Synthesis and Characterization of “Hairy Urchin”-like Polyaniline by Using β-cyclodextrin as a template

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Synthesis and Characterization of "Hairy Urchin"-like Polyaniline by Using β-Cyclodextrin as a Template

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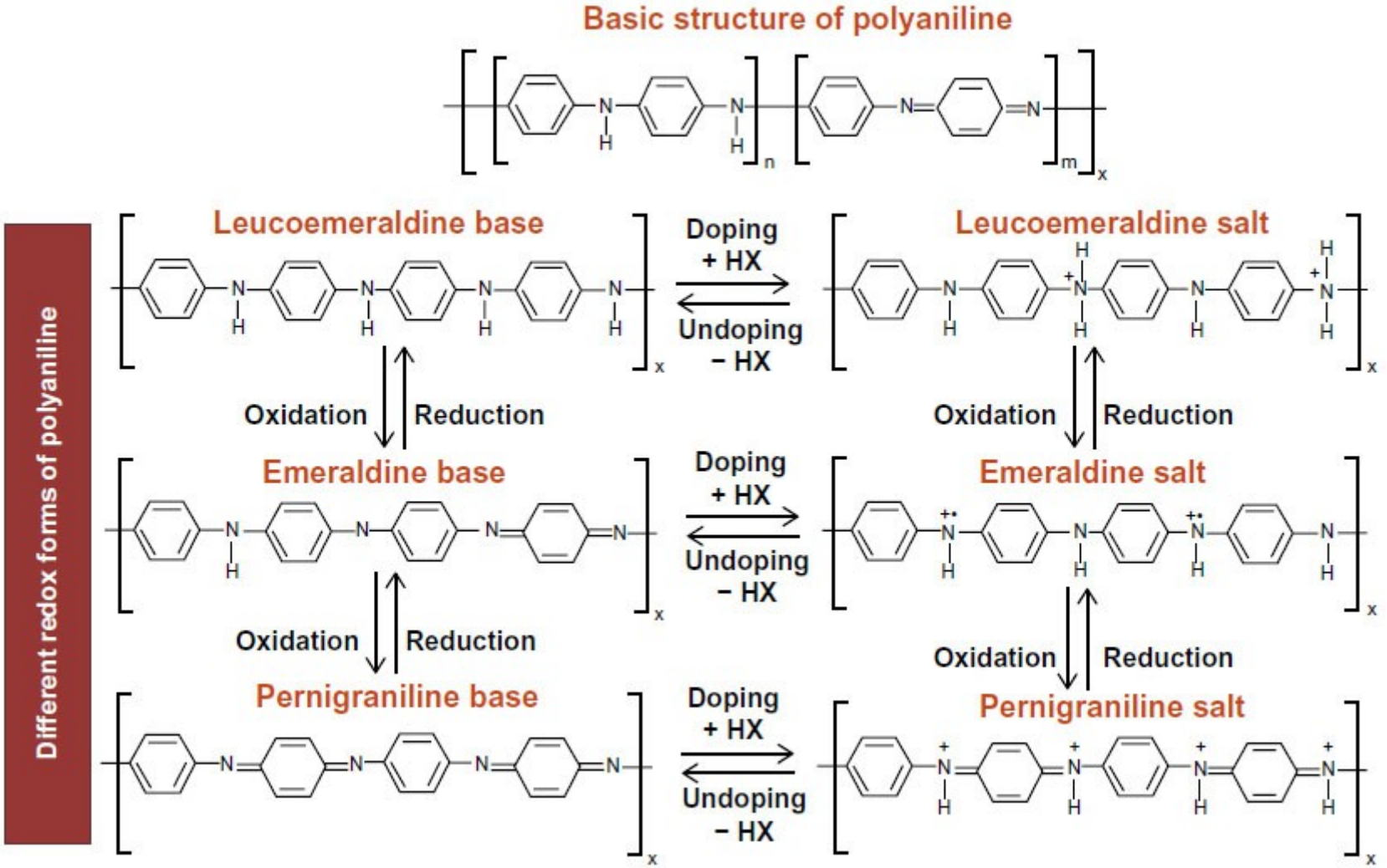
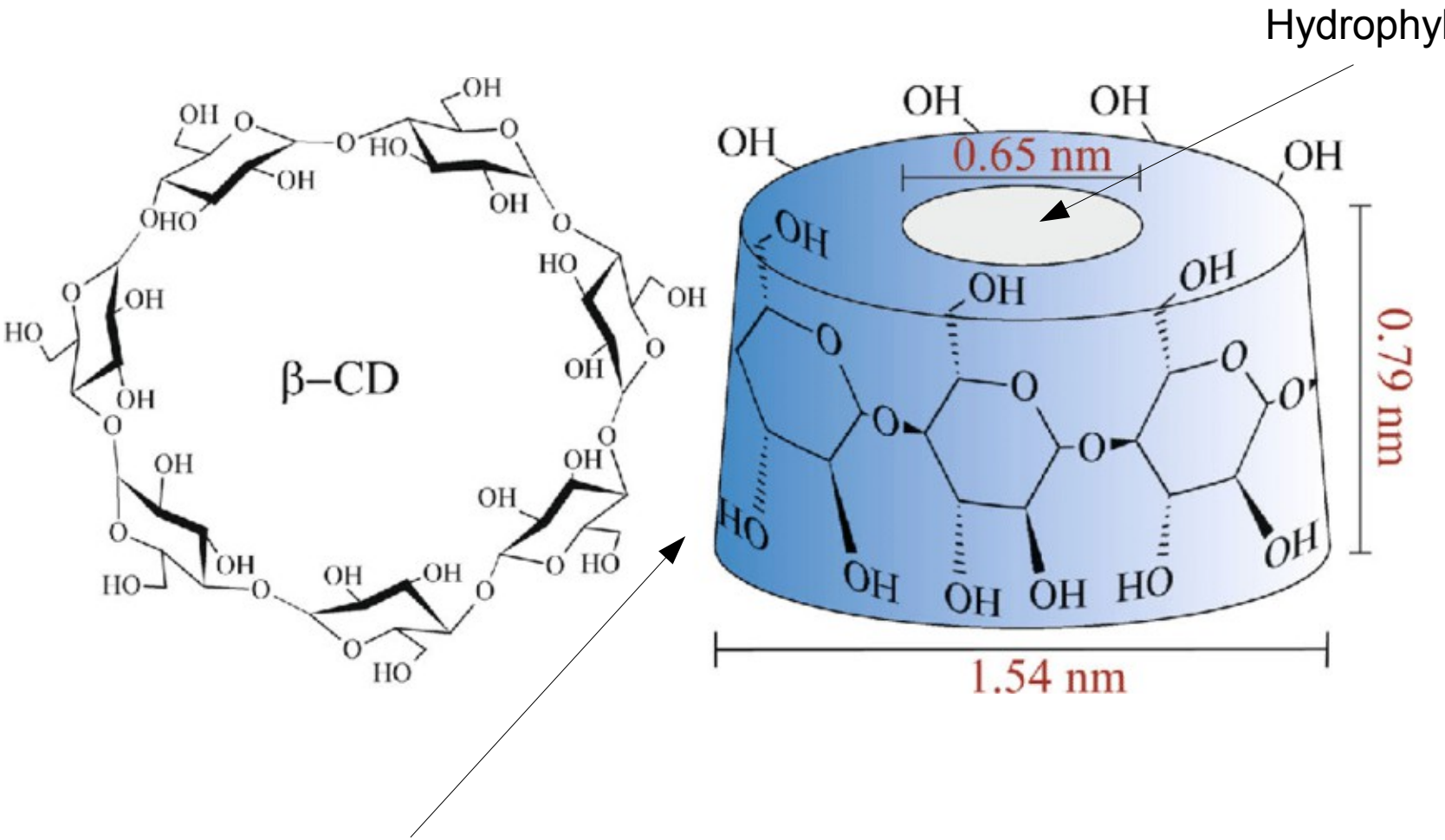
Introduction - Polyaniline

- It is a semiconductor polymer.



