

Electronic Supplementary Information (ESI)

Enhanced Photovoltaic Performance with Co-Sensitization of Quantum Dots and an Organic Dye in Dye-Sensitized Solar Cells

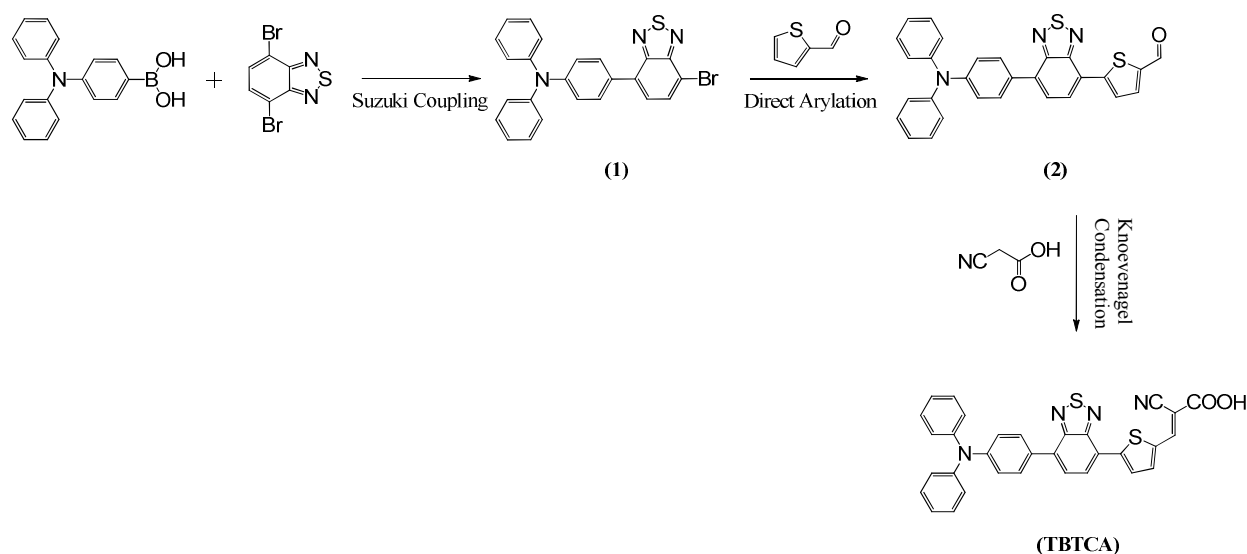
Camilla Lelii,^a Mounji G. Bawendi,^{*b} Paolo Biagini,^{*c} Po-Yen Chen,^d Marcello Crucianelli,^a Julio M. D'Arcy,^d Francesco De Angelis,^a Paula T. Hammond^{*d} and Riccardo Po^c

General Procedures. All reactions were performed using standard glass vessels under an inert nitrogen atmosphere. All the solvents were purchased from Sigma Aldrich and, unless otherwise specified, they have been used without further purification. K₂CO₃ (Carlo Erba), MgSO₄ (Carlo Erba), TiO₂ paste, T/SP - 20 nm (Solaronix), N719 (Solaronix), TBTCA was prepared according to a modification of the literature procedures^{1,2}, while all the other chemicals employed were acquired from Aldrich and they were all used as received.

¹H-NMR spectra were recorded on a 400 MHz Avance (Bruker) in CD₂Cl₂, reference peak: δ(¹H)= 5.30 ppm. UV-Vis Absorption spectra were recorded in solution using quartz cuvettes, 1 cm pathway length, with Agilent Cary 5000 UV-Vis-NIR spectrophotometer, in double beam mode. Fluorescence emission spectra were performed in hexane solution, using a FluoroMax-3 HORIBA Jobyn Ivon. The excitation wavelength was set at 360 nm for QDs and 400 nm for TBTCA. All measurements were performed at room temperature. DCI-MS analysis were carried out on a Finnigan Mat 95S magnetic mass spectrometer, loading a drop of sample solution in CH₂Cl₂ on the metal emitter placed on the top of a direct insertion probe.

