ELECTRONIC SUPPLEMENTARY INFORMATION

Synthesis and Dye Sensitized Solar Cell Applications of Bodipy Derivatives with Bis-dimethylfluorenyl Amino Donor Groups

Yusuf Çakmak, *[a] Safacan Kolemen,[a] Muhammed Buyuktemiz,[b] Yavuz Dede,[b] Sule Erten-Ela,*[c]

[a]Department of Chemistry, Bilkent University, Ankara, 06800, Turkey

[b] Department of Chemistry, Faculty of Science, Gazi University, Teknikokullar, Ankara 06500, Turkey

[c]Institute of Solar Energy, Ege University, Izmir, 35100, Turkey. TEL: 0090 232 3111231; E-mail: suleerten@yahoo.com

COMPUTATIONAL DETAILS

Electronic structure analysis of dyes **TB6** and **TB7** were performed with Density Functional Theory[3-6] employing the B3LYP[5-11], functional and Stevens-Basch-Krauss split valence efective core potentials (ECP) CEP-31G.[13] This level of theory was previously shown to yield reasonable results for similar systems.[14-15] For both cases, symmetry is turned off and unrestricted DFT formalism is followed. Spin contaminations of the Kohn Sham wave functions were checked and found to be negligible in all cases. Harmonic vibrational frequency calculations ensured that Hessian matrix does not contain any negative eigenvalue, i.e. all reported geometries correspond to minimum points on the potential energy surface. Excitations were studied with the TD-DFT formalism. The Polarizable Continuum Model (PCM) is used to model the dielectric medium of methanol solvent. Computations were carried out using Gaussian 09[16]. Molecular orbitals are plotted using 0.3 iso-value.

DEVICE FABRICATION:

The construction of the dye sensitized solar cell device requires first cleaning of the fluorine doped tin oxide (FTO) coated glass substrates in acetone and isopropanol by using an ultrasonic bath. FTO (SnO2:F, Pilkington TEC-15; Rsheet:15O/&), electrically conductive oxide-coated glasses were used as transparent electrodes. TiO_2 electrodes consist of an adsorbent mesoporous layer with 20 nm anatase TiO_2 particle size in 7 mm thicknesses and a second light scattering layer with 400 nm anatase TiO_2 particle size of 5 mm thicknesses. Dye solutions were prepared in chlorobenzene-methanol (1:1) mixture with a concentration of 0.5 mM BODIPY. TiO_2-coated electrodes, after sintering at 450^0C for 30 min and cooling to 100^0C, were kept overnight in BODIPY solutions for adsorption. BODIPY adsorbed TiO_2-coated glasses were washed with pure chlorobenzene and dried *in vacuo*. Platinized FTO glasses were used as counter electrode. Platinization of counter electrodes were done by coating of FTO glasses with 1% solution of hydrogen hexachloroplatinate (Aldrich) in 2-propanol and annealing at 400^0C for 30 min. Cells were prepared in sandwich geometry. Surlyn-1702 (DuPont) frame was used as a spacer and a thermoplastic sealant between the two electrodes. Cells prepared in this way were then sealed by heating at 100^0C. Electrolyte was filled into the space created by Surlyn-1702 between the electrodes under vacuum using a small hole pre-drilled on the counter electrode with the help of a diamond drill. After filling the electrolyte, a small hole was sealed again using a piece of Surlyn-1702 and a piece of cover glass. The electrolyte consisted of 0.6M N-methyl-N-butyl-imidazolium iodide (BMII) + 0.1 M LiI + 0.05 M I_2 + 0.5 M 4-*tert*-butylpyridine (TBP) in acetonitrile/valeronitrile (85/15 v/v). Active areas of the cells were adjusted to 0.159 cm^2 with a special mask. Dye sensitized solar cells were characterized by current-voltage ($J-V$) measurement. All current-voltage measurements ($J-V$) were done under 100 mW/cm^2 light intensity and AM 1.5 conditions. 450 W Xenon light source (Oriel) was used to give an irradiance of various intensities. The spectral output of the lamp was matched in the region of 350–700 nm with the aid of Schott K113 Tempax sunlight filter. $J-V$ data collection was made by using Keithley 2400 Source-Meter and LabView data acquisition software. The incident