Introduction – β-cylcodextrin

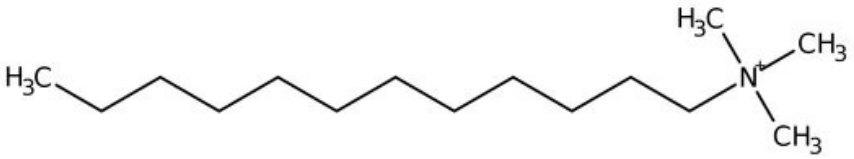


Objectives

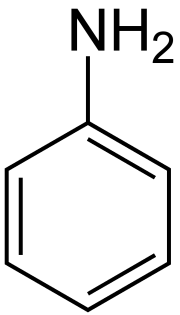
- Synthese and structural analysis of host-guest compounds of various amounts of β-cyclodextrins (β- CD) with aniline, and their polymerization in water using microemulsion polymerization. Synthesis nanosctruture investigated the influence of ferric chloride and [βCD] in the shape and size. Analyze the electronic transport behavior of the different structures.

Materials

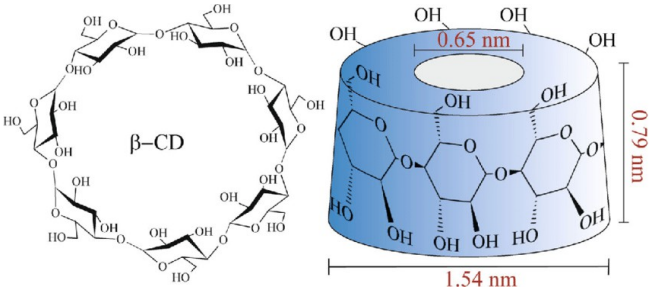
- Cationic surfactant dodecyltrimethylammonium chloride (DoTAC).



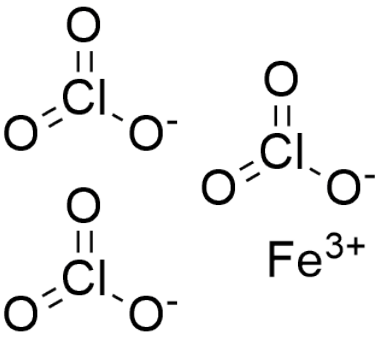
- Aniline



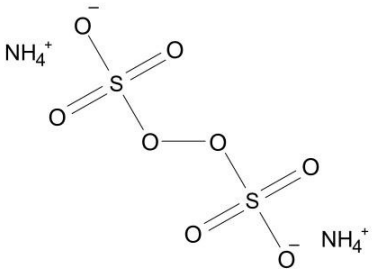
- β-cyclodextrin (β-CD)



- Ferric chloride ($FeCl_3$)



- Ammonium persulfate (APS)



Synthesis aniline-βCD inclusion compound

- Aniline (7.2 mM).
- β-cyclodextrin (7.2, 9, 10.8 and 12.6 mM).

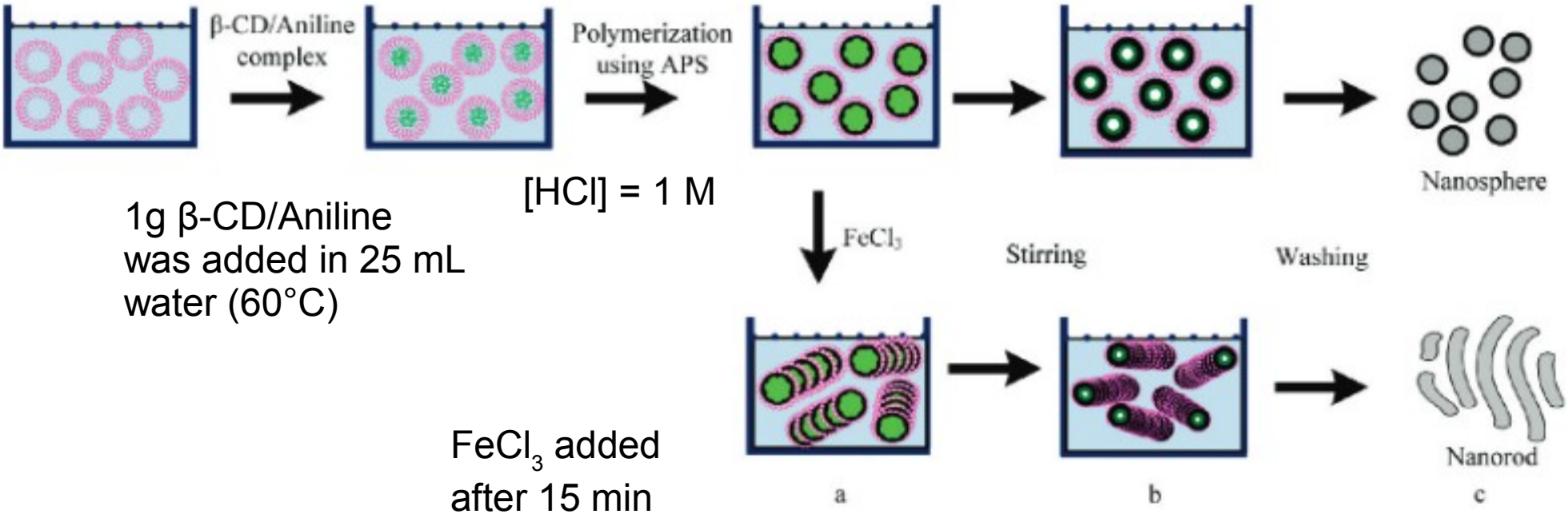
100 mL water

- This solution was stirred for 4 h at room temperature.
- After placed in refrigerator for 24 h at 0 °C.
- The crystals product were filtered and washed with 20 mL of cold water.
- The water-soluble inclusion complex (IC) was dried at room temperature.

Synthesis PANI nanomaterials

Solution with
7.2 mM DoTAC

[APS] = 7.2 mM



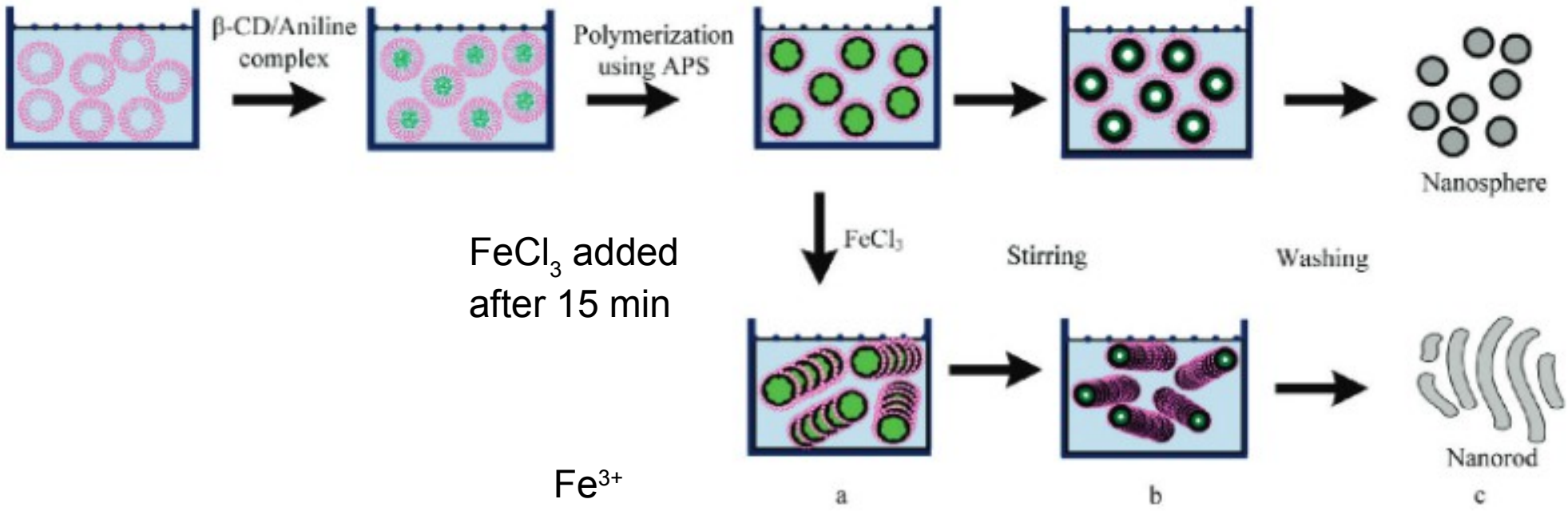
1g β-CD/Aniline
was added in 25 mL
water (60°C)