Synthesis and characterization of 2-cyano-3-{5-[7-(4-diphenylamino-phenyl)benzo[1,2,5]thiadiazol-4-yl]-thiophen-2-yl}-acrylic acid (TBTCA)

TBTCA was synthesized through multistep reaction modifying the methods reported in literature.^{1,2}



Scheme S1. Synthetic steps of TBTCA dye

[4-(7-Bromo-benzo[1,2,5]thiadiazol-4-yl)-phenyl]diphenylamine (1) In a three neck flask containing 4,7-dibromobenzo[1,2,5]thiadiazole (6.63 g, 22.6 mmol) in toluene (80 ml), an aqueous solution (80ml) of K_2CO_3 (20.73 g, 150 mmol) was added and the mixture was degassed. Then a degassed solution of N,N-diphenyl-4-aminophenylboronic acid (4.34 g, 15.0 mmol) in n-propanol (50 ml) was added under nitrogen flux. Finally $\text{Pd}(\text{Ph}_3)_4$ (0.36 g, 0.3 mmol) was added and the mixture was refluxed overnight. When the reaction was completed, water was added to quench the reaction. The product was extracted with CH_2Cl_2 (3 x 25 ml), the organic layer was collected, dried over anhydrous MgSO_4 and evaporated under vacuum. The crude solid was purified by flash chromatography with n-heptane/ CH_2Cl_2 (70:30, v:v) as eluent, obtaining 3.20 g (47% yield) of **(1)** as dark yellow solid. ^1H NMR (400 MHz, CD_2Cl_2 , δ): 7.89 (d, 1H), 7.81 (d, 2H), 7.55 (d, 1H), 7.31-7.27 (t, 4H), 7.14 (d, 6H), 7.09-7.05 (t, 2H).

5-[7-(4-Diphenylamino-phenyl)-benzo[1,2,5]thiadiazol-4-yl]thiophene-2-carbaldehyde (2) K_2CO_3 (0.430 g, 3.1 mmol), $\text{Pd}(\text{OAc})_2$ (0.009 g, 0.04 mmol), $\text{PCy}_3 \cdot \text{HBF}_4$ (0.044 g, 0.12 mmol), pivalic acid (0.031, 0.30 mmol) and **(1)** (0.95, 2.07 mmol) were placed in a screw-capped vial equipped with a magnetic stirring bar and purged with nitrogen. Then toluene (20 ml) and 2-thiophenecarboxaldehyde (0.5 ml, 5.35 mmol) were added. The reaction mixture

was vigorously stirred at 110°C for 16 h. then the mixture was cooled to room temperature, diluted with CH₂Cl₂ and H₂O. The aqueous phase was extracted with CH₂Cl₂, dried over anhydrous MgSO₄ and evaporated in vacuum. The crude product was purified by flash chromatography, with n-heptane/EtOAc (90:10, v:v) as eluent, affording 0.52 g (51% yield) of **(2)** as orange solid.

¹H NMR (400 MHz, CD₂Cl₂, δ): 9.95 (s, 1H); 8.20 (d, *J*_{HH} = 7.5 Hz, 1H), 8.08 (d, *J*_{HH} = 8.9 Hz, 2H), 7.91 (d, *J*_{HH} = 3.9 Hz, 1H), 7.76 (d, *J*_{HH} = 7.5 Hz, 1H), 7.30 (t, *J*_{HH} = 7.9 Hz, 4H), 7.16 (d, *J*_{HH} = 8.6 Hz, 6H), 7.10 (t, *J*_{HH} = 7.3 Hz, 2H).

2-cyano-3-{5-[7-(4-diphenylamino-phenyl)benzo[1,2,5]thiadiazol-4-yl]-thiophen-2-yl}-acrylic acid (TBTCA). To a flask containing **(2)** (0.47 g, 0.96 mmol), cyanoacetic acid (0.14 g, 1.65 mmol) and piperidine (0.4 ml, 4.05 mmol), acetonitrile was added (50 ml). The mixture was refluxed, under nitrogen atmosphere, overnight. Then the mixture was cooled at room temperature and HCl 1 M (15 ml) was added and a dark powder precipitated off. The solid was recovered by filtration, then it was washed with water, diethyl ether and MeOH and finally dried under vacuum obtaining 0.42 g (79% yield) of **TBTCA** as a dark violet solid.