photon-to-current conversion efficiencies (IPCE) were taken in the equipment of QE-R Enlitech. All of the dye scan efficiently convert visible light to photocurrent in the region from 300 nm to 700 nm.
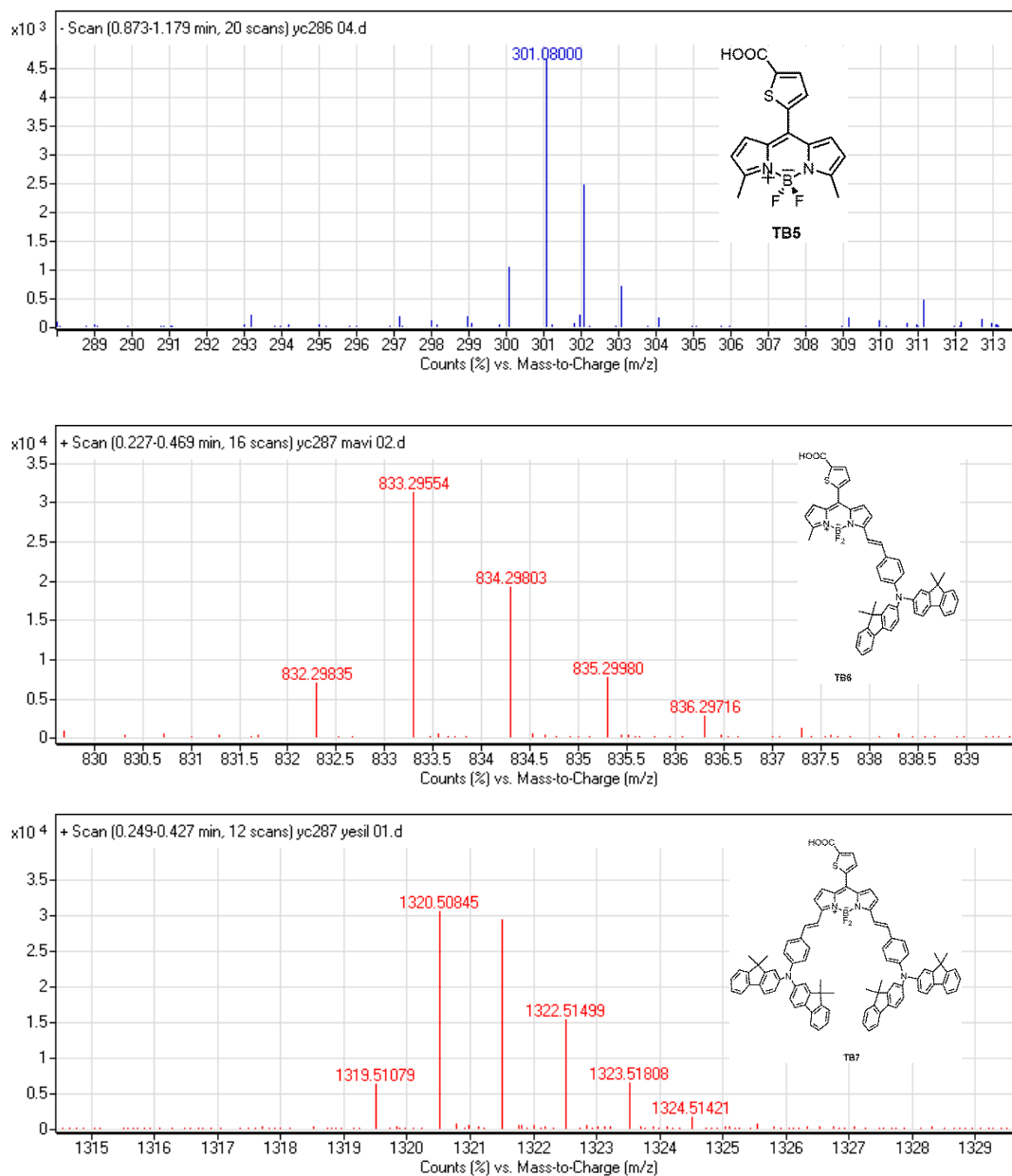
SYNTHETIC CHARACTERIZATION

