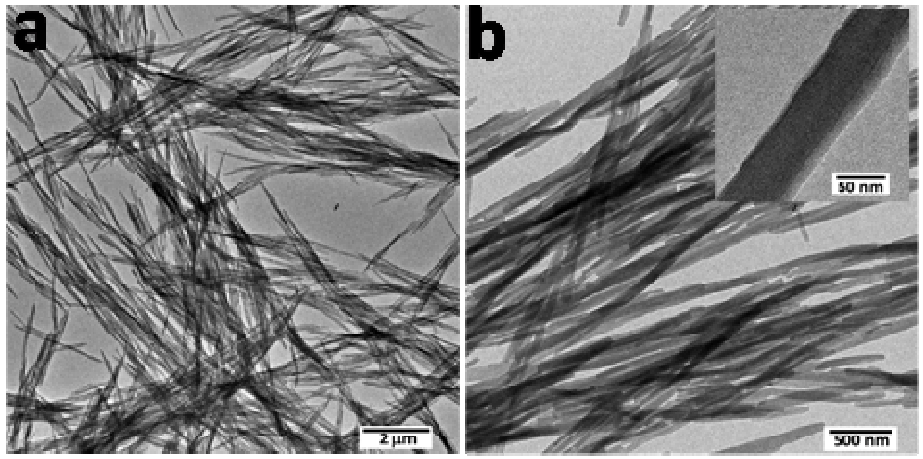




Extremely long fluorescent WIRES of PTCDI by 2L-HT method

Chemical reaction mediated self-assembly of highly insoluble PTCDA





1D fibers without any side chains

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Dr. Angel Marti
Dr. Kavin Keller, UT Austin
Shared Equipment Authority

Staff Members
Chemistry Department
MEMS Department

Funding
National Science Foundation

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