# Supporting Information

# Metal-Free Organic Sensitizers with Sterically Hindered Thiophene Unit for Efficient Dye-Sensitized Solar Cells

*Erika Kozma*[a,*], *Isabella Concina*[b], *Antonio Braga*[b], *Laura Borgese*[c], *Laura E. Depero*[c], *Alberto Vomiero*[b,*], *Giorgio Sberveglieri*[b], *Marinella Catellani*[a]

a) CNR Institute of Macromolecular Studies of Milano, Via Bassini 15, 20133 Milano, Italy

b) CNR IDASC SENSOR Lab and Chemistry & Physics Department, University of Brescia, Via Valotti 9 , 25133 Brescia, Italy

c) INSTM and Chemistry for Technologies Laboratory, University of Brescia, Via Branze 28, 25133 Brescia, Italy

* Corresponding authors:

Erika Kozma: e-mail: erika.kozma@ismac.cnr.it

Alberto Vomiero: e-mail: alberto.vomiero@ing.unibs.it

## Table of Contents

# Synthetic procedures and characterization

## 1. General methods

Unless otherwise specified, all reactions and manipulations were performed under nitrogen atmosphere using standard Schlenk techniques. All solvents used were purified by standard procedures, or purged with nitrogen before use.

Tributyl(thiophen-2-yl)stannane, dithieno[3,2-*b*:2′,3′-*d*]thiophene, 4-bromo-N,N-diphenylaniline were purchased from Aldrich.

5-bromothiophene-2-carbaldehyde and 5-Bromo-2,2'-bithiophene-5'-carboxaldehyde were purchased from TCI Europe.

3,4-Dibutylthiophene[1], N,N-Diphenyl-(4-thiophen-2-yl-phenyl)amine[2], N, N-Diphenyl-4-(5-(tributylstannyl)thiophen-2-yl)aniline[3] and 5-tributylstannyl-dithieno[3,2-b:2’,3’-d]thiophene[4] were prepared according to the literature.

All chromatographic separations were carried out on silica gel (60M, 230-400 mesh).

$^1$H NMR spectra were recorded on a Bruker 270-MHz or 400-MHz spectrometer. Absorption spectra were recorded on a Perkin Elmer Lambda 9 spectrophotometer.

Cyclic voltammetry measurements were performed under nitrogen atmosphere in a three electrode single-compartment cell using platinum electrodes and SCE as standard electrode with a tetrabutylammonium tetrafluoroborate solution (0.1 M) in acetonitrile.

Photoluminescence (PL) spectra of DEK1 and DEK2 (in chloroform solutions) were recorded using 490 nm light excitation from a xenon lamp and a monochromator coupled to a N2 cooled CCD detector.

