

Supplementary Information for

**Photochromic one-dimensional nanostructures based on dithienylethene:
fabrication by light-induced precipitation and reversible transformation in the
nanoparticle state**

Abhijit Patra,^{a, #} Rémi Métivier,^a François Brisset^b and Keitaro Nakatani^a

^a PPSM, ENS Cachan, CNRS, UniverSud, 61 av President Wilson, 94230 Cachan France

^b ICMMO - Bât 410, Université Paris-Sud 15, rue Georges Clémenceau 91405 Orsay Cedex France

[#] Present address: Macromolecular Chemistry, University of Wuppertal,

Gaußstraße 20, 42119 Wuppertal, Germany

CONTENTS

Pages

2	I. Instrumentation
2 – 4	II. Fabrication of CMTE nanomaterials
4 – 7	III. Characterization and morphology details of the nanomaterials

I. Instrumentation

UV-visible spectra were recorded on a Varian Cary 5 UV-visible spectrophotometer. Photochromic reaction was induced *in situ* by means of a Hg/Xe lamp (Hamamatsu, LC6 Lightningcure, 200 W) equipped by 405 nm narrow band interference filter (Ealing Electro-Optics Inc. 405.8/8.7 for $\lambda_{\text{irr}} = 405$ nm and DMZ 20-2 for $\lambda_{\text{irr}} = 546$ nm). The irradiation power was measured using a photodiode from Ophir (PD300-UV).

Time-dependent absorption profiles were recorded by probing the sample continuously with a Xenon lamp during the photochromic reaction. Absorption changes were monitored by a CCD camera (Princeton Instruments) mounted on a spectrometer (Roper Scientific). Kinetic profiles were analyzed by an Igor-implemented home-made procedure.

II. Fabrication of CMTE nanomaterials

Experimental details regarding laser-induced fabrication technique. In a typical fabrication procedure, few mg of CMTE crystals in the open form (light yellow crystalline powder, CMTE-OF) were taken into a quartz cuvette containing an aqueous (ultrapure water, Millipore MilliQ, resistivity = 18 M Ω cm) solution of sodium dodecylsulphate (SDS, Aldrich). The concentration of surfactant should be at least higher than that of critical micellar concentration (8.2×10^{-3} mol L $^{-1}$) in order to substantially stabilize the suspension of nanoparticles. The mixture was stirred and simultaneously exposed to the third harmonics of a nanosecond Nd:YAG laser at 355 nm (30 mJ pulse $^{-1}$ cm $^{-2}$, 7 ns full-width at half-maximum, 10 Hz repetition rate) for 5-6 min at room temperature. The initial light yellow opaque suspension was gradually transformed to a pinkish turbid colloidal solution.

Experimental details regarding continuous-wave light-induced precipitation technique. ~ 0.3 mg of CMTE-OF crystals was taken into a quartz cuvette containing 3 mL of an aqueous solution of SDS. The mixture was stirred for 1 h. Then the suspension was irradiated for 30 min at 405 nm (power ~ 18 mW). Light irradiation induces the change of color from yellow to reddish pink and an increase of scattering which indicates the formation of colloids (Fig. S1). The resultant reddish pink suspension was filtered completely or partially through nanoporous alumina membrane (Anodisc 13, Whatman). These membranes were used for FESEM and optical imaging. B to A conversion was induced by irradiation at 546 nm (power ~70 mW).

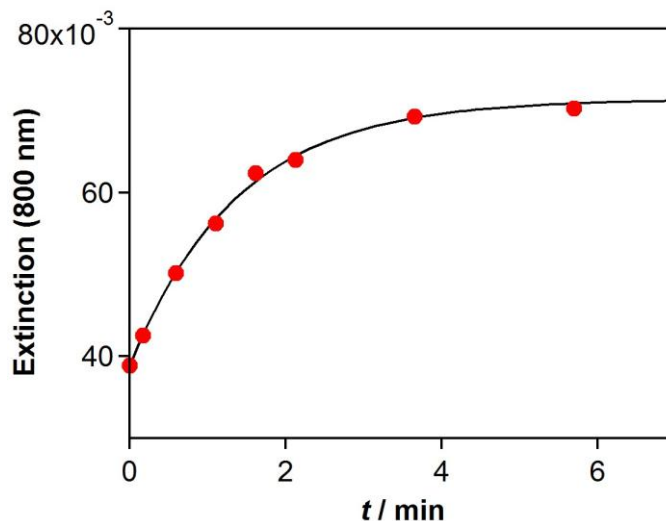


Fig. S1. Time profile of extinction at 800 nm during irradiation at 405 nm.

