Photoinduced formation of bi-thiophene Radical cation via a hole-transfer process from CdS nanocrystals

Alessandro Iagatti[a], Rebecca Flamini, Morena Nocchetti and Loredana Latterini*

Dipartimento di Chimica and Centro Eccellenza Materiali Innovativi Nanostrutturati (CEMIN), Università di Perugia, Via Elce di Sotto 8, 06123 Perugia, Italy

[a]Present address: European Laboratory for Non Linear Spectroscopy (LENS), Università di Firenze, via Nello Carrara 1, 50019 Sesto Fiorentino, Florence, Italy and INO - CNR, Istituto Nazionale di Ottica – Consiglio Nazionale delle Ricerche, Largo Fermi 6, 50125 Florence, Italy

*E-mail: loredana.latterini@unipg.it

1. Estimation of quenching rate constant

2. TEM Image

3. XRD pattern and Instrumental set-up description

4. Luminescence decay curves and phase-shift data together with the Instrumental set-up description

1. Estimation of quenching rate constant

Smoluchowski equation: $k_q = [(4\pi N/1000)(R_f + R_q)(D_f + D_q)]$, where R_f and R_q are the radii of the CdS colloids (1.6 nm, it was taken the average value from DLS data) and bi-thiophene molecules (ca. 0.3 nm, determined on the basis of atom distances from reference 24 of the manuscript and approximating the molecules to a spherical shape); D_f and D_q are their diffusion coefficients determined by the Stokes-Einstein equation assuming the same radii. These equations were used considering the CdS nanocrystals as a fluorophore and the bi-thiophene (whose dimensions under the working conditions are known in the literature) as the quencher.
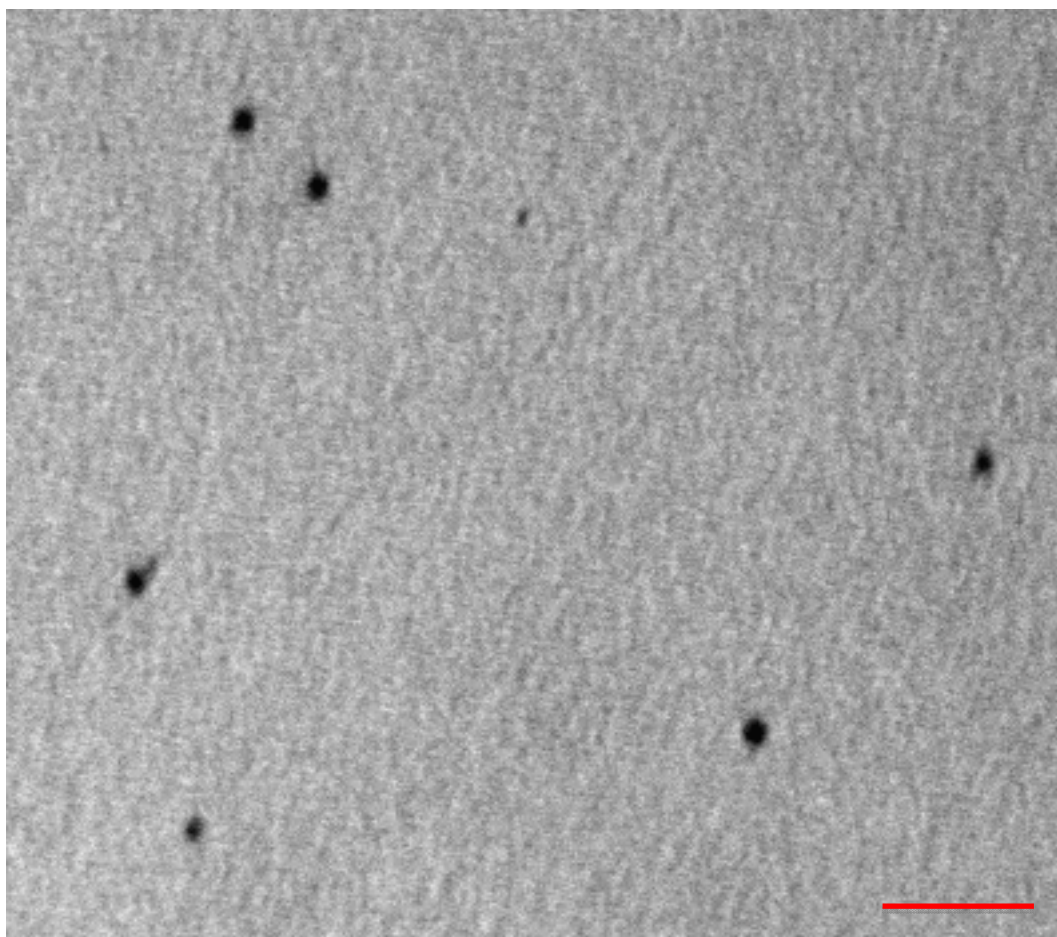
2. TEM Image