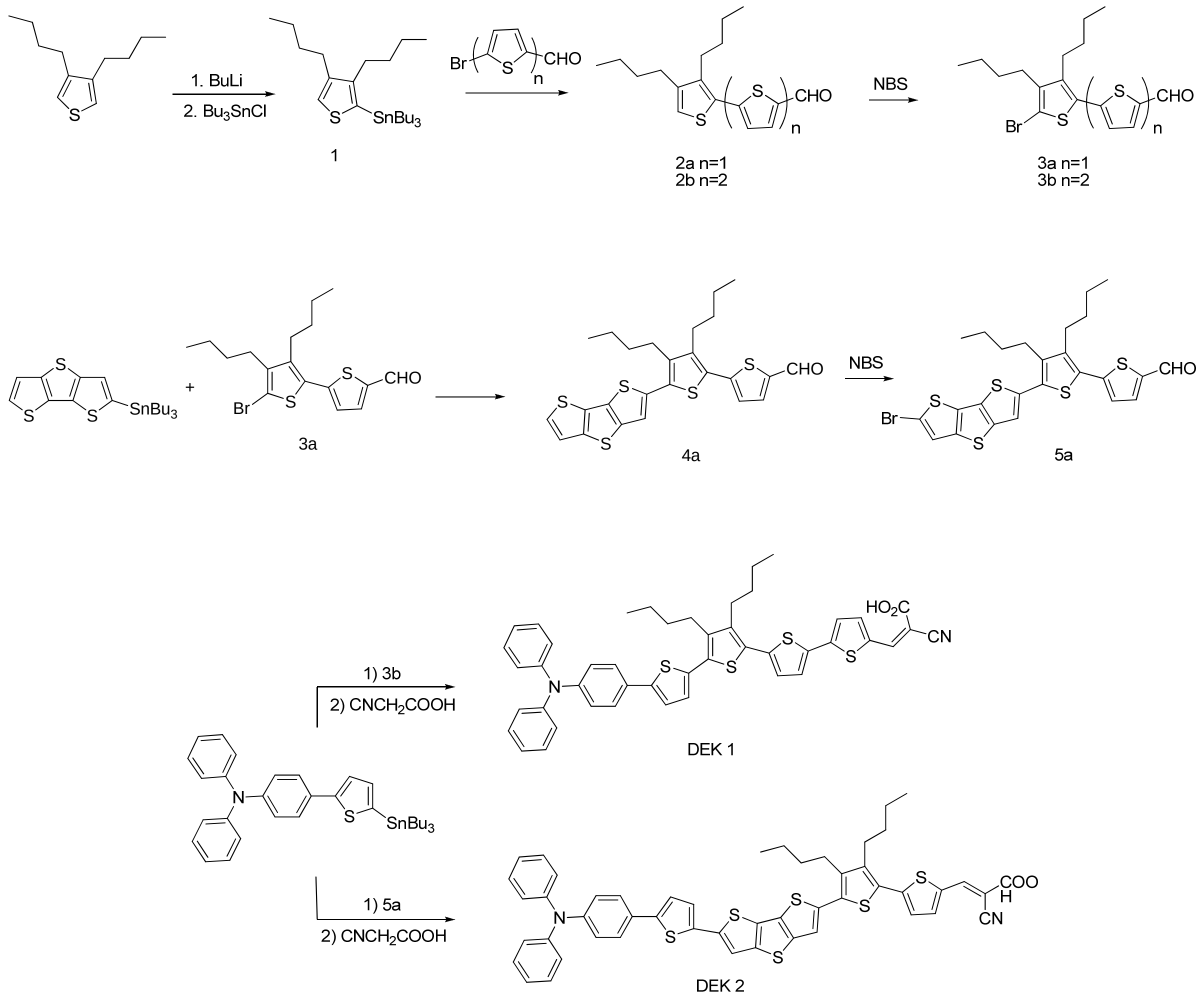

**Figure S1.** Synthetic scheme for the preparation of DEK1 and DEK2

## *General procedure for the preparation of DEK 1*

*2-Tributylstannyl-3,4-dibutyl-thiophene* (**1**)*:* To a solution of 500 mg of 3,4-dibutyl-thiophene[1] (2.55 mmol, M=196) and 5 ml of dry THF, a solution of 1.9 ml of BuLi (1.46M, 2.77 mmol, 1.08 Eq) and 5 ml THF dry was dropwise added.

When the addition was finished, the reaction mixture was brought to 0°C and 0.83 ml of $Bu_3SnCl$ (M=325.5, d=1.2, 996 mg, 3 mmol, 1.2 Eq) were added.

The reaction was mixed at room temperature overnight and then quenched with water and extracted with chloroform. The solvent was removed and the slightly yellow oil was used further without any further purification.

*3,4-dibutyl-5”-formyl-2,2′:5′,2″-terthiophene (**2b**)*

270 mg of 2-tributylstannyl-3,4-dibutyl-thiophene **1** (0.55 mmol) was treated with 152 mg of 5’-bromo-2,2’-bithiophene-5-carbaldehyde (0.55 mmol) in the presence of 10 mg $Pd(PPh_3)_2Cl_2$ in 10 ml of dry DMF and refluxed for 6 hours. After the completion of the reaction, the mixture was cooled, quenched with water and extracted in chloroform. After the removal of the solvent, a brownie oil was obtained, which was then passed through the column chromatography using hexane/ethyl acetate=10:0.5 as eluent, when yellow crystals were obtained (185 mg, 85%). $^1$H-NMR (500 MHz, TCE): 9.6 (s, 1H), 8.1 (d, 1H), 7.9 (d, 1H), 7.7 (d, 2H), 7.5 (s,1H), 2.60 (t, 4H), 1.6 (m, 4H), 1.3 (m, 4H), 0.9 (t, 6H).

*5-bromo-3,4-dibutyl-5”-formyl-2,2’:5’,2”-terthiophene (**3b**)*

To a solution of 70 mg of 3,4-dibutyl-5”-formyl-2,2′:5′,2″-terthiophene **2b** (0.18 mmol), 5 ml of $CHCl_3$ and 5 ml of AcOH, 32.1 mg (0.18 mmol) of NBS were added in a single portion. The mixture was refluxed for 1 hour. After the completion of the reaction (60 min) the mixture was cooled, quenched with water and extracted in chloroform. After the removal of the solvent, the crude product was recrystalized and orange crystals were obtained (83 mg, 98.5%).