Determination of the composition of the nanorods. We have determined the composition of the nanorods obtained by the continuous-wave light-induced precipitation technique by means of the following procedure. The colloidal suspension of nanorods were filtered through nanoporous alumina membrane (pore size 100 nm) and dried. Complete dissolution of the nanorods was performed in chloroform. The absorption spectrum of the resulting solution was recorded, and the relative proportions of CMTE-OF and CMTE-CF were determined by deconvolution of the spectrum of the mixture by the spectra of the pure CMTE-OF and CMTE-CF in chloroform. The results displayed on Fig. S2 show that the CMTE nanorods are composed of more than 90% of CF.

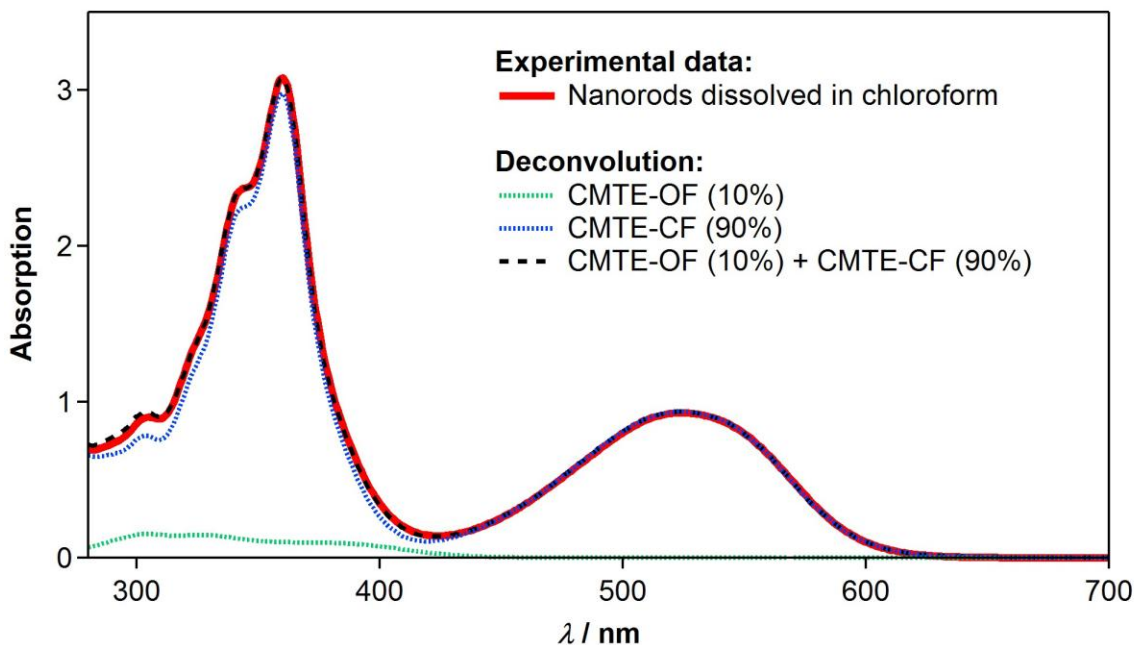


Fig. S2. Deconvolution analysis of the absorption spectrum of nanorods dissolved in chloroform.

Estimation of the solubility data. Solubility of CMTE-OF in water / SDS medium was measured by analyzing a saturated suspension of CMTE-OF. 5.5 mg of CMTE-OF crystals were stirred in 25 mL of surfactant solution for 1-2 days. Filtration of the suspension and measurement of absorption spectra allowed the determination of the amount of dissolved and undissolved CMTE-OF. Solubility of CMTE-CF in water / SDS was obtained by applying the same method, on a saturated suspension of CMTE obtained by prolonged irradiation at 405 nm. In the latter case, both forms are present (OF and CF) and a deconvolution procedure (described in the previous paragraph) was necessary to determine the exact amount of dissolved and undissolved CMTE-CF. The solubility of CMTE-OF (resp. CMTE-CF) in water / SDS was determined to be 120 mg L⁻¹ (resp. 20 mg L⁻¹).

