

Photoinduced hole transfer forming polymer quantum dot nano composites

Xichen Cai, Puran K. De, Kelechi C. Anyaogu, Ravi M. Adhikari, Sujeewa S. Palayangoda and Douglas C. Neckers *

Center for Photochemical Sciences, Bowling Green State University, 132 Overman Hall, Bowling Green, Ohio 43403.

Contents

A, Experimental Section.

B, The UV absorption changes of BTSCdSe and BTC₅SCdSe after ≥ 450 nm irradiation for 30 minutes (Figure S1).

C, TEM images of BTC₅SCdSe before and after ≥ 450 nm irradiation for 30 minutes.

A, Experimental Section

Preparation of 5-(5-mercaptopentyl)-2,2'-bithiophene (BTC₅SH). Dry, distilled tetrahydrofuran (20 ml) and 2,2'-bithiophene (1 mmol) were added in a dry round bottom flask. The mixture was flushed with argon for 15 minutes and cooled to 0 °C with ice. To this mixture *tert*-butyllithium in hexanes (1.2 mmol) was slowly added while stirring vigorously. The mixture was warmed to room temperature while stirring for five hours. 1,5-Dibromopentane (1.3 mmol) in tetrahydrofuran was added and the mixture refluxed for five hours after which it was cooled and ammonium chloride solution was added. The mixture was separated using ethyl acetate, dried and the solvent evaporated. A green, oily product [5-(5-bromopentyl)-2,2'-bithiophene] was obtained (70 %). The HRMS (EI) measured mass value is 313.9796 and calculated mass value is 313.9799. The 5-(5-bromopentyl)-2,2'-bithiophene (0.7 mmol) was mixed with thiourea (1.5 mmol) in dry ethanol and the mixture refluxed for 24 hours. The mixture was then cooled to room temperature, sodium hydroxide solution added and the resulting mixture refluxed for another five hours. Subsequently the mixture was neutralized with hydrochloric acid, extracted with ether, washed with water several times and dried over MgSO₄. After evaporation of the solvent, crude product was subjected to silica gel column (20% dichloromethane in hexanes) producing pure white powder (90 % yield). ¹H NMR (300 MHz, CDCl₃) δ 1.35 (1H), 1.5 (2H), 1.7 (4H), 2.5 (1H), 2.7 (1H), 2.8 (2H), 6.7 (1H), 6.95 (2H), 7.05 (1H), 7.15 (1H); ¹³C NMR (300 MHz, CDCl₃) δ 24, 27, 30, 31, 33, 122.5, 123, 123.2, 128, 135, 138, 145; The HRMS (EI) measured mass value is 268.0415 and calculated mass value is 268.0414.

Electron Microscopy. TEM images were taken on a ZEISS EM10 transmission electron microscope operating at 80 kV. The nanoparticles were dropcast from toluene solutions onto formvar-carbon coated 300-mesh copper grids and air-dried before viewing under the TEM. SEM images were recorded on a Hitachi S-2700 electron microscope at 15 kV. Samples for SEM were prepared by placing a few drops of the nanoparticle solution onto a glass cover slip placed on an aluminum stub. The samples were allowed to dry before viewing under the electron microscope. To enhance contrast and the quality of the SEM images, samples were sputter-coated with gold/palladium.

Ultraviolet-Visible Absorption, Excitation and Fluorescence Spectroscopy. Ultraviolet-Visible (UV) absorption spectra were measured using MultiSpec-1501 (Shimadzu). The excitation spectra, emission spectra and emission lifetimes were

measured using a SPEX Fluorolog-3 (Jobin Yvon Inc.) equipped with Time Correlated Single Photon Counting (TCSPC).

Femtosecond Transient Absorption Measurements. The femtosecond time-resolved apparatus at the Ohio Laboratory for Kinetic Spectrometry at Bowling Green State University, USA, has been described elsewhere.¹ A Spectra-Physics Hurricane system was used as the laser source. The pump beam 478 nm was focused into the sample cell where it was overlapped with the probe beam white light continuum (effective useful range, 460–800 nm) at an angle of *ca.* 5°. The probe light was coupled into a 400 μm optical fiber connected to a CCD spectrograph (Ocean Optics, PC 2000). The delay line and the CCD spectrograph were computer-controlled by a LabVIEW (National Instruments) software routine developed by Ultrafast Systems, LLC. The sample was flowed through a quartz cell with an optical path of 2 mm that was connected to a solution reservoir and a pump system (Micropump Corp.). All measurements were carried out at room temperature, $20 \pm 2 \text{ C}^\circ$.