Anal. calcd for C₃₂H₂₀N₄O₂S₂: C 69.04, H 3.62, N 10.06, S 11.52; found: C 67.2, H 3.48, N 9.46, S 11.11. ¹H NMR (400 MHz, DMSO-*d*₆, δ): 8.63 (s, 1H), 8.44 (d, *J*_{HH} = 7.6 Hz 1H), 8.38 (d, *J*_{HH} = 4.1 Hz, 1H), 8.19 (d, *J*_{HH} = 4.1 Hz, 1H), 8.08 (d, *J*_{HH} = 8.8 Hz, 2H), 8.03 (d, *J*_{HH} = 7.6 Hz, 1H), 7.45-7.41 (t, *J*_{HH} = 7.9 Hz, 4H), 7.20-7.16 (m, 8H). DCI-MS *m/z* (%): 512.9 (60) [M⁺ – CO₂], 556.9 (100) [M⁺].

Electrochemical Characterization of TBTCA

The cyclic voltammetric (CV) characterization was carried out using an Autolab PGSTAT 12 potentiostat/galvanostat (EcoChemie, The Netherlands) run by a PC with GPES software. The dye TBTCA was analyzed as a film drop coated onto the working electrode from 1,2-dichlorobenzene solution 1·10⁻³ M, using acetonitrile solvent (Carlo Erba, HPLC grade) with 0.1 M tetrabutylammonium tetrafluoroborate TBATFB (Fluka, electrochemical grade) as

supporting electrolyte, and were deaerated with argon purging. The working cell included a Glassy Carbon GC disk embedded in Teflon® (Amel, surface 0.071 cm²); a Platinum counter electrode (Metrohm); and an aqueous saturated calomel electrode (SCE, Amel) as the reference electrode. According to IUPAC recommendations the data have been referred to the Fc⁺/Fc redox couple (ferricinium/ferrocene), having a formal potential of 0.390 V vs our operating reference electrode.

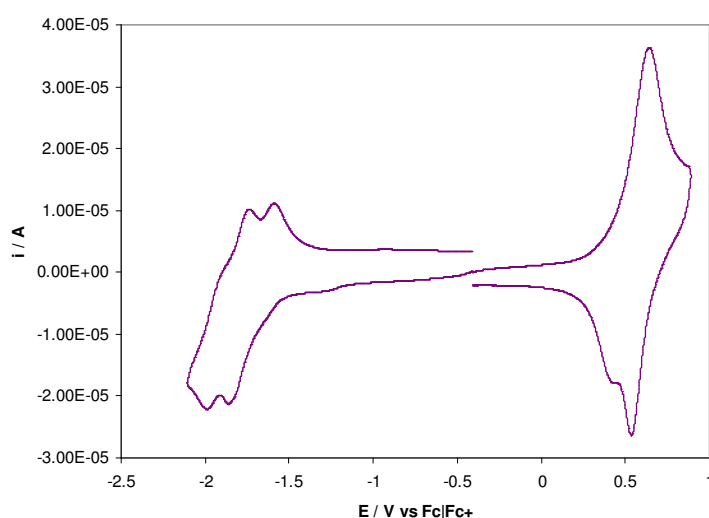


Figure S1. Voltammogram of TBTCA, v scan 200 mV/s

E_{HOMO} : -5.17 eV

E_{LUMO} : -3.27 eV

BG: 1.90 eV

Spectroscopic Characterization of TBTCA

Absorption spectra of TBTCA were recorded in solution using quartz cuvettes 1 cm pathway length, with UV-Vis Perkin Elmer mod. LAMBDA 950 spectrophotometer, in double beam mode. Measurements were performed at room temperature.

Fluorescence emission spectra were performed using a HORIBA Jobin Yvon Fluorolog 3.

Measurements were performed at room temperature.

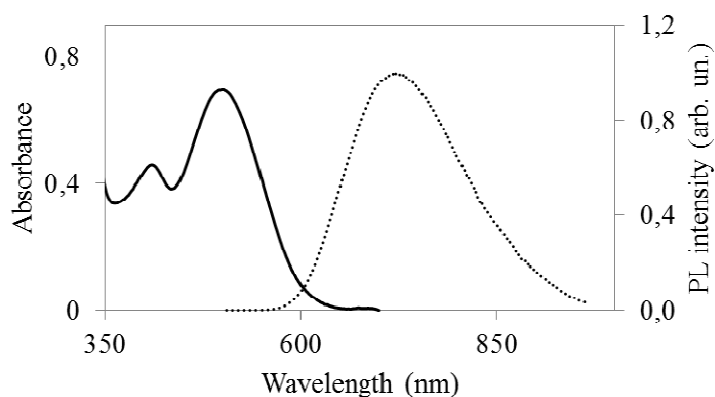


Figure S2. Absorption (bold line) and emission (dotted line) spectra of TBTCA in dichloromethane solution.