Attempts of light-induced precipitation of CMTE in different solvents. All our trials to perform light-induced nanoprecipitation of CMTE in any other solvent than the water / SDS medium were unsuccessful. CMTE, in both its open and closed forms, is well-soluble in most of the organic solvents, whereas it is quite insoluble in pure water. As for examples, absorption spectra of CMTE recorded in CH₃CN and CHCl₃ under similar concentration range that used in aqueous SDS medium, are plotted in Fig. S3. The absence of scattering before and after irradiation at 405 nm suggests that no light-induced precipitation is occurred in these cases.

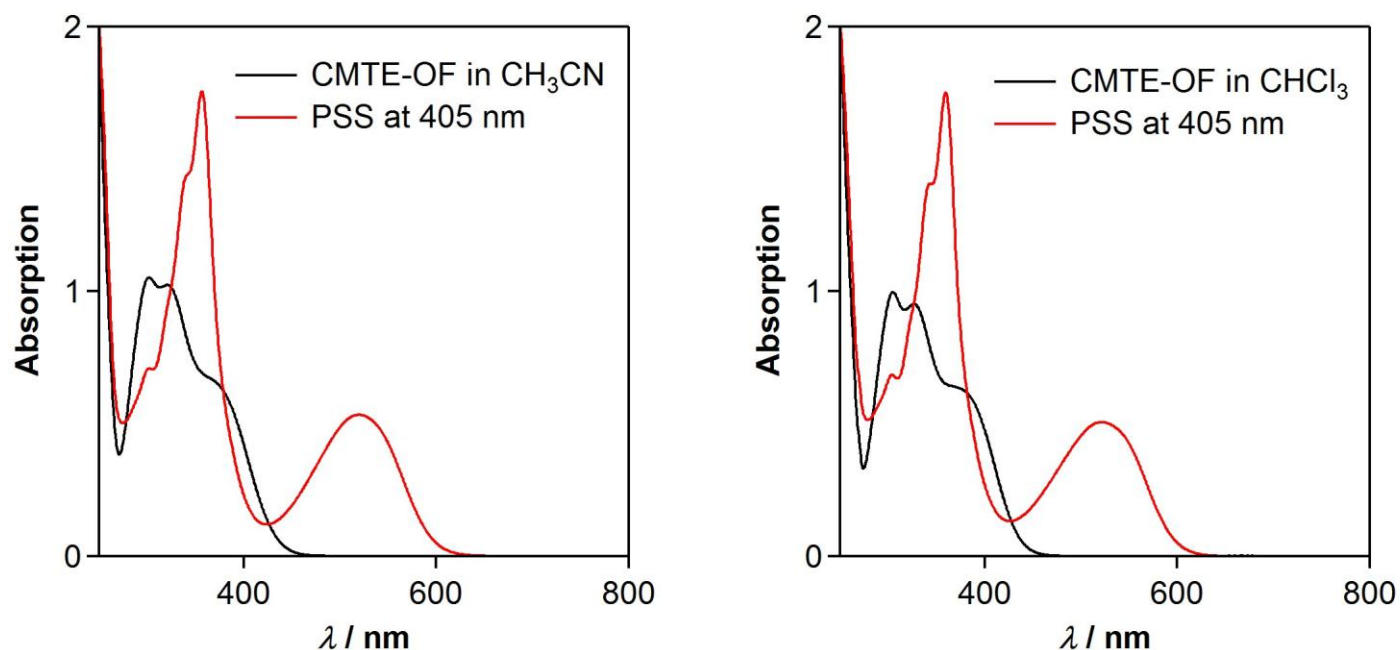


Fig. S3. Absorption spectra of CMTE in its open form (black) and at the photostationary state (PSS, red) at 405 nm, in acetonitrile (left) and in chloroform (right).

III. Characterization and morphology details of the nanomaterials

The size and morphology of the nanoparticles were examined using a Zeiss Supra 55 VP field emission scanning electron microscope (FESEM).

The samples were collected on a 100 nm pore alumina membrane (Anodisc 13, Whatman) through filtration of the colloidal solution. The samples prepared for FESEM were coated by a thin layer of sputtered gold prior to imaging and microscopy was carried out using a beam voltage of 15 kV. FESEM measurements of nanoparticle deposited membrane used for solid state switching were carried out without prior gold coating and beam voltage of 1 kV was used. Size distribution histograms were obtained from FESEM images by an Igor-implemented procedure (Wavemetrics).

