Electronic Supplementary Material (ESI) for Chemical Communications

Reversible Modulation of Photoluminescence from Conjugated Polymer Nanotubes by incorporation of Photochromic Spirooxazine Molecules

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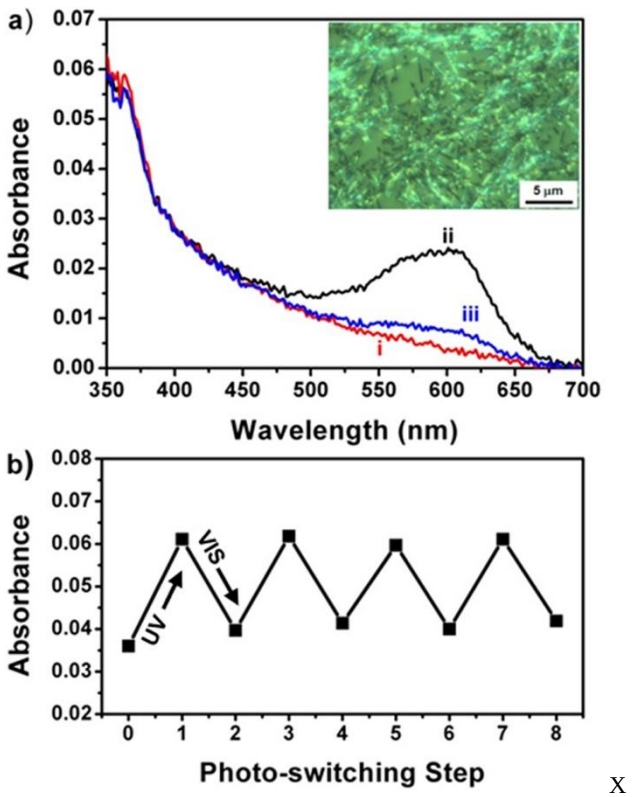

Fig. S1(a) UV-visible absorption spectra of a SO-PMMA nanowire matt following visible (i)-UV(ii)-visibleible (iii). Inset: optical image of cycled matt; (b) reversible modulation of matt absorption intensity following alternating steps of UV and visible irradiation.

Supporting information

† Electronic Supplementary Information (ESI) available:

Preparation of Thin Films. All thin films were prepared and stored in an inert atmosphere glove box system. PFA thin films were fabricated from a 20 mg/mL solution of PFA in anhydrous THF. Spirooxazine-doped PMMA thin films were prepared from an anhydrous THF solution containing 10 mg/mL of PMMA and 5 mg/mL of SO. Both solutions were spin-coated onto acid cleaned glass cover slips at 3,000 rpm for 1 min. Spirooxazine-doped PFA films were spin-coated onto cleaned cover slips at 2,000 rpm for 1 min from a THF solution containing 20 mg/mL of PFA and 5 mg/L of SO.

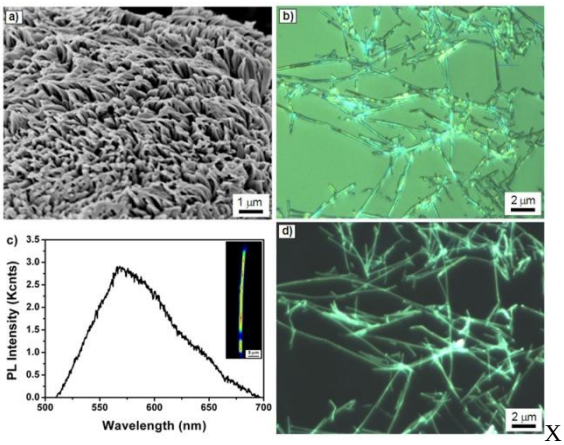

Fig. S2 (a) Scanning electron microscopy (SEM) image of freestanding SO-PMMA nanowire array; bright-field (b) and fluorescence (c) optical microscopy images PFA nanowire mat; d) emission spectrum of individual PFA nanowire. Inset: fluorescence intensity image of PFA nanowire.

Scanning Electron Microscopy (SEM) of Nanotube Arrays. SEM images of nanotube arrays were acquired using a field emission SEM (JSM-6700F, JEOL UK Ltd.) operating at beam voltages between 3 and 7 kV. For imaging of nanotube arrays, nanotube filled porous alumina membranes were mounted onto SEM stubs using carbon pads and then dipped into NaOH solution (3 M, 1h) to selectively dissolve the template and leave freestanding forests of doped tubes.