UV-VIS (CH_2Cl_2) absorption: $\lambda_{\text{max}}/\text{nm} = 309, 422, 501$ $\epsilon(\lambda=501 \text{ nm})/\text{mol}^{-1}\text{cm}^{-1} = 17790$;

emission $\lambda_{\text{max}}/\text{nm} = 720$

Spectroscopic Characterization of N719

Absorption spectra of N719 were recorded in solution using quartz cuvettes 1 cm pathway length, with UV-Vis Perkin Elmer mod. LAMBDA 950 spectrophotometer, in double beam mode. Measurements were performed at room temperature.

Fluorescence emission spectra were performed using a HORIBA Jobin Yvon Fluorolog 3.

Measurements were performed at room temperature.

N719 exhibits very low photoluminescence emission (Fig. S3) and the spectrum could appear artificial, hence we show only the maximum of emission.

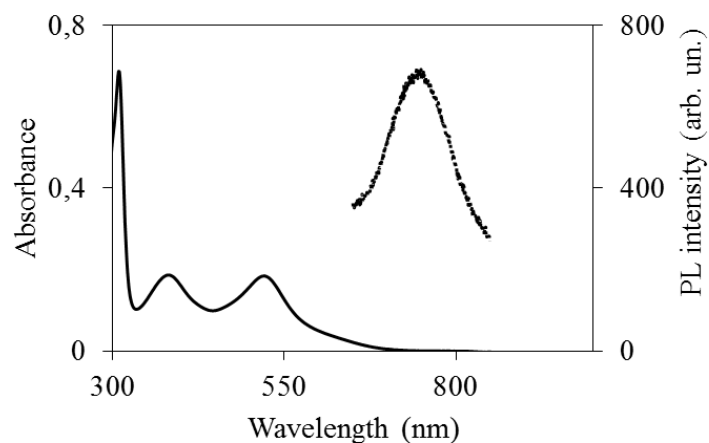


Figure S3. Absorption (bold line) and emission (dotted line) spectra of N719 in Ethanol solution.

Spectroscopic Characterization of CdSe₄₉₅ and CdSe₅₄₅

Absorption spectra of QDs were recorded in solution using quartz cuvettes 1 cm pathway length, with Agilent Cary 5000 UV-Vis-NIR spectrophotometer, in double beam mode.

Measurements were performed at room temperature.

Fluorescence emission spectra were performed using a FluoroMax-3 HORIBA Jobyn Ivon.

Measurements were performed at room temperature.

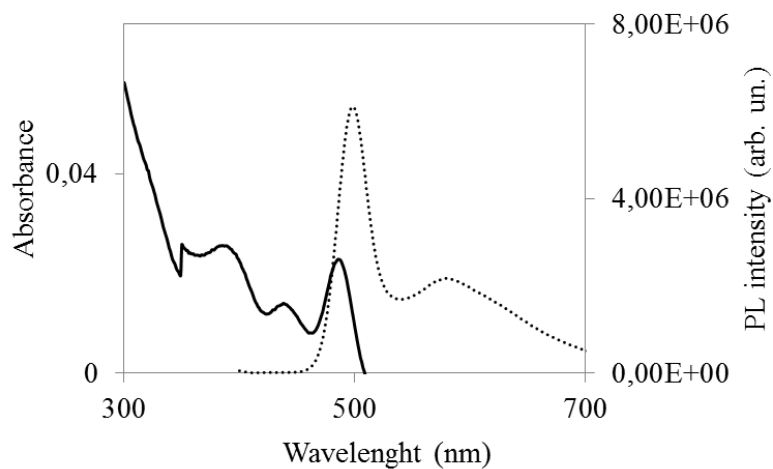


Figure S4. Absorption (bold line) and emission (dotted line) spectra of CdSe₄₉₅ in hexane solution.