$FeCl_3$ added
after 15 min

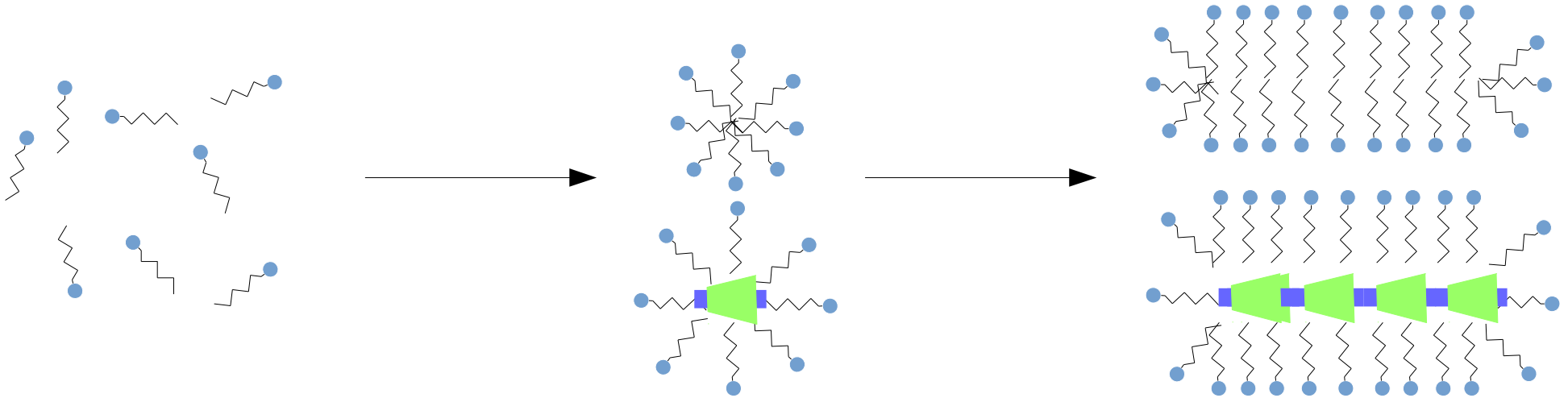
The polymerization
reaction was carried out
for 6 h

The PAni nanomaterials were precipitated in methanol (60 mL) and acetone (60 mL)

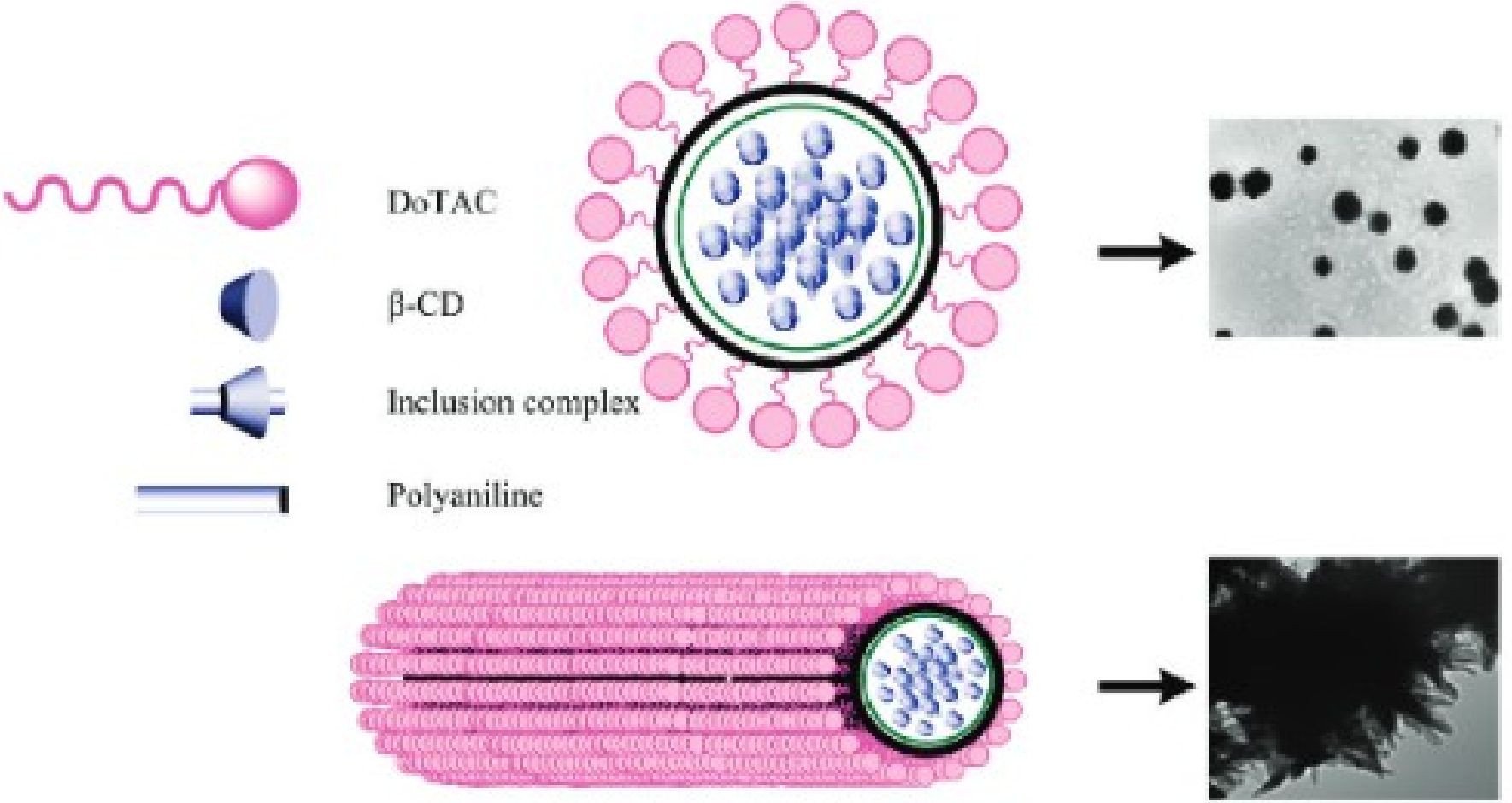
Synthesis PANI nanomaterials



CMC 0.016 mM and the concentration for sphere-to-rod transformation 0.35 mM for DoTAC.

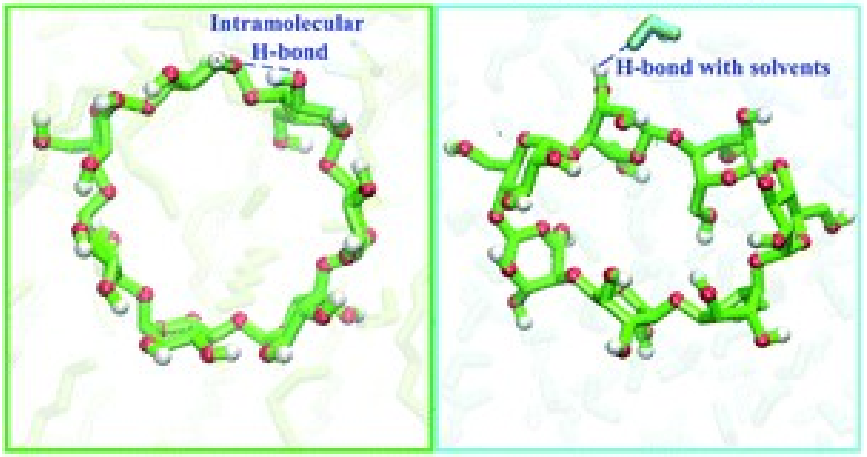


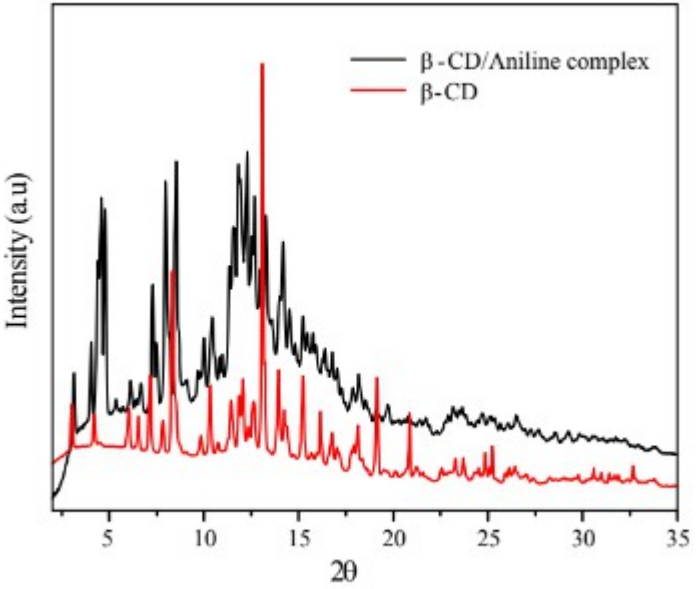
Synthesis PANI nanomaterials



The aqueous solution of the Ani/β-CD complex is instinctively entered into the aqueous core of the micelles due to its hydrophilicity nature of complex. Resulting PAni/β-CD complex molecules surrounded inside the micelles. In this case, the specific