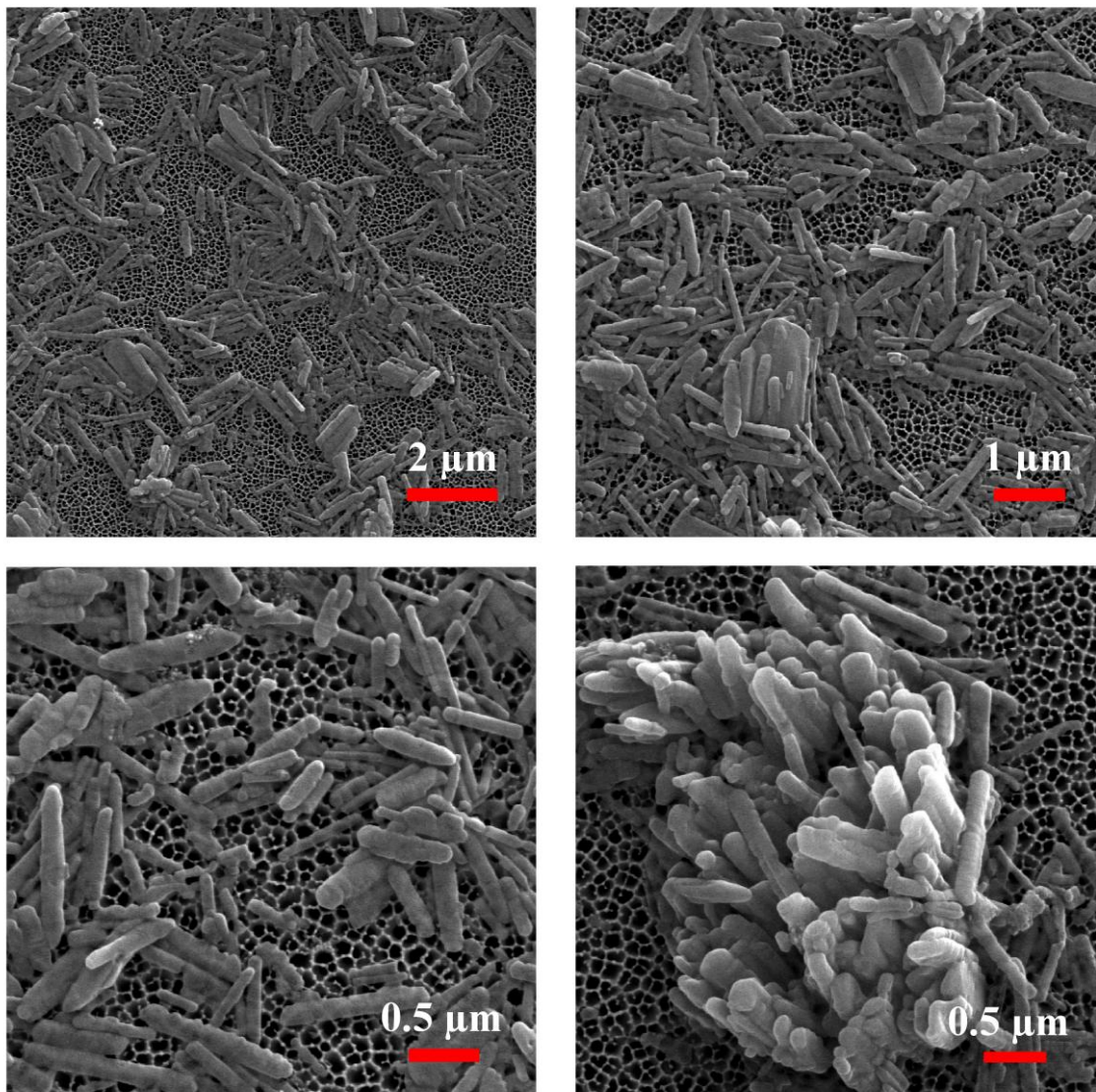


Fig. S4. FESEM images of CMTE nanorods obtained by irradiation of aqueous-SDS dispersion of CMTE-OF at 405 nm for 30 min (18 mW).