Mass Spectra

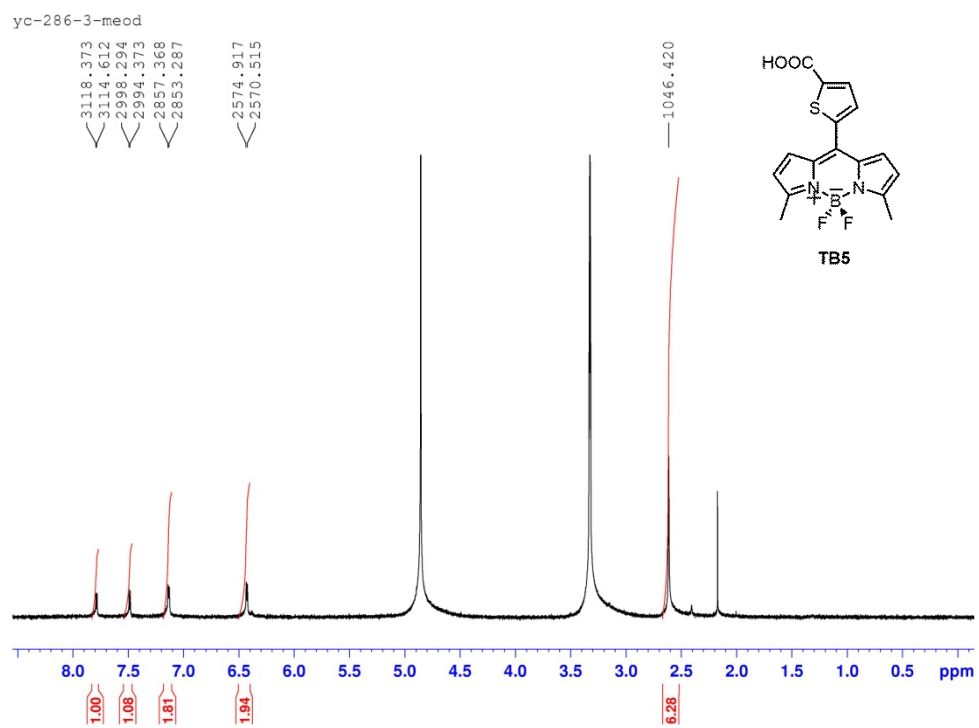Figure S1: Mass Spectra of TB5, TB6, TB7

¹H and ¹³C NMR Spectra

yc-286-3-meod

3118.373
3114.612
2998.294
2994.373
2857.368
2853.287
2574.917
2570.515
1046.420

HOOC

TB5

8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 ppm

1.00 1.08 1.81 1.94 6.28
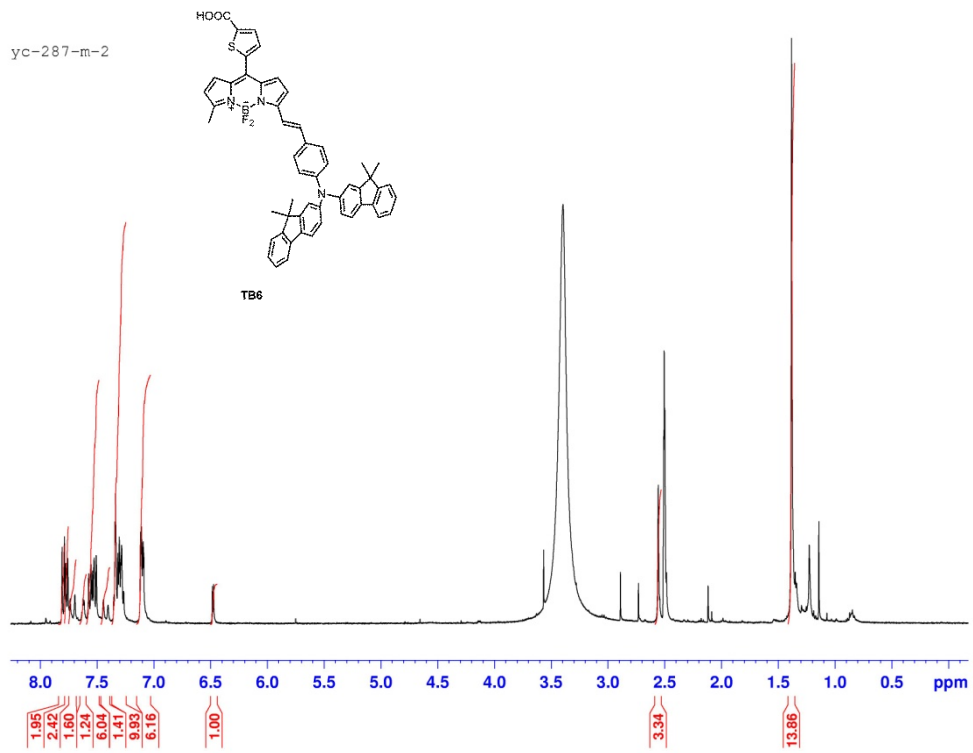
Figure S2: ¹H NMR Spectrum of TB5