Figure S1. TEM images of CdS nanocrystals (scale bar is 20 nm).

3. XRD pattern and Instrumental set-up description

The X-ray powder diffraction (XRPD) patterns were taken with a Philips X'PERT PRO MPD diffractometer operating at 40 kV and 40 mA, step size 0.0170 2θ degree and step scan 20 s, using the CuKα radiation and an X'Celerator detector.[3]
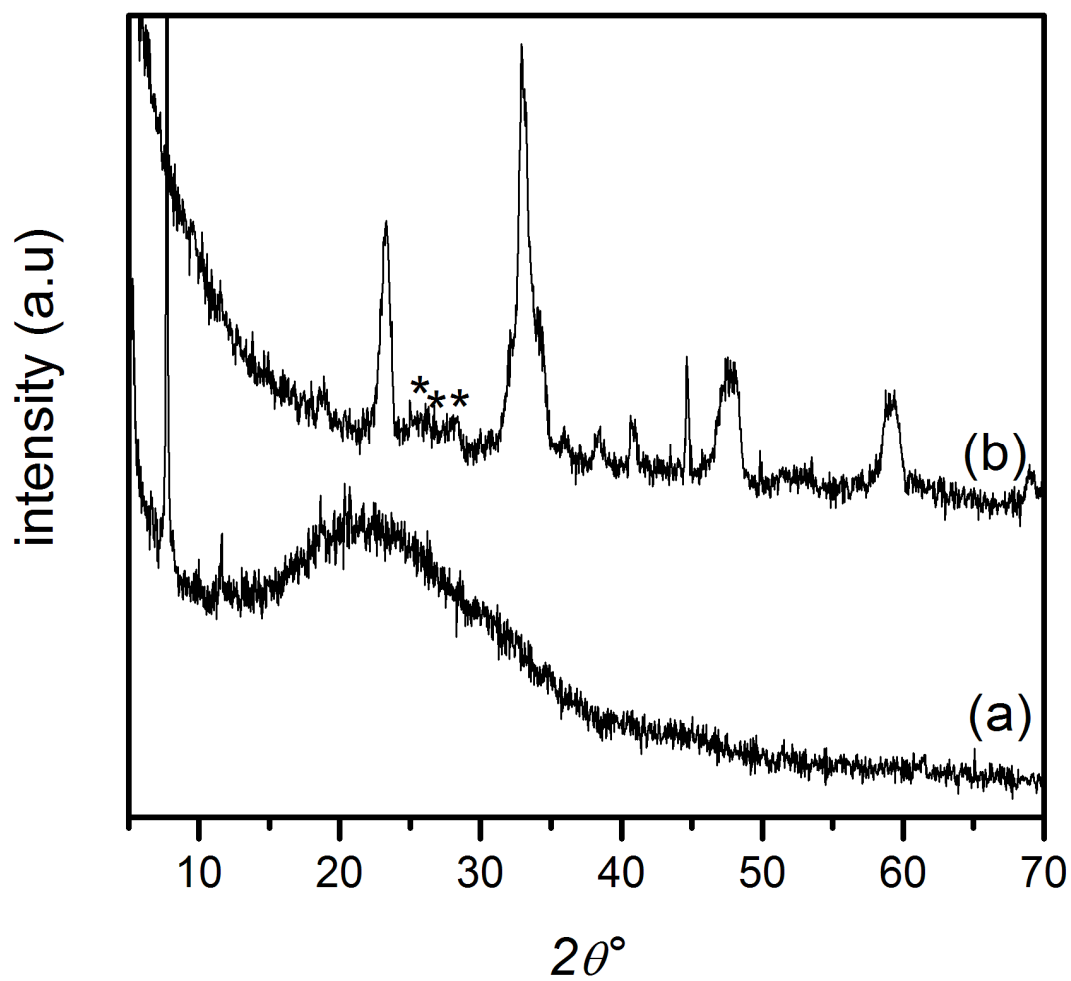

Figure S2. XRD of as prepared CdS nanoparticles (a) and CdS nanoparticles calcinated at 350° C (b).