Results – βCD/Aniline compuonds

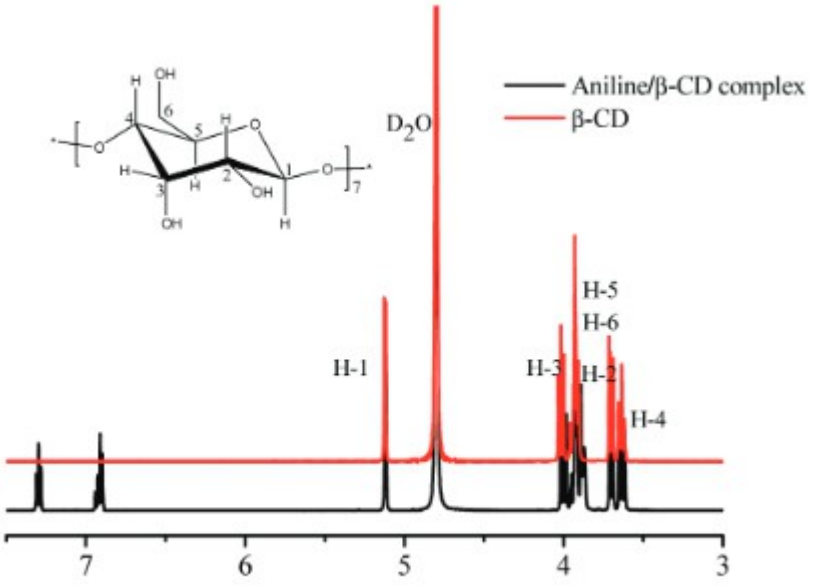




Wide angle X-ray diffraction

This measurement was in water solution.

The shift in the peak is because have complex inclusion and aniline was inside cyclodextrin cavity.

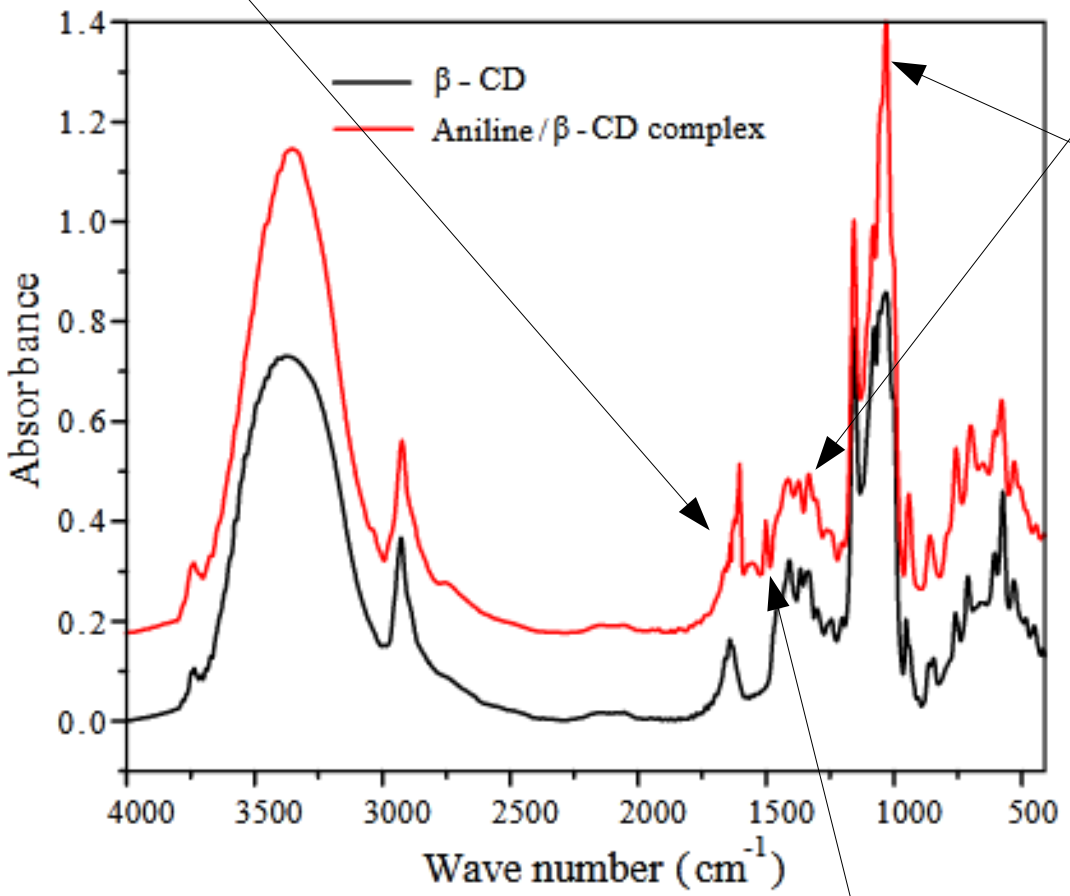


H NMR spectra

Results – βCD/Aniline compuonds

1602 cm^{-1} C=C stretching of the benzenoid rings.

1332 cm^{-1} C-N stretching of the aromatic amine of aniline.



Aromatic C-H vibration observed at 1156 cm^{-1}

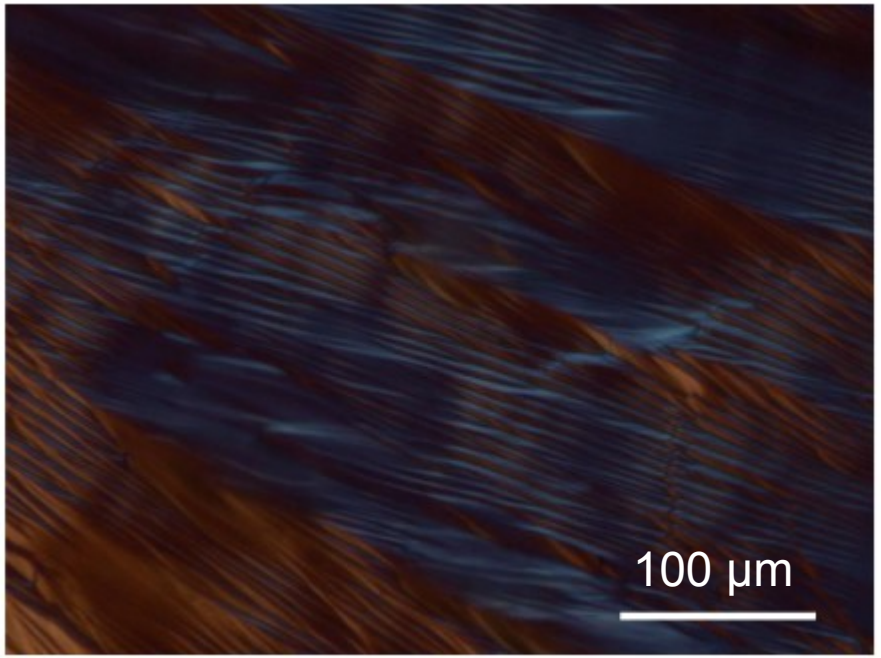
Fourier-transform infrared (FTIR)

1478 cm^{-1} was shifted due to the presence of β-CD host molecule.