yc-287-m-2

TB6
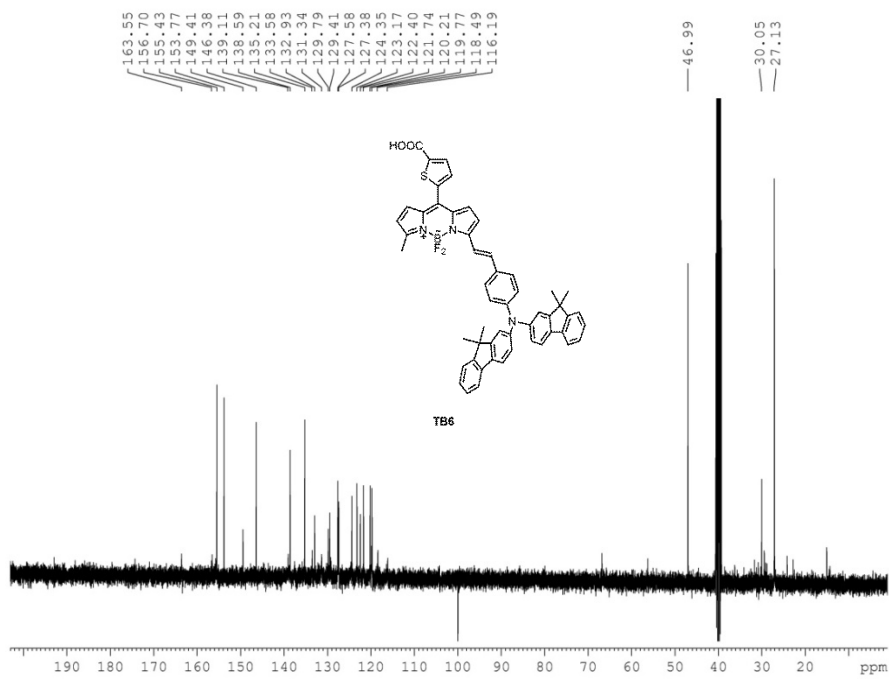
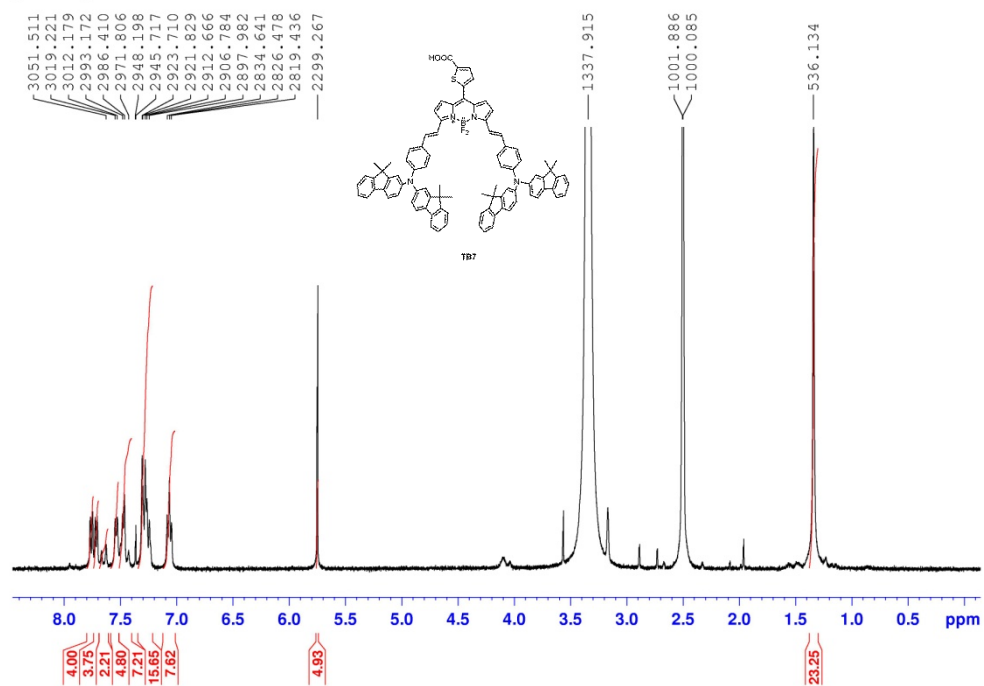Figure S3: ^{1}H NMR and ^{13}C Spectra of TB6