4. Luminescence decay curves and phase-shift data together with the Instrumental set-up description

The fluorescence lifetimes, τ_F, were measured by a Spex Fluorolog-τ2 system, which uses the phase-modulation technique (excitation wavelength modulated in the 0.5-330 MHz range; time resolution ca.10 ps). The frequency-domain intensity decays (phase angle and modulation Vs. frequency) were analyzed with the Globals Unlimited (rev. 3) global analysis software.[1,2]
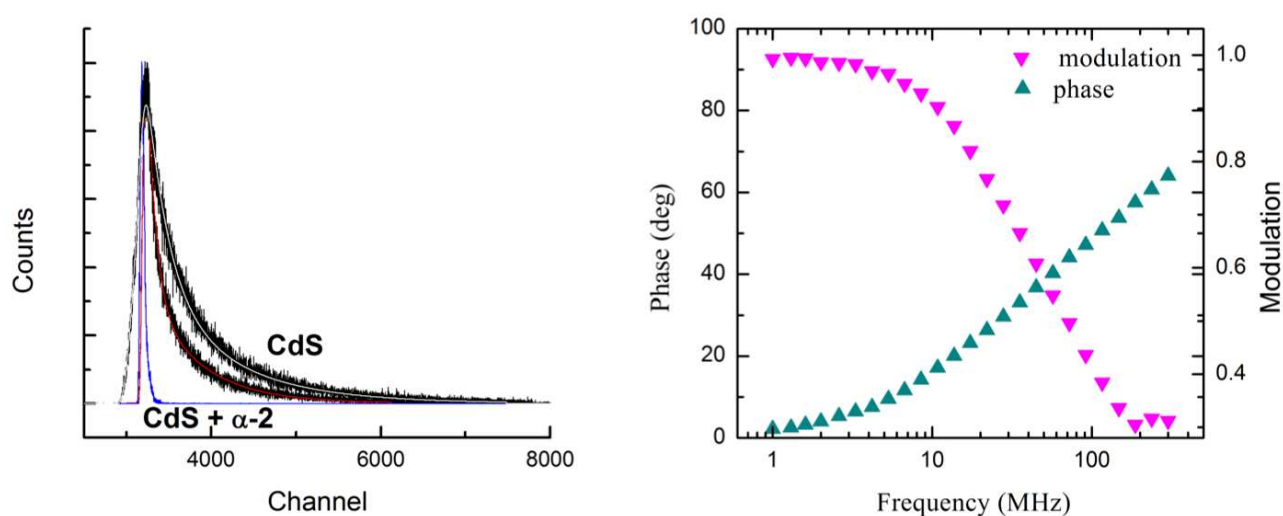

Figure S3. Luminescence decay curves (left panel) CdS nanoparticles recorded (λ_{exc} = 370 nm) in the presence and in the absence of bi-thiophene molecules; phase-shift curves of CdS luminescence (right panel) recorded (λ_{exc} = 370 nm) in the presence of bi-thiophene molecules (6.5×10^{-4} M).

References

1. Beechem, J. M.; Gratton, E.; Ameloot, M.; Kutson, J. R.; Brand, L. Fluorescence Spectroscopy: Vol. 1 Principles and Techniques; Lakowicz, J. R., Ed.; Plenum Press: New York, **1988**; and references therein.

2. Aloisi, G. G.; Elisei, F.; Latterini, L.; Mazzucato, U.; Rodgers, M. A. J. Excited State Behavior of Diarylethenes in the Subnanosecond Timescale: The Role of an Upper Singlet, *J. Am. Chem. Soc.* **1996**, *118*, 10879-10887.

3. Nocchetti, M.; Donnadio, A.; Ambrogi, V.; Andreani, P.; Bastianini, M.; Pietrella, D.; Latterini, L. Ag/AgCl nanoparticle decorated layered double hydroxides: synthesis, characterization and antimicrobial properties, *Mater. Chem. B*, **2013**, *1*, 2383-2393