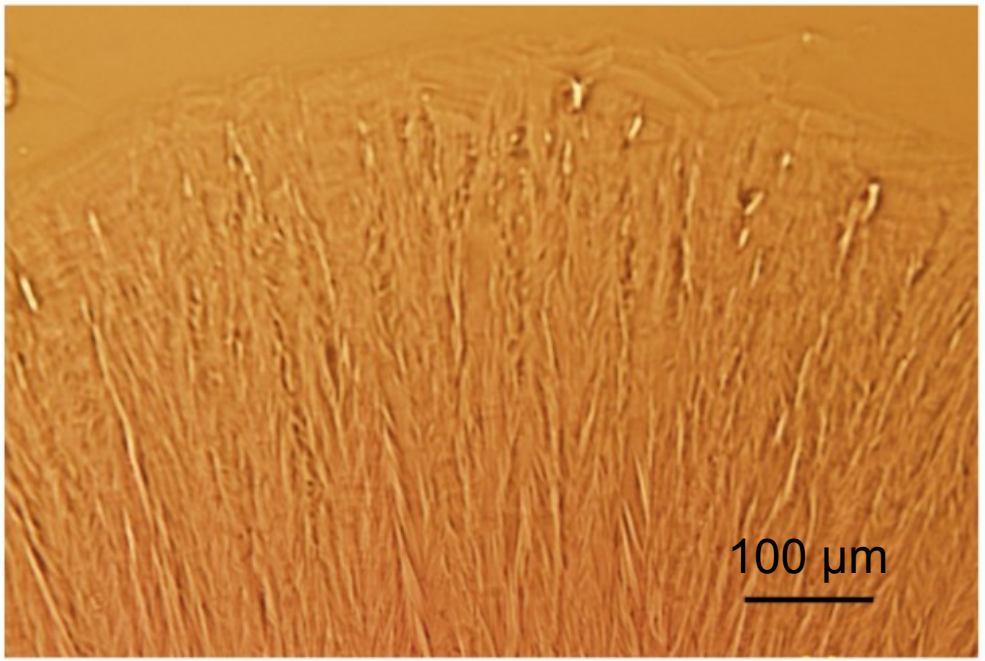
Characteristic bands at 3349, 1622, 1029, and 867 cm^{-1} of β-CD were found in the aniline/β-CD inclusion complex

Formation of Rodlike Micelle Phase

The anisotropic refractive index of the DoTAC rodlike micelle phase alters the polarization of transmitted polarized light to blue and reddish-pink texture.



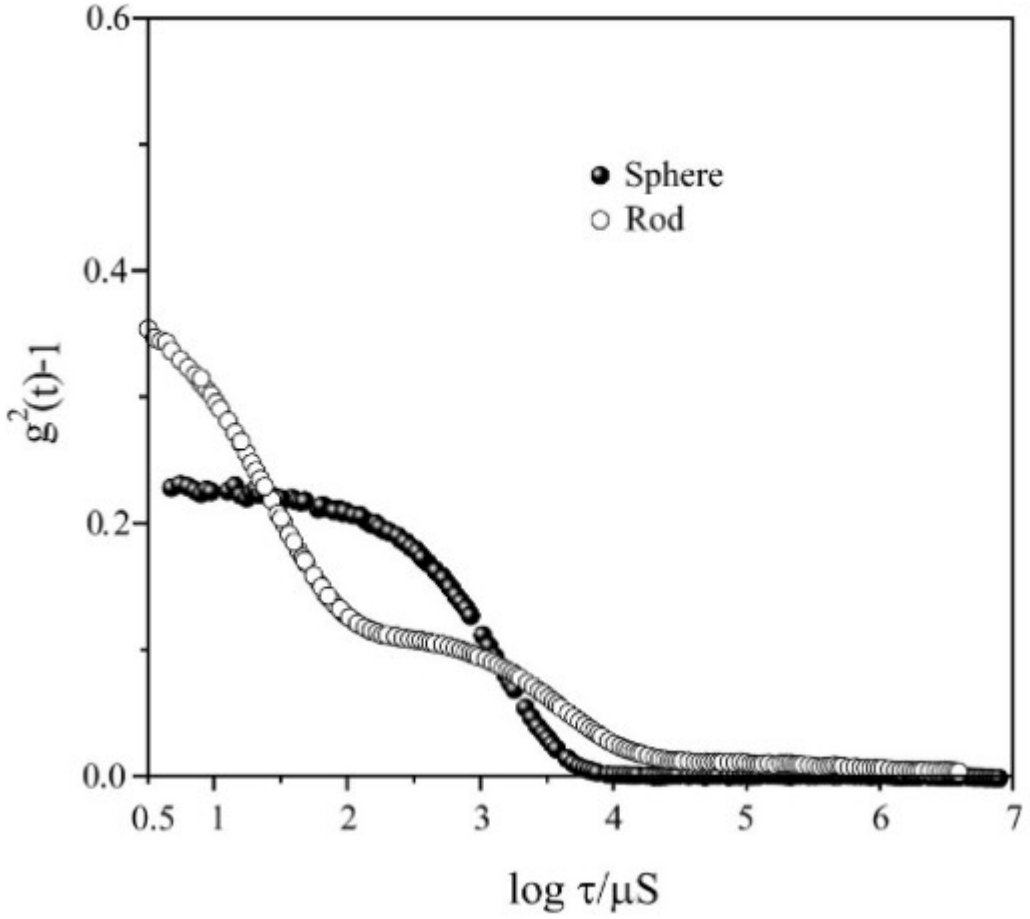
POM photograph

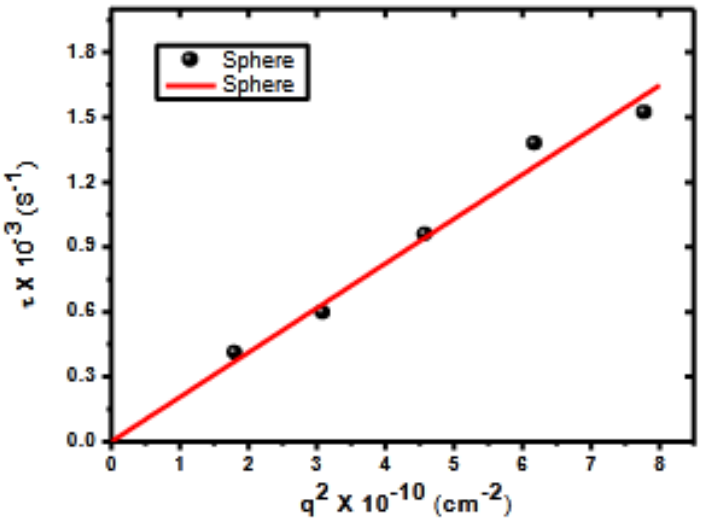


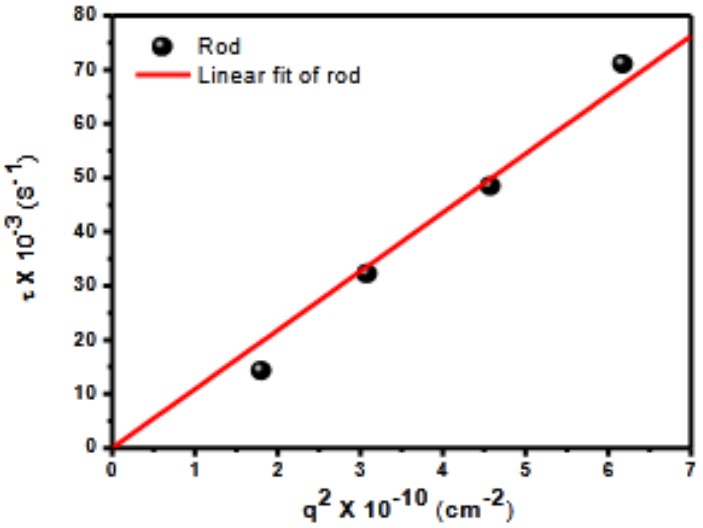
Confocal laser scanning microscopy

The yellow collor is a emisson resulting the molecules inside the rod-like micelles.
The aggregation DoTAC rods is encouraged for evaporation the water.