yc-287-y-2
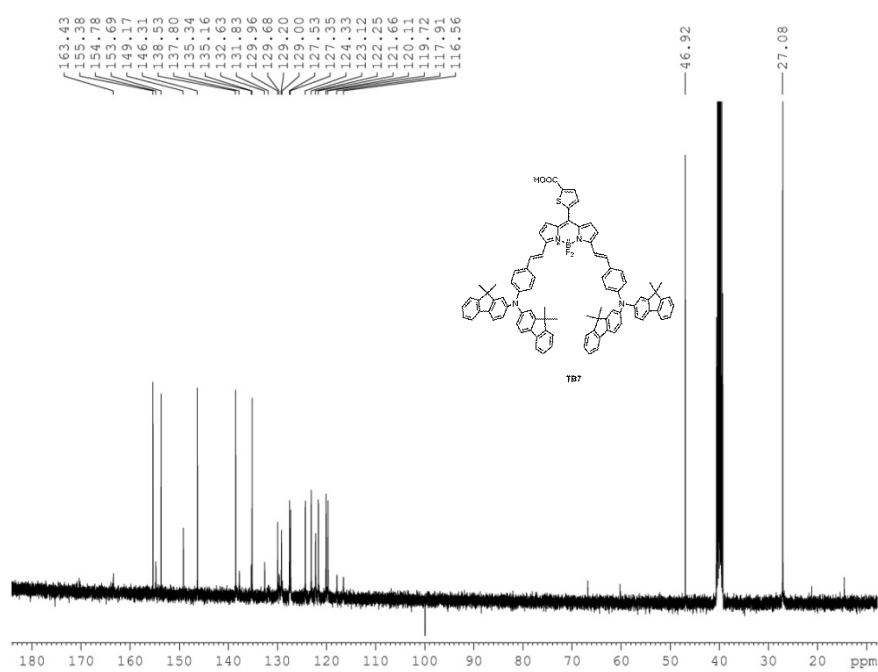
Figure S4: ^{1}H NMR and ^{13}C Spectra of TB7
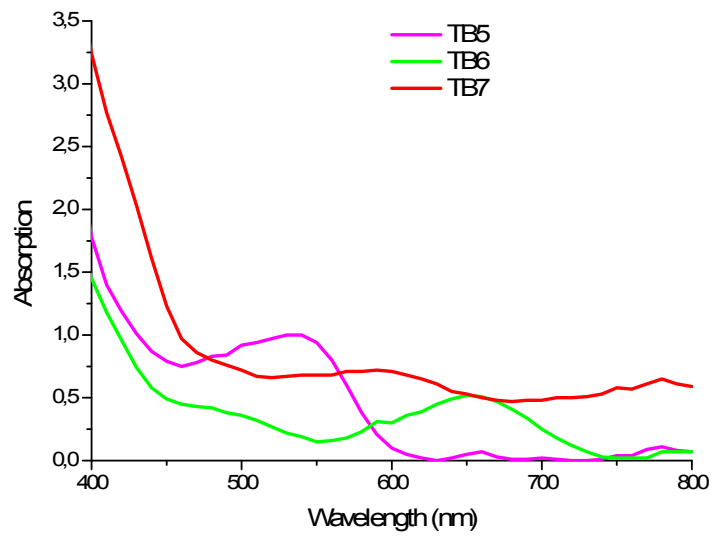
CHARACTERIZATION OF DSSC

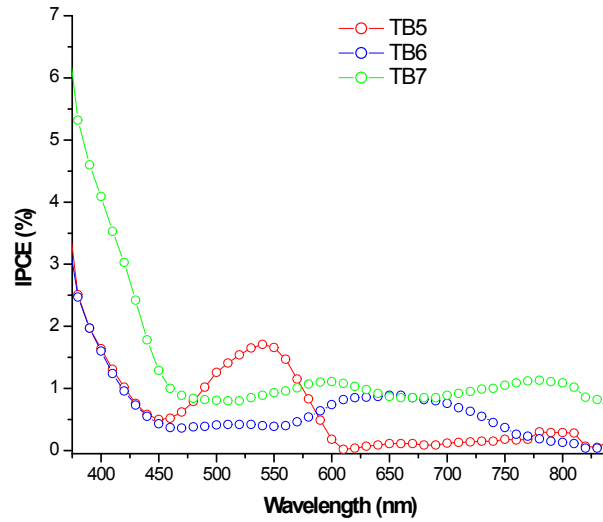Figure S5: Absorption Spectra of dyes absorbed on TiO$_2$

Figure S6. Incident photon to current conversion efficiencies as a function of wavelength for the liquid electrolyte based DSSCs.
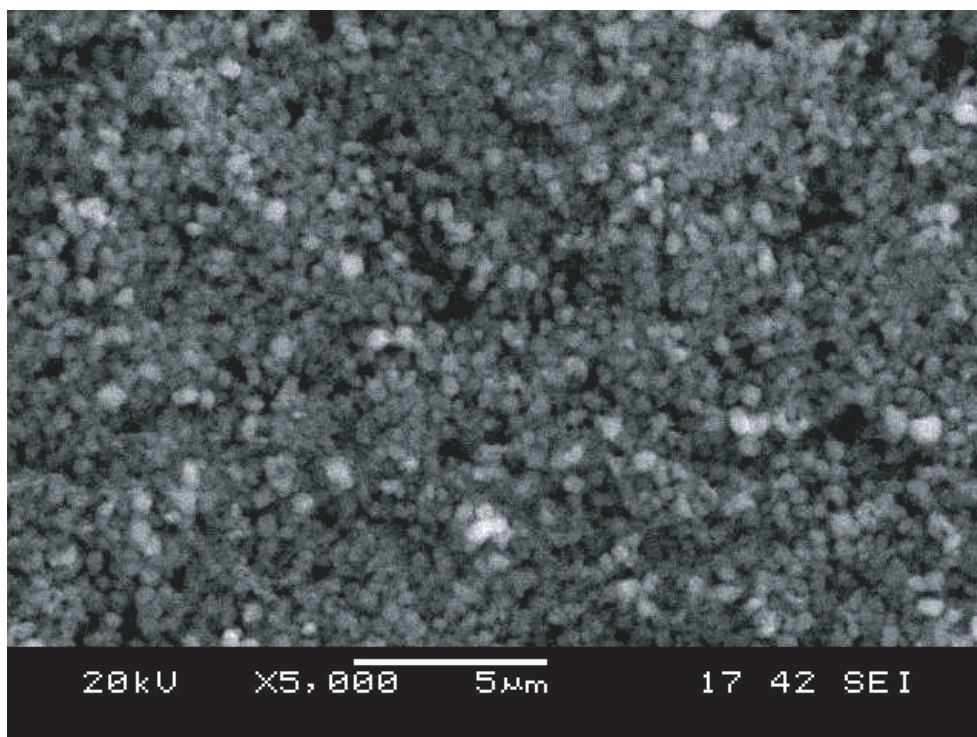
Figure S7. Scanning electron microscopy image (SEM) of TiO$_2$ Electrode