*5”’-(4-diphenylamino-phenyl)-3”,4”-dibutyl-[2,2’,5’,2”,5”,2”’]quaterthiophenyl-5-carbaldehyde*

50 mg 5-bromo-3,4-dibutyl-5”-formyl-2,2’:5’,2”-terthiophene **3b** (0.1 mmol), 66 mg N, N-diphenyl-4-(5-(tributylstannyl)thiophen-2-yl)aniline[2,3] (0.1 mmol), 2 mg $Pd(PPh_3)_2Cl_2$ were dissolved in 10 ml of dry DMF and refluxed for 4 hours. After the completion of the reaction, the mixture was cooled, quenched with water and extracted in chloroform. After the removal of the solvent, a brownie oil was obtained, which was then passed through the column chromatography

using hexane as eluent, when orange-red crystals were obtained (55 mg, 77%). $^1$H-NMR (270MHz, TCE): 9.8 (s, 1H), 7.7 (d, 1H), 7.46 (d, 2H), 7.33-7.35 (d, 2H), 7.31 (d, 1H), 7.28 (m, 4H), 7.03-7.14 (m, 10H), 2.75 (m, 4H), 1.49 (m, 4H), 1.24 (m, 4H), 0.97 (t, 6H)

*2-cyano-3-[5'''-(4-diphenylamino-phenyl)-3'',4''-dibutyl-[2,2',5',2'',5'',2''']quaterthiophenyl-5-yl]acrylic acid (**DEK1**)*

25 mg 5'''-(4-diphenylamino-phenyl)-3'',4''-dibutyl-[2,2',5',2'',5'',2''']quaterthiophenyl-5-carbaldehyde (0.035mmol), 4.5 mg cyanoacetic acid (0.05 mmol), 2 mg ammonium acetate were dissolved in 0.7 ml acetic acid and 0.7 ml THF. The reaction mixture was refluxed for 20 hours. The solution was then cooled to room temperature to yield a dark red solution. After the removal of the solvent, the crude product was purified on column chromatography using chloroform/methanol=4:1 as eluent, when a dark red solid was obtained (20 mg, 73%).

$^1$H-NMR (500 MHz, DMSO-d$_6$): 8.07 (s, 1H), 7.68 (d, *J* = 3.9 Hz, 1H), 7.61 (d, *J* = 8.6 Hz, 2H), 7.47-7.52 (m, 2H), 7.41 (m, 1H), 7.34 (t, *J* = 7.8 Hz, 4H), 7.24 (m, 2H), 7.07 (m, 6H), 6.99 (m, 2H), 2.69 (t, 4H), 1.52 (m, 8H), 0.98 (t, 6H)

$^{13}$C-NMR (125 MHz, DMSO-d$_6$) 163.7, 153.2, 148.5, 146.6, 146.3, 144.2, 137.8, 136.5, 133.8, 129.8, 128.2, 127.2, 125.5, 125.0, 124.1, 123.9, 121.6, 118.7, 97.1, 35.7, 28.3, 22.8, 13.8

IR (KBr, cm$^{-1}$) 2213 (C≡N), 1701 (C=O), 1593 (COOH)

HR-MS (TOF MS ESI) m/z: 781.0988 [M$^+$] calcd. for $C_{46}H_{40}N_2O_2S_4$ (M$^+$): 781.0966

***General procedure for the preparation of DEK 2***

*3,4-dibutyl-5'-formyl-2,2'-bithiophene (**2a**)*

250 mg of 2-tributylstannyl-3,4-dibutyl-thiophene **1** (0.515 mmol) was treated with 1 mg of 5-bromothiophene-2-carbaldehyde (0.515 mmol) in the presence of 5 mg Pd(PPh$_3$)$_2$Cl$_2$ in 5 ml of dry DMF and refluxed for 6 hours. After the completion of the reaction, the mixture was cooled, quenched with water and extracted in chloroform. After the removal of the solvent, a brownie oil was obtained, which was then passed through the column chromatography using hexane as eluent, when an orange oil was obtained (126 mg, 80%). $^1$H-NMR (500 MHz, TCE): 9.6 (s, 1H), 7.9 (d, 1H), 7.7 (d, 1H), 7.4 (s, 1H), 2.6 (t, 4H), 1.6 (m, 4H), 1.3 (m, 4H), 0.9 (t, 6H).