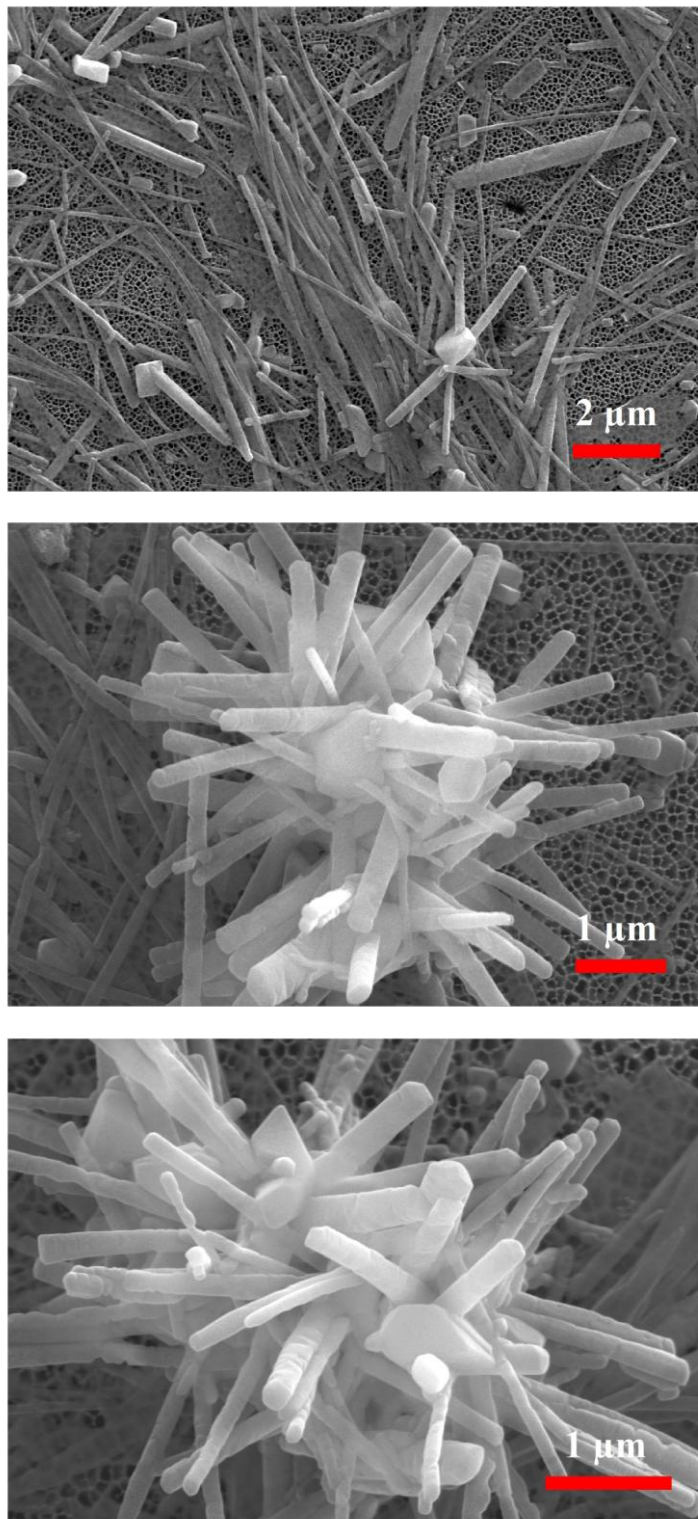


Fig. S5. FESEM images of CMTE nanowires and nanorods obtained by irradiation of aqueous-SDS dispersion of CMTE-OF at 405 nm for 1 h in the second cycle.