Formation of Rodlike Micelle Phase







$$g^{(2)}(t) = 1 + \beta \left| g^{(1)}(t) \right|^2$$

$$\frac{1}{\Gamma} = \tau = \frac{1}{q^2 D} = \frac{1}{q^2}\left[\frac{6\pi\eta_0 R_h}{k_B T}\right]$$

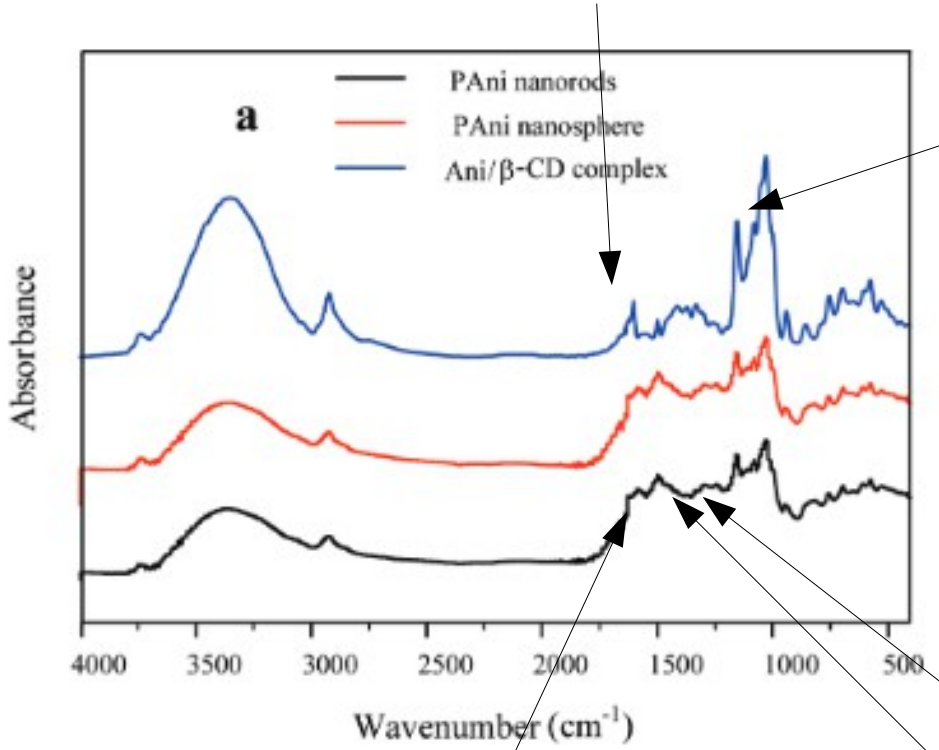
$$q = 4\pi n \sin(\theta/2)/\lambda$$

The R_h sphere is 112 and rod radius is 15 nm.

micelle solutions. In the correlation function of the spheres, one decay point is clearly observed. This may point out that the spherical micelles revealed only translational motion. Two decay points obtained in the case of rodlike micelles due to the change in molecular motions of micelles, which may be related to the rotational motion.[25,26] While the spheres showed one peak attributed to the diameter of the micelle, the rodlike micelles shows two peaks associated with the radius and length of the micelle.[25] The hydrodynamic radii (R_h) of micelles were calculated from the diffusion coefficients (D) by means of the Stokes−Einstein equation (Figure S5, Supporting Information), yielding the hydrodynamic radius R_h. The R_h values of 112 and 15 nm were obtained for sphere and rod radius, respectively.

Fabrication of PANI Nanoparticles

1602 cm^{-1} from the C=C stretching mode in the aniline/β-CD complex



Fourier-transform infrared (FTIR)

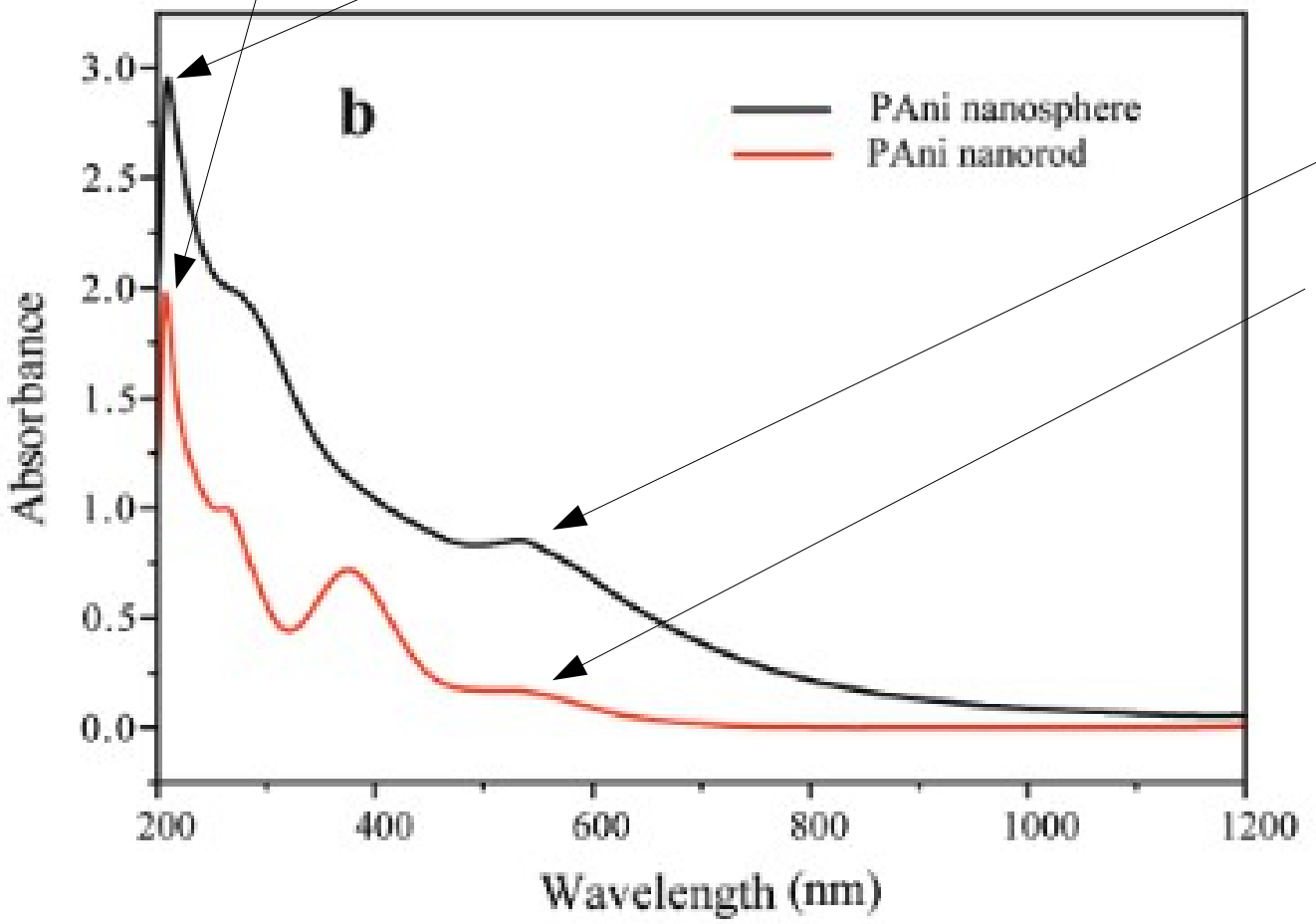
1157 cm^{-1} has been associated with high electrical conductivity and a high degree of electron delocalization in PAni.

1296 cm^{-1} band is assigned to the C-N stretching of the secondary aromatic amine of Pani and 1245 cm^{-1} could be interpreted as a C-N-C stretching vibration in the polaron structure.

Bands at 1582 and 1494 cm^{-1} are attributed to the C=C stretching deformation mode of the quinoid and benzenoid rings.