*5-bromo-3,4-dibutyl-5'-formyl-2,2′-bithiophene (**3a**)*

To a solution of 100 mg of 3,4-dibutyl-5'-formyl-2,2′-bithiophene **2a** (0.32 mmol), 5 ml of $CHCl_3$ and 5 ml of AcOH, 58.2 mg (0.32 mmol) of NBS were added in a single portion. The mixture was refluxed for 1 hour. After the completion of the reaction the mixture was cooled, quenched with water and extracted in chloroform. After the removal of the solvent an orange oil was obtained (97 mg, 79%).$^1$H-NMR (500 MHz, TCE): 9.5 (s, 1H), 7.9 (d, 1H), 7.7 (d, 1H), 2.7 (t, 4H), 1.7 (m, 4H), 1.3 (m, 4H), 0.9 (t, 6H).

*5'-dithieno[3,2-b:2',3'-d]thiophen-3',4'-dibutyl-2,2'-bithiophene-5-carbaldehyde (**4a**)*

100 mg 5-bromo-3,4-dibutyl-5'-formyl-2,2′-bithiophene **3a** (0.26 mmol), 126 mg 5-tributylstannyl dithieno[3,2-b:2',3'-d]thiophene[4] (0.26 mmol), 10 mg $Pd(PPh_3)_2Cl_2$ were dissolved in 10 ml of dry DMF and refluxed for 4 hours. After the completion of the reaction, the mixture was cooled, quenched with water and extracted in chloroform. After the removal of the solvent, a brownie oil was obtained, which was then passed through the column chromatography using hexane as eluent, when orange oil was obtained (85 mg, 65%). $^1$H-NMR (270 MHz, TCE): 9.73 (s, 1H), 8.10 (d, 1H), 7.80 (s, 1H), 7.69 (d, 2H), 7.54 (s, 1H), 2.60 (m, 4H), 1.62 (m, 4H), 1.25 (m, 4H), 0.9 (t, 6H).

*5'-(5'-bromo-dithieno[3,2-b:2',3'-d]thiophen)-3',4'-dibutyl-2,2'-bithiophene-5-carbaldehyde (**5a**)*

To a solution of 50 mg of 5'-dithieno[3,2-b:2',3'-d]thiophen-3',4'-dibutyl-2,2'-bithiophene-5-carbaldehyde **4a** (0.1 mmol), 3 ml of $CHCl_3$ and 3 ml of AcOH, 17.8 mg (0.1 mmol) of NBS were added in a single portion. The mixture mixed at r.t. for 3 hours. After the completion of the reaction the mixture was cooled, quenched with water and extracted in chloroform. After the removal of the solvent, an orange oil was obtained (55 mg, 95%). $^1$H-NMR (270 MHz, TCE): 9.8 (s, 1H), 8.05 (d, 1H), 7.86 (s, 1H), 7.73 (d, 1H), 7.55 (s, 1H), 2.63 (m, 4H), 1.62 (m, 4H), 1.28 (m, 4H), 0.93 (t, 6H).

*5”’-(N,N-diphenyl-(4-thiophenyl-2-yl-phenylamine))-3’,4’-dibutyl-dithieno[3,2-b:2’,3’-d]thiophen-[2,2’,5’,5’’]-bithiophene-5-carbaldehyde*

55 mg 5’-(5’-bromo-dithieno[3,2-b:2’,3’-d]thiophen)-3’,4’-dibutyl-2,2’-bithiophene-5-carbaldehyde (0.09 mmol), 64 mg N, N-Diphenyl-4-(5-(tributylstannyl)thiophen-2-yl)aniline (0.1 mmol), 5 mg $Pd(PPh_3)_2Cl_2$ were dissolved in 10 ml of dry DMF and refluxed for 6 hours. After the completion of the reaction, the mixture was cooled, quenched with water and extracted in chloroform. After the removal of the solvent, the crude product was then passed through the column chromatography using hexane/ethyl acetate 9/1 as eluent, when a red solid was obtained (70 mg, 94%). $^1$H-NMR (270 MHz, dmso-d6): 9.9 (s, 1H), 8.03 (d, 1H), 7.74 (d, 1H), 7.57 (d, 2H), 7.30-7.46 (m, 8H), 6.96-7.11 (m, 8H), 2.74 (m, 4H), 1.49 (m, 8H), 0.93 (t, 6H)

*2-cyano-3-[5”’-(N,N-diphenyl-(4-thiophenyl-2-yl-phenylamine))-3’,4’-dibutyl-dithieno[3,2-b:2’,3’-d]thiophen-[2,2’,5’,5’’]-bithiophene-5-yl]acrylic acid (**DEK2**)*

50 mg 5”’-(N,N-diphenyl-(4-