SEM images of TiO$_2$ electrode was given in Figure S7. Both sensitizers have been used to manufacture solar cell devices to explore current-voltage characteristics using 7(transparent) + 5(scattering) μm TiO$_2$ transparent layers. Preparation and characterization of double-layer TiO$_2$ electrode are previously described by Wang et al.[16]

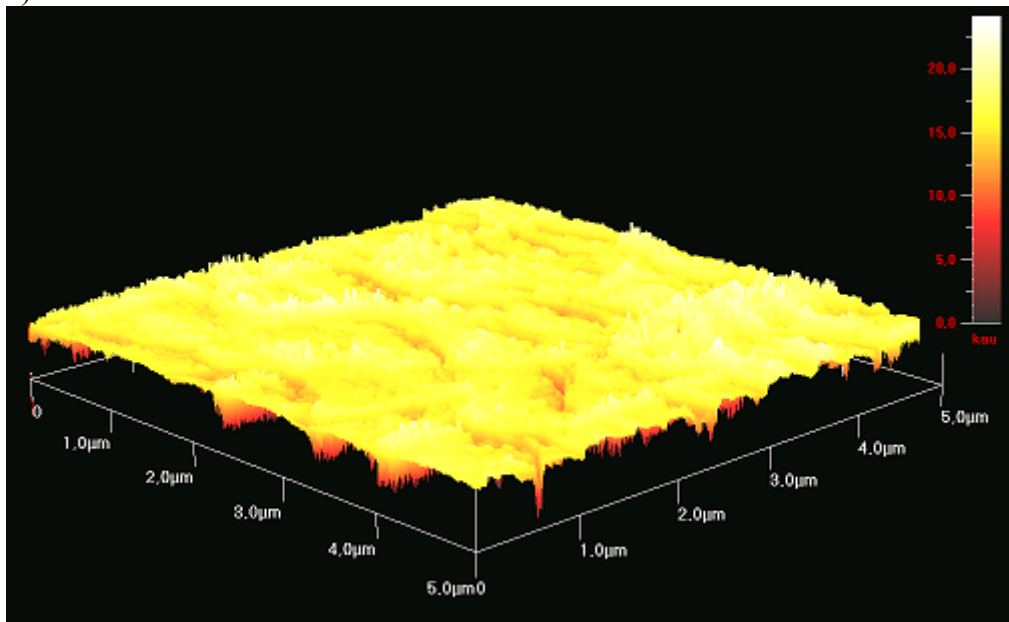***Atomic Force Microscopy Images of the Films***

Morphology of the films were observed by Atomic Force Microscopy using Ambios AFM equipment. Atomic force microscopy (AFM) is used to observe film surface morphology of TiO$_2$ (a), TB5 on TiO$_2$ (b), TB6 on TiO$_2$ (c), TB7 on TiO$_2$ (d). AFM images of films in noncontact mode are presented in Fig. S7.
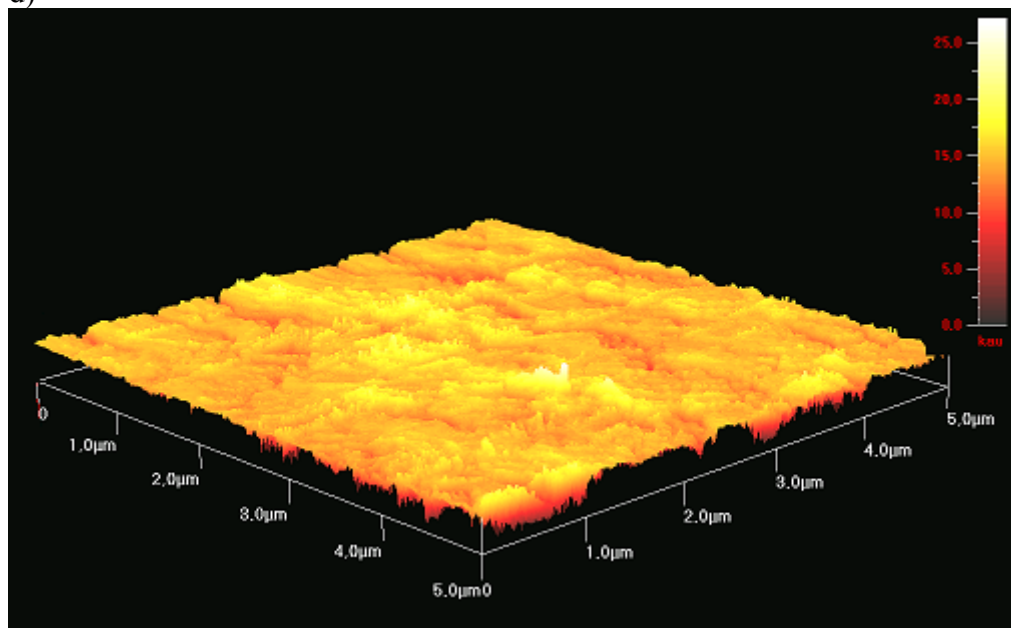