Reversible Modulation of Light Absorption in SO-doped PMMA Thin Films. Absorption spectra of prepared SO-PMMA films were measured for each film as a function of irradiation conditions. The light source employed for irradiation was a Xenon lamp (FL-450XOFR 450 W) coupled to the Triax 180 monochromator (0.19 m; 1200 g/mm grating; 2 mm slit width). For UV irradiation, a wavelength of 360 ± 3 nm was selected and the sample was illuminated for 10 min at an excitation power of 0.75 mW/cm^2. For visible irradiation, a wavelength of 580 ± 3 nm was selected and the sample was illuminated for 20 min at an excitation power of 0.50 mW/cm^2. Absorption spectra were acquired using the Agilent diode-array spectrophotometer described above. Modulation of absorption following alternating steps of UV and visible irradiation was graphically represented by plotting the nanotube spectral absorption intensity, measured

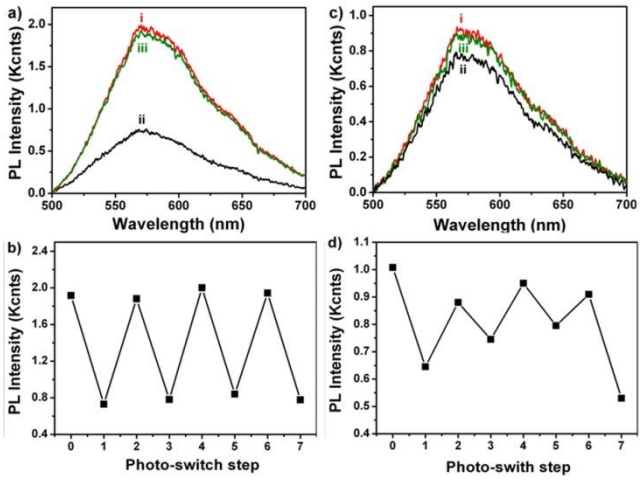

Fig. SI3 Emission spectra from a single SO-PFA nanotube following vis (i)-UV (ii)-visible (iii) irradiation. (a) SO-PFA 20% w:w; (c) SO-PFA 1% w:w. Reversible modulation of nanotube emission following alternating steps of UV and visible irradiation. (b) SO-PFA 20% w:w; (d) SO-PFA 1% w:w.

at the wavelength of maximum absorption after each photo-switch step.

Luminescence Microscopy of Nanotube Mats. Emission microscopy images of individual nanotubes, drop deposited from aqueous suspension onto cleaned glass microscope slides, were acquired using a calibrated epi-fluorescence microscope (Zeiss Axioskop II Plus, Carl Zeiss U.K.) equipped with a CCD camera (Optronics DEI-750). A 100 W arc lamp was employed, together with an appropriate filter set (Zeiss 01), enabling 350 - 380 nm optical excitation and collection of resulting luminescence above 380 nm. Images were analysed using Image Pro Express software (Media Cybernetics Inc., USA).

Emission Microscopy and Spectroscopy of Single Nanotubes. All single nanotube measurements were carried out using a time-resolved scanning confocal fluorescence microscope (MicroTime 200, PicoQuant) equipped with a XY piezoelectric scanning stage (P-733-2CL, Physik Instrumente). System operation was controlled by a dedicated software package (MicroTime 200 Version 4.0 software, PicoQuant). The horizontally polarized output of a 468.8 nm pulsed picosecond laser diode (59 ps; 40 MHz repetition rate; 4.8 nm max. spectral width; LDH-P-C-470, PicoQuant) was spectrally filtered using a 467 nm band pass filter (Z467/10X, Chroma) and then converted to circularly polarised light using a broadband quarter waveplate (AQWP05M-630, Thorlabs). The collimated laser beam was then directed into the entrance port of an inverted microscope (IX 71, Olympus) using a dichroic mirror (480dcrx, Chroma). A 100X oil immersion objective (1.4 NA, UPlan SAPO, Olympus) was used both for focusing the excitation light onto the sample on the piezoelectric scanning stage and for collecting the resulting photoluminescence (immersion oil: n = 1.48 refractive index; Type FF, Cargille-Sacher Laboratories, Inc.). Typically, the sample comprised a nanotube mat deposited onto a cleaned glass cover slip at sub-monolayer coverage and sealed into a home-built vacuum cell. The collected luminescence was first spectrally filtered using a 500 nm long pass filter (HQ500LP, Chroma) to reject backscattered excitation light, and then spatially filtered by focusing onto a 150 µm diameter pinhole to reject out-of-focus signals. Single nanotube emission intensity images were recorded by raster scanning the sample through the laser focus spot and recording the luminescence using an avalanche photodiode (SPCM-AQR-14, Perkin-Elmer). All emission intensity images were recorded with a pixel integration time of 2 ms and an incident excitation power < 0.1 nW/cm2 to prevent sample photo-bleaching.

Single nanotube emission spectra were recorded by directing the photoluminescence from a single nanotube onto the entrance slit of a 0.3 m monochromator (SP-2356, 300 g/mm grating, 500 nm blaze, Acton Research) equipped with a thermoelectrically cooled, back illuminated CCD (Spec10:100B, Princeton Instruments). Spectra were typically recorded using an incident excitation power < 0.1 nW/cm2, a slit width of 500 µm and an integration time of 10 s.