Fabrication of PANI Nanoparticles

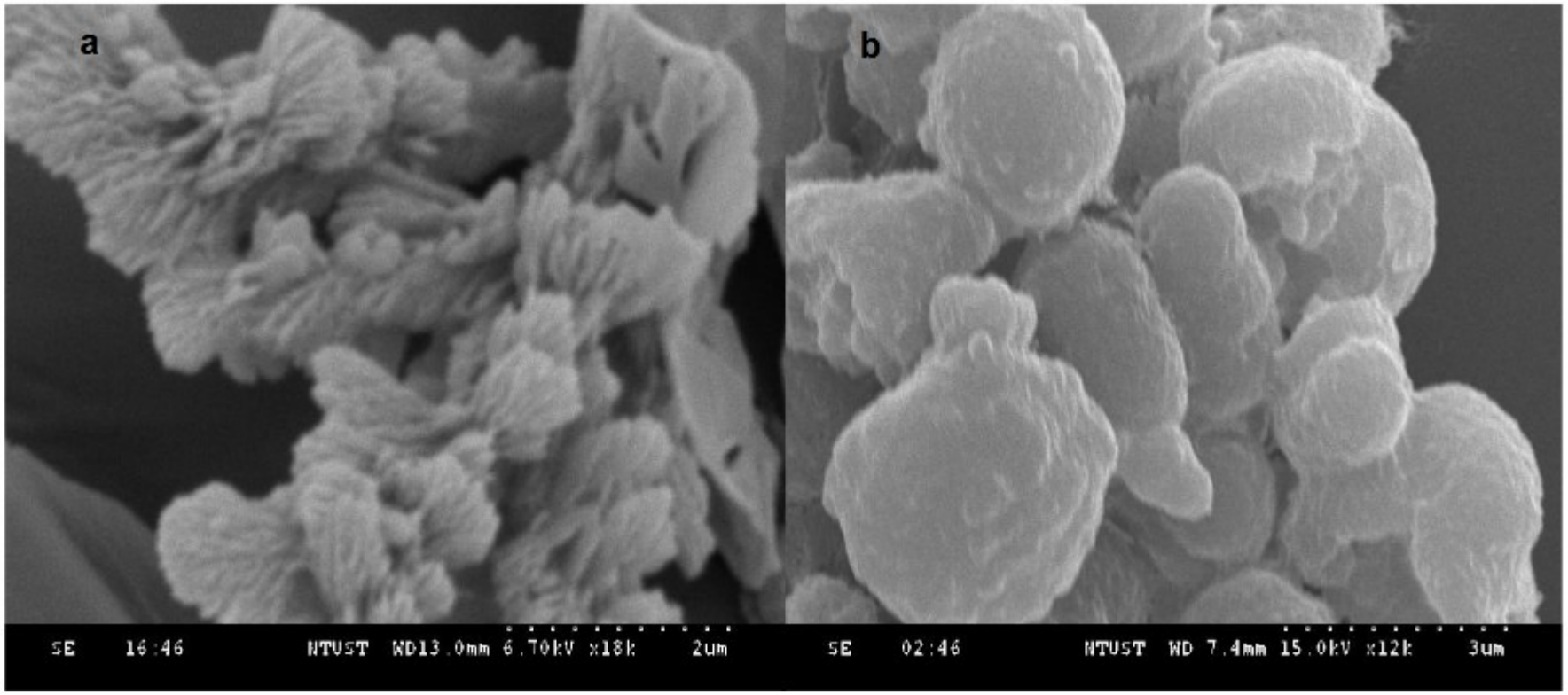
263 nm (nanofiber) and 286 nm (nanoparticle) the π-π* transition of PANI



The red shift from 532 to 539 nm is due to the longer conjugation length in the oriented PAni microsize fibers compared to the spheres

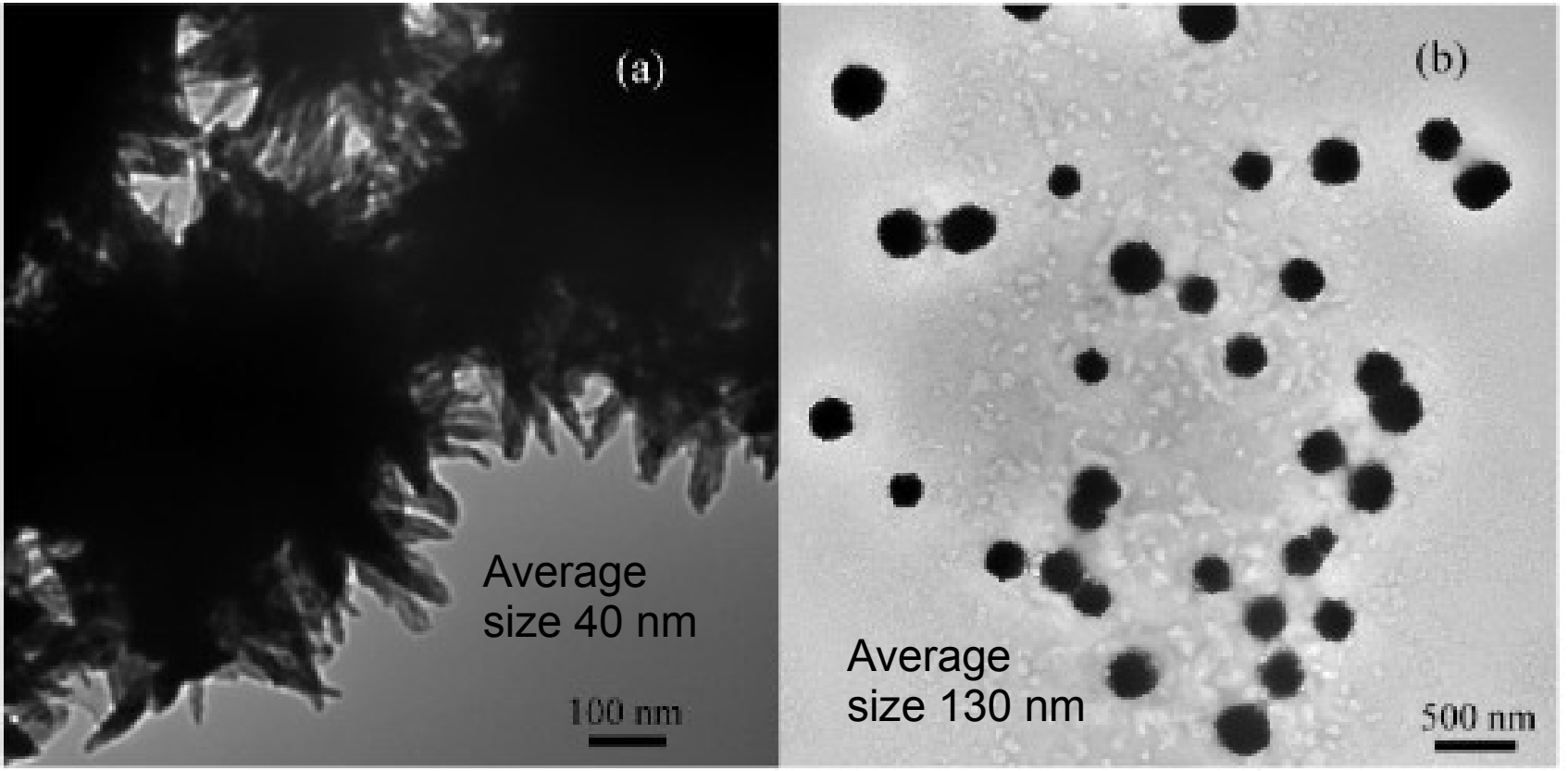
UV-vis spectroscopy (UV)

Fabrication of PANI Nanoparticles



Scanning electron microscope (SEM)