a)
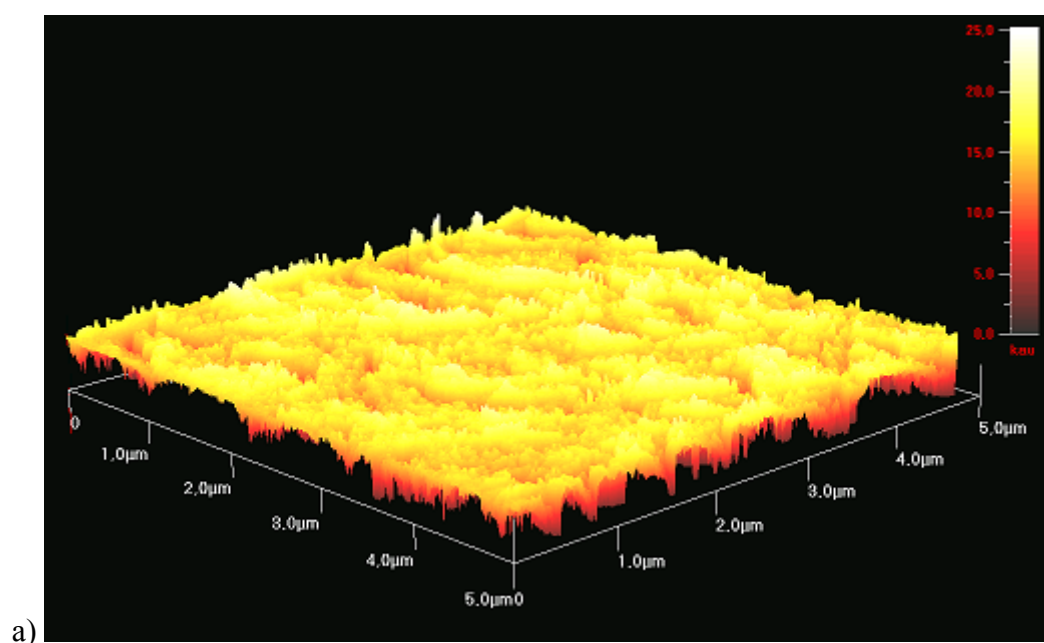
b)
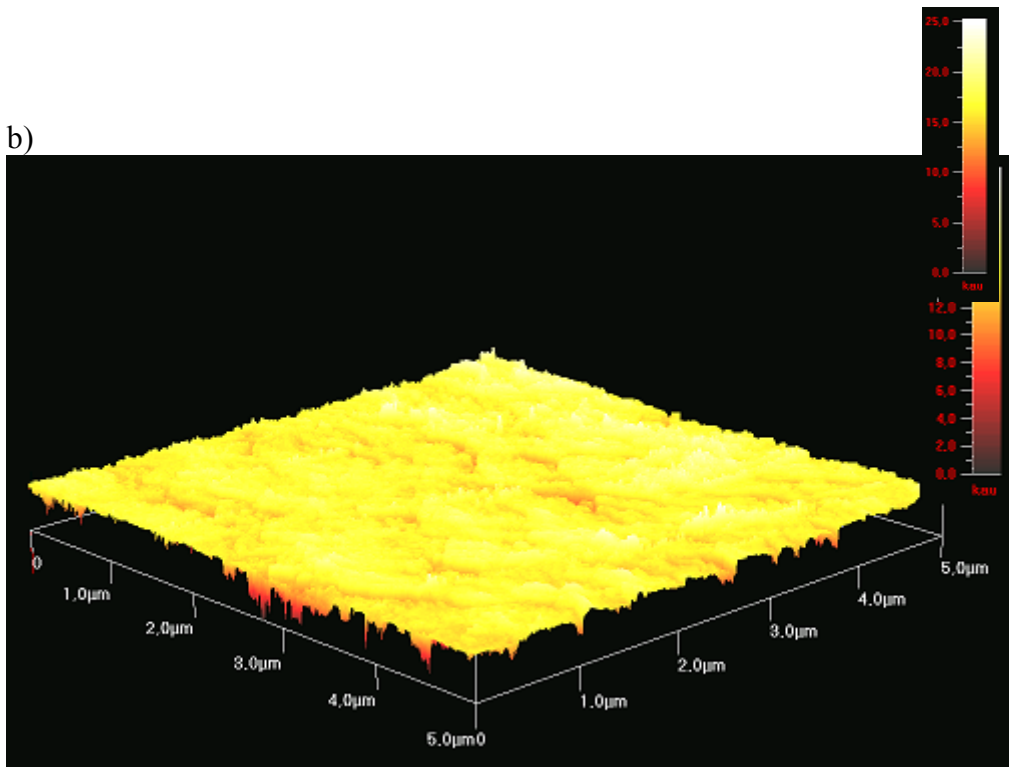
c)