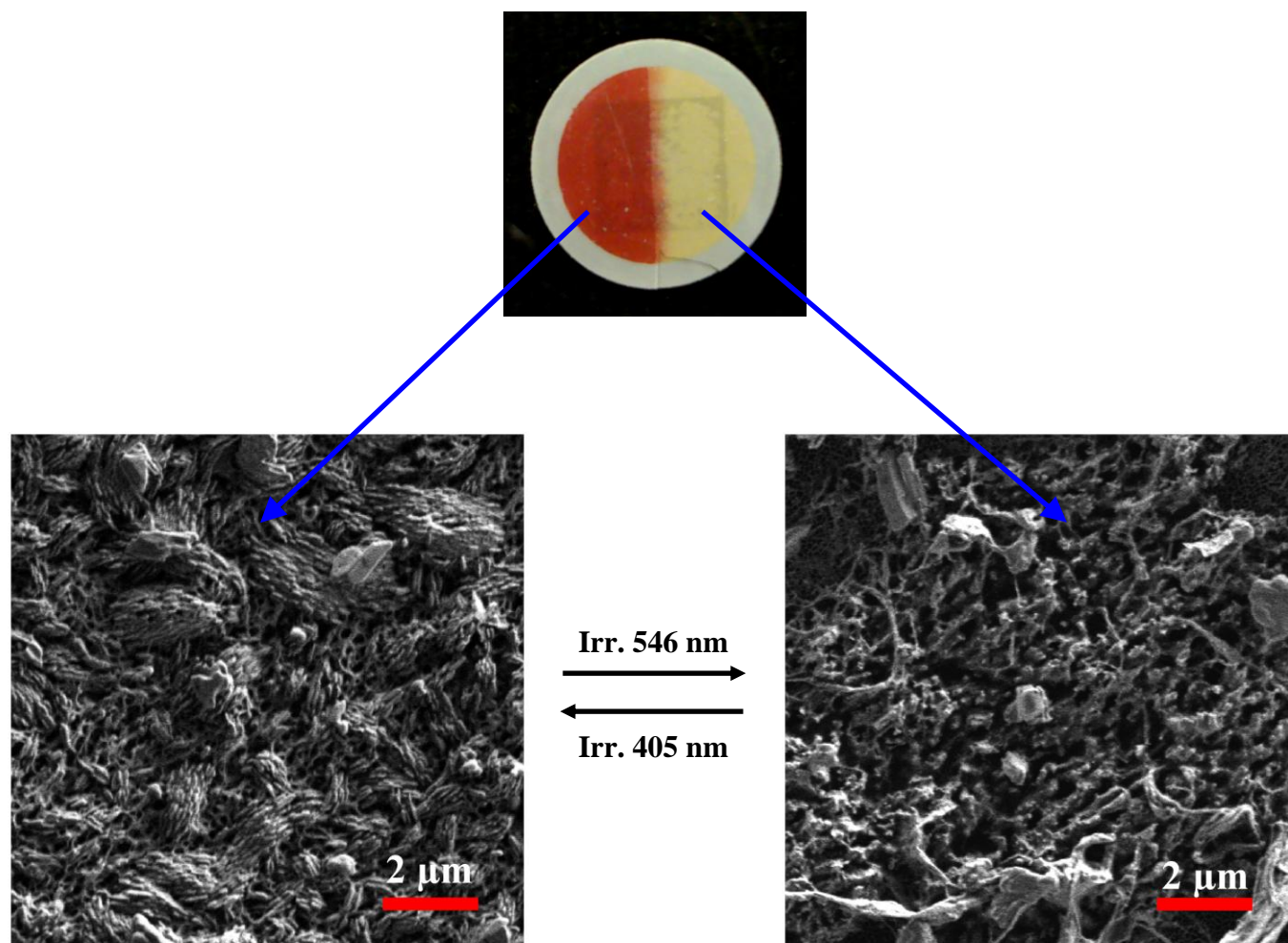


Fig. S6. FESEM images of CMTE nanoparticles deposited on an alumina membrane after 10 times alternate 405 and 546 irradiations.

The experiment was carried out as following: pinkish colloidal dispersion containing nanorods of CMTE-CF was filtered through nanoporous alumina membrane. The membrane was air dried and irradiated repeatedly with alternate 546 and 405 nm light. It was ensured that the color of the membrane should completely transform red to yellow or vice versa after each irradiation (30 s to 1 min). After the 10th cycle, half part of the membrane was masked with black paper and the remaining half was irradiated with 546 nm light. Both parts of the membrane were imaged under FESEM separately.

The reason behind the net-like structures obtained after irradiation at 546 nm is not very clear at the present time. It is obvious that the irradiation at 546 nm leads to the transformation from CMTE-CF to CMTE-OF and that causes the breakdown of the rod like morphology. Unlike in the colloidal dispersion, where most of the CMTE-CF nanorods are dissolved in the medium upon irradiation at 546 nm, solid-state transformation occurs in the constrained environment of porous membrane. SDS micelles may play significant role and pave the way to net-like morphology under irradiation at 546 nm.