Fabrication of PANI Nanoparticles

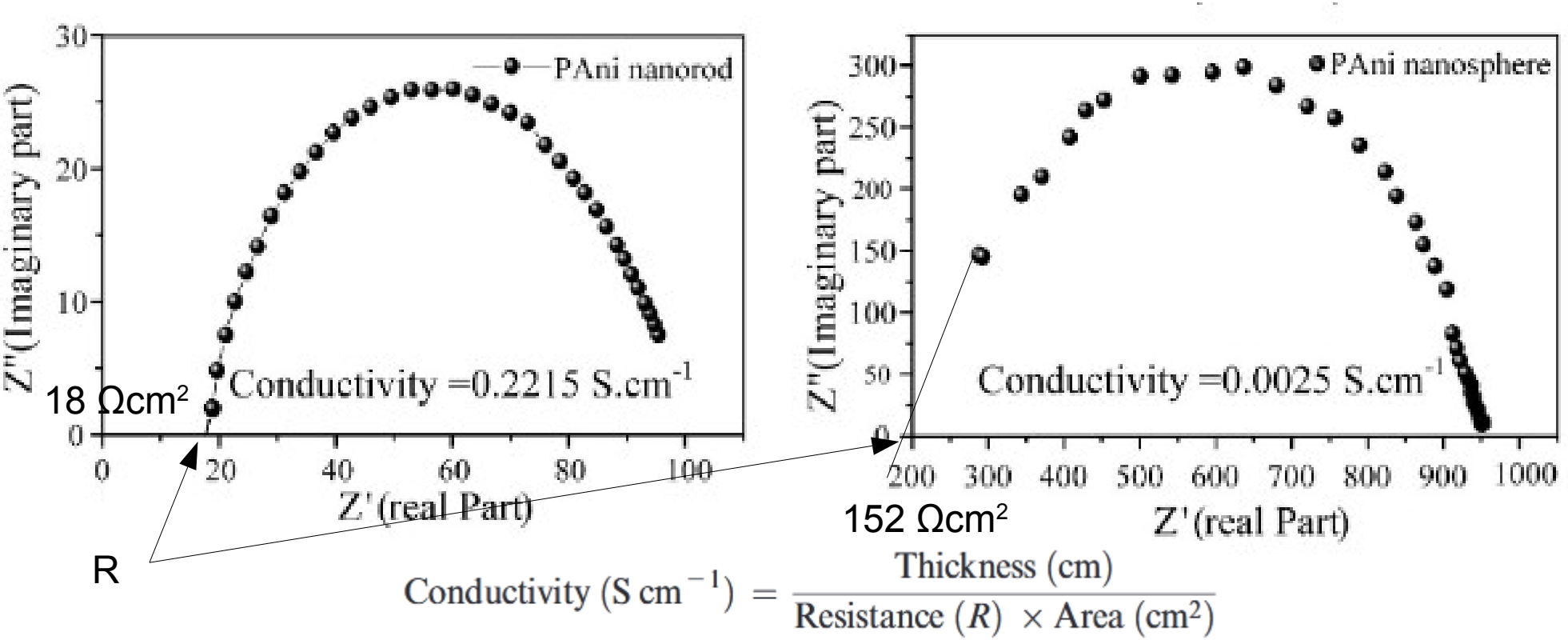


Nanorods

Nanoparticles

Transmittance electron microscopy (TEM)

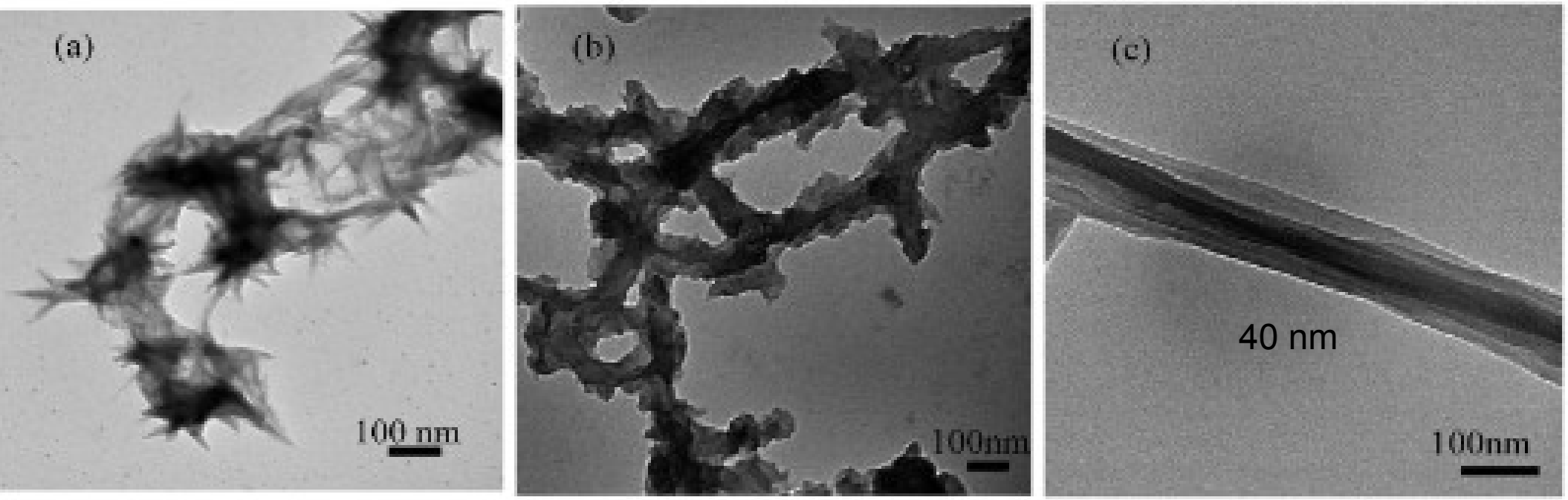
Electronic Transport Behavior



$$\text{Conductivity (S cm}^{-1}) = \frac{\text{Thickness (cm)}}{\text{Resistance } (R) \times \text{Area (cm}^2)}$$

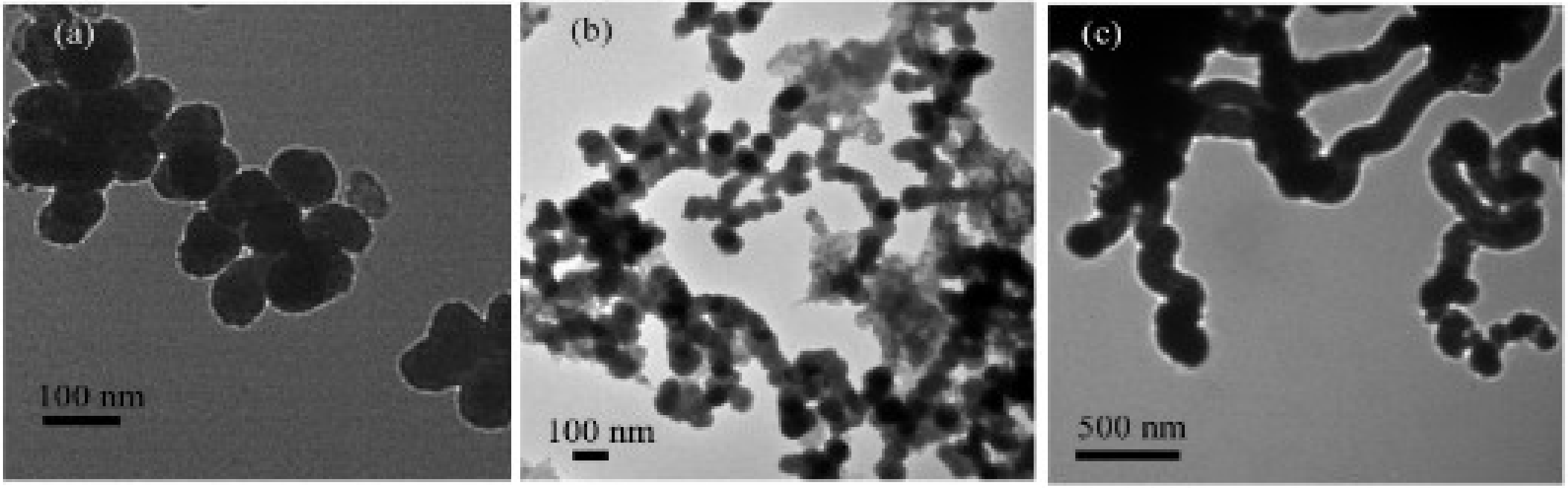
The sample showed a higher order fiber nature and has high conductivity, whereas nanoparticles sample has 3 orders less conductance than ordered structures.

[βCD] Influence



TEM image of PAni nanorods prepared from (a) 9, (b) 10.8, and (c) 12.6 mmol of β-CD in the presence of FeCl3.

[βCD] Influence



TEM image of PAni nanosphere prepared from (a) 9, (b) 10.8, and (c) 12.6 mmol of β-CD in the absence of FeCl3.

Conclusion

- The PAni nanorod and nanosphere were synthesized using β-CD-mediated microemulsion polymerization and as molecular host component.
- The rodlike micelle phase was developed through a cooperative interaction between aqueous FeCl3 solution and aniline in an aqueous medium with β-CD.
- The DoTAC rodlike micelle template in the presence of β-CD was demonstrated as an efficient tool to architect conducting PAni nanorod.
- Average particle size of the PAni nanometerials was controlled by the amount of β-CD and the structure change.

Thank you