Nanosecond Transient Absorption Measurements. Nanosecond transient absorption measurements were performed on a kinetic spectrometric system previously described.^{2,3} The excitation pulse (532 nm, 12-19 mJ/pulse) is the second harmonic of a Q-switched Nd:YAG laser. The excitation pulse width is ~ 7 ns. Transients produced are followed temporally and spectrally by a computer-controlled kinetic spectrophotometer. The sample solutions were adjusted with absorbance of 0.15-0.33 at the excitation wavelength in 1-cm² quartz cuvettes. Fresh samples were used for obtaining each kinetic trace. All measurements have been made at room temperature.

B, The UV absorption changes of BTSCdSe and BTC₅SCdSe after ≥ 450 nm irradiation for 30 minutes

The UV absorption changes of BTSCdSe and BTC₅SCdSe after ≥ 450 nm light irradiation for 30 minutes are shown in Figure S1. The UV absorption of BTSCdSe is increased and blue shifted from 323 nm to 315 nm. The shoulder absorption around 390 nm is decreased and absorption around 450 nm is increased. Such absorption changes indicate the possibility of polymerization of BTSCdSe.⁴ No obvious changes are observed in BTC₅SCdSe.

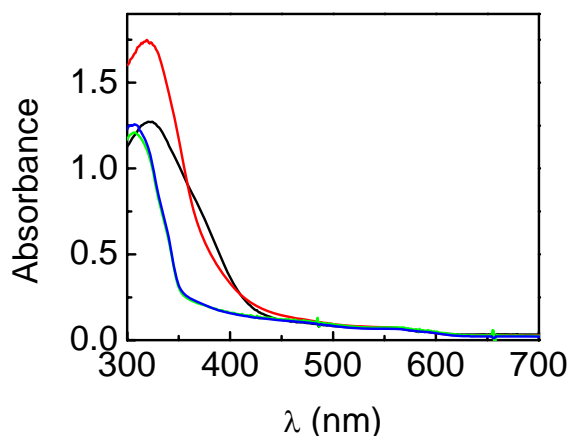


Figure S1 UV absorption spectra of BTSCdSe before (black line) and after (red line) and BTC₅SCdSe before (blue line) and after (green line) ≥ 450 nm light irradiation.

C, TEM images of BTC₅SCdSe before and after ≥ 450 nm irradiation for 30 minutes.

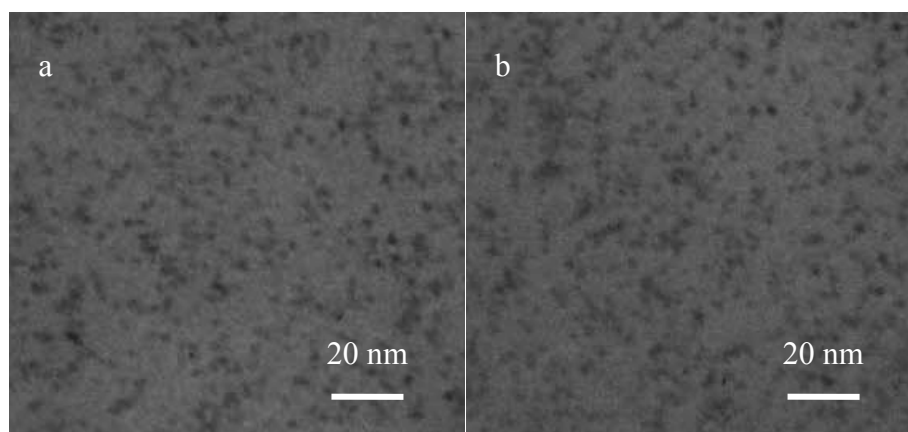


Figure S2 TEM images of BTC₅SCdSe before (a) and after (b) ≥ 450 nm light irradiation for 30 minutes.

- (1) Gentili, P. L.; Danilov, E.; Ortica, F.; Rodgers, M. A. J.; Favaro, G. *Photochem. Photobiol. Sci.* **2004**, 3, 886.
- (2) Shah, B. K.; Neckers, D. C. *J. Am. Chem. Soc.* **2004**, 126, 1830.
- (3) Ford, W. E.; Rodgers, M. A. J. *J. Phys. Chem.* **1994**, 98, 3822.
- (4) Cai, X.; Anyaogu, K. C.; Neckers, D. C. *J. Am. Chem. Soc.* **2007**, 129, 11324.