d)

Figure S7. AFM images of mesoporous TiO$_2$ (a), TB5 on TiO$_2$ (b), TB6 on TiO$_2$ (c), TB7 on TiO$_2$ (d)

References

1   Kohn, W., Becke, A. D. & Parr, R. G. Density functional theory of electronic structure. *J. Phys. Chem.* **100**, 12974-12980 (1996).

2   Parr, R. G. & Yang, W. *Density Functional Theory of Atoms and Molecules*. (Oxford University Press, 1989).

3   Becke, A. D. Density-Functional Thermochemistry. 3. The Role of Exact Exchange. *J. Chem. Phys.* **98**, 5648-5652 (1993).

4   Becke, A. D. Density-Functional Exchange-Energy Approximation With Correct Asymptotic-Behavior. *Phys. Rev. A* **38**, 3098-3100 (1988).

5   Lee, C. T., Yang, W. T. & Parr, R. G. Development of the Colle-Salvetti Correlation-Energy Formula Into a Functional of the Electron-Density. *Phys. Rev. B* **37**, 785-789 (1988).

6   Slater, J. C. *Quantum Theory of Molecules and Solids, Vol. 4: The Self-Consistent Field for Molecules and Solids*. (McGraw-Hill, 1974).

7   Vosko, S. H., Wilk, L. & Nusair, M. Accurate Spin-Dependent Electron Liquid Correlation Energies for Local Spin-Density Calculations - a Critical Analysis. *Can. J. Phys.* **58**, 1200-1211 (1980).

8   Stephens, P. J., Devlin, F. J., Chabalowski, C. F. & Frisch, M. J. Ab Initio Calculation of Vibrational Absorption and Circular Dichroism Spectra Using Density Functional Force Fields doi:10.1021/j100096a001. *J. Phys. Chem.* **98**, 11623-11627 (1994).

9   Hertwig, R. H. & Koch, W. On the parameterization of the local correlation functional. What is Becke-3-LYP? *Chem. Phys. Lett.* **268**, 345-351 (1997).

10   Stevens, W. J., Basch, H. & Krauss, M. Compact Effective Potentials and Efficient Shared-Exponent Basis-Sets for the 1st-Row and 2nd-Row Atoms. *J. Chem. Phys.* **81**, 6026-6033 (1984).

11   Cakmak, Y. *et al.* Designing Excited States: Theory-Guided Access to Efficient Photosensitizers for Photodynamic Action. *Angew. Chem. Int. Ed.* **50**, 11937-11941 (2011).

12   Duman, S., Cakmak, Y., Kolemen, S., Akkaya, E. U. & Dede, Y. Heavy Atom Free Singlet Oxygen Generation: Doubly Substituted Configurations Dominate S1 States of Bis-BODIPYs. *J. Org. Chem.* **77**, 4516-4527 (2012).

13   Buyuktemiz, M., Duman, S. & Dede, Y. Luminescence of BODIPY and Dipyrrin: An MCSCF Comparison of Excited States. *J. Phys. Chem. A* **117**, 1665-1669 (2013).

14   Gaussian 09 (Gaussian, Inc., Wallingford, CT, USA, 2009).

15   Vijay, D., Varathan, E. & Subramanian, V. Theoretical design of core modified (oxa and thia) porphyrin based organic dyes with bridging thiophene linkers. *Journal of Materials Chemistry A* **1**, 4358-4369, doi:10.1039/c3ta10270j (2013).

16   (a) C. Li, W. Wang, X. Wang,et al Chem. Lett., 2005, **34**, 554.