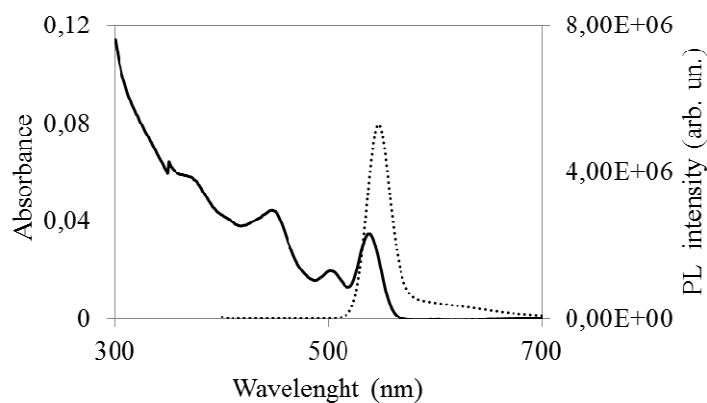


Figure S5. Absorption (bold line) and emission (dotted line) spectra of CdSe₅₄₅ in hexane solution.

Characterization of QDs/TiO₂ film

Transmission Electron Microscopy – Energy Dispersive Spectroscopy (TEM – EDS)

Preparation of the sample: CdSe-sensitized TiO₂ electrode was scratched to a vial containing ethanol (1-2 mL) and sonicated for 5 min. Few drops of this solution were applied to a formvar/carbon coated copper grid 400 mesh and dried in air. TEM imaging analysis was performed using JEOL JEM-2100F Field Emission Electron Microscope at 200 kV accelerating voltage and illumination angle $\alpha=1$.

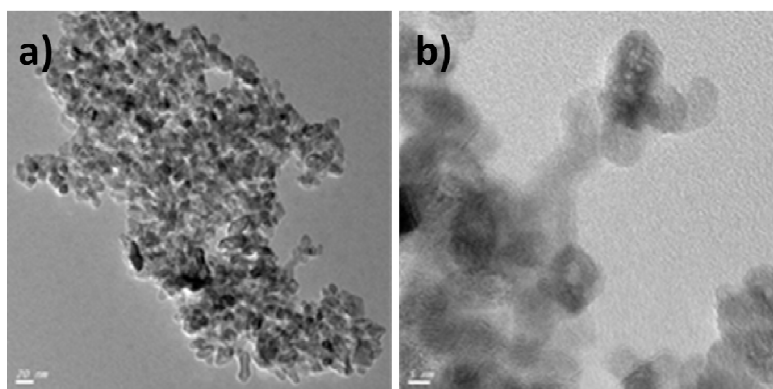


Figure S6. TEM images of TiO₂ film sensitized with CdSe quantum dots. a) entire sample of TiO₂ film scratched from the conductive FTO glass and suspended in EtOH; b) magnification of the sample shown in a.

It is not possible to identify CdSe nanocrystals from TEM images (Fig. S6). Only using EDS tool we can detect Cd and Se peaks though they are very tiny. EDS spectrum is shown in the figure S7: Copper peaks are due to the grid used as support for TEM experiments.

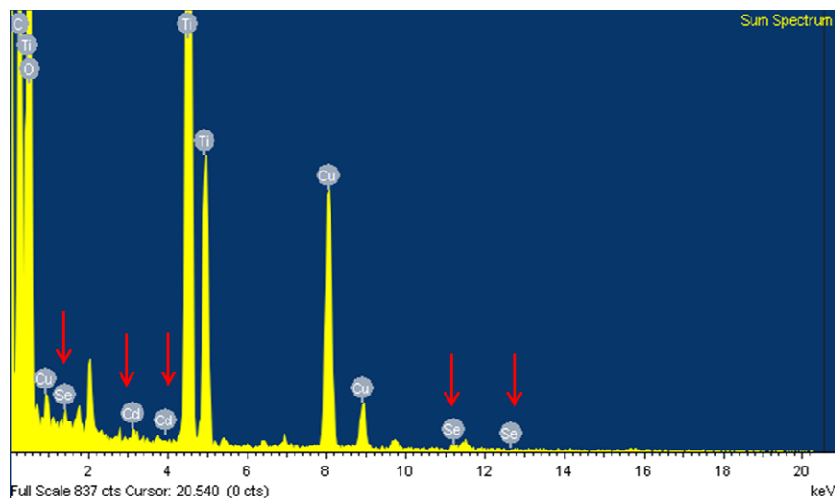


Figure S7. EDS spectrum of TiO₂ film sensitized with CdSe quantum dots.

Cd and Se peaks (indicated by red arrows) are very tiny compared to Ti and O ones. Copper signals are due to the grid used for TEM analysis.

Moreover, with EDS tool, it is possible mapping Cd and Se elements on the overall sample as shown in Fig. S8.

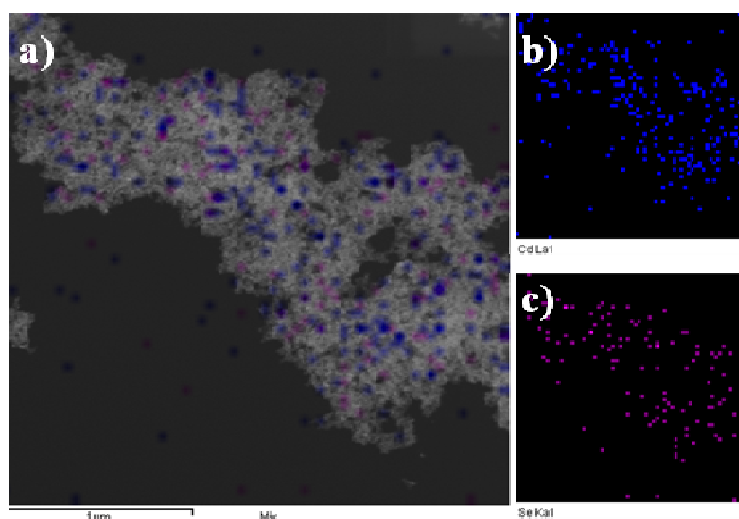


Figure S8. Map of Cd and Se atoms on TiO₂ through EDS analysis. a) map of Cd and Se over TEM image of the sample; b) map of Cd; c) map of Se.

X-Ray Photoelectron Spectroscopy (XPS)

The experiments were performed on TiO₂ film with PHI VersaProbe II XPS. X-ray source was monochromatic Al K alpha, 200um spot size, 50W; The error associated to each measure is about 10% of the value.

Surface Analysis

Survey analyzer pass energy: 187.85 eV, step size: 0.8 eV.

XPS spectra (Fig. S9) of two different points of the surface are similar and clearly show Cd peaks; Se3d peak overlaps a minor Ti3s one.

The Table S1 below summarizes the percentage of the elements detected.

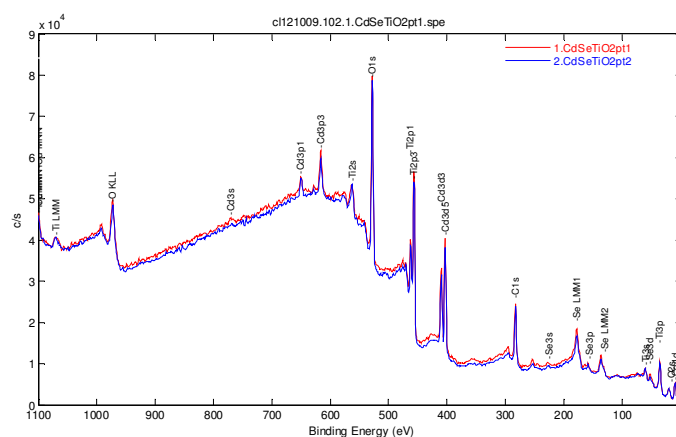


Figure S9. XPS spectrum performed on the surface of TiO₂ film sensitized with CdSe.

Spectra of the point 1 (red line) and point 2 (blue line).

Table S1. Atomic concentration on the surface of TiO₂ film sensitized with CdSe quantum dots.

	C1s	O1s	Ti2p	Se3d	Cd3p3
Point 1 surface (%)	33.80	43.74	15.12	1.20	6.15
Point 2 surface (%)	33.65	44.88	15.03	0.82	5.62
Mean (atomic %)	33.72	44.31	15.07	1.01	5.88
Standard Deviation	0.11	0.81	0.06	0.27	0.37

Depth Profile

Depth profile analysis was performed sputtering high energy Ar^+ ions on the sample over the time. Total depth profile to reach glass: 220 min at $I_{\text{gun}} = 4\text{kV}$, $3\mu\text{A}$, $2\times 2\text{ mm}$ raster.

Analyzer pass energy 117.40 eV; step size 0.5 eV.

Spectral data (Fig. S10) obtained from point 1 after 10 minutes sputter and table of atomic concentration (Table S2) are shown below.

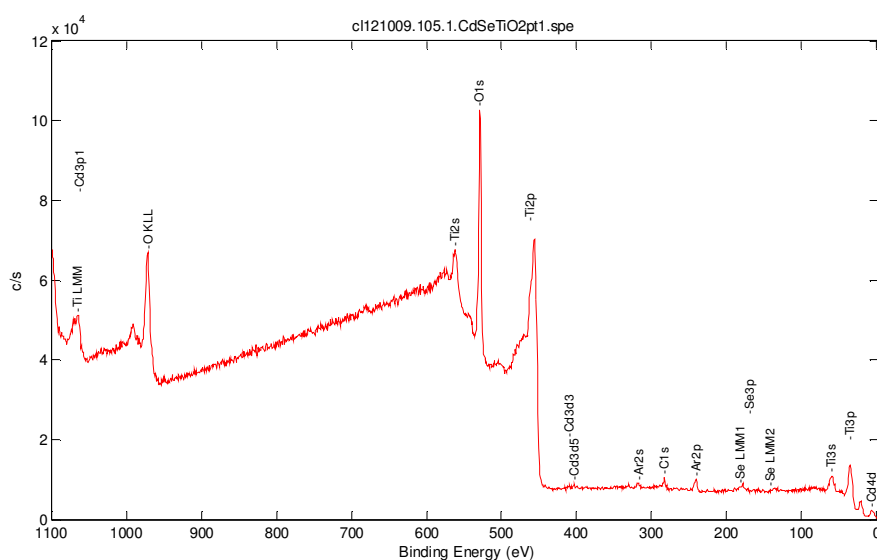


Figure S10. XPS spectrum performed on TiO_2 film sensitized with CdSe quantum dots after 5 minutes sputter.

Spectrum shows strong Ti and O; trace of C, Cd and Se, as also summarized by the atomic percentage (Table S2)

Table S2 Atomic concentration of the TiO_2 film sensitized with CdSe quantum dots after 10 minutes of sputtering

	C1s	O1s	Ti2p	Se3p3	Cd3d5
Atomic %	6.18	64.26	29.41	0.08	0.08

Electrical Characterization of solar devices.

Photovoltaic measurements were performed using an AM 1.5 solar simulator (Photo Emission Tech.). The power of the simulated light was calibrated to 100 mW cm^{-2} by using a reference

silicon photodiode with a power meter (1835-C, Newport) and a reference silicon solar cell to reduce the mismatch between the simulated light and AM 1.5. I–V curves were obtained by applying an external bias to the cell and measuring the generated photocurrent with a Keithley model 2400 digital source meter. The voltage step and delay time of photocurrent were 10 mV and 40 ms, respectively.

Table S4 shows the photovoltaic parameters of solar devices. The values are an average on a set of four devices per each sensitizer, made in different days. They confirm that the best values reported on the paper are consistent with the mean.

Table S4. Photovoltaic parameters average values of DSSCs and QDDSSCs

Entry	Sensitizer	J_{SC} (mA/cm ²)	V_{OC} (V)	FF	η (%)
1	N719	13.1 ± 0.5	0.76 ± 0.01	0.69 ± 0.03	7.0 ± 0.6
2	N719–CdSe495	10.6 ± 0.8	0.70 ± 0.04	0.73 ± 0.02	5.9 ± 0.7
3	N719–CdSe545	10.0 ± 1.0	0.67 ± 0.01	0.74 ± 0.02	5.0 ± 0.6
4	TBTCA	8.1 ± 0.4	0.633 ± 0.003	0.74 ± 0.03	3.8 ± 0.2
5	TBTCA–CdSe495	9.2 ± 0.6	0.67 ± 0.01	0.75 ± 0.01	4.7 ± 0.4
6	TBTCA–CdSe545	7.7 ± 0.5	0.643 ± 0.004	0.74 ± 0.02	3.6 ± 0.3

References

- 1 M. Velusamy, K. R. J. Thomas, J. T. Lin, Y. -C. Hsu and K. -C. Ho, *Org. Lett.*, 2005, **7**, 1899.
- 2 D. J. Schipper and K. Fagnou, *Chem. Mater.*, 2011, **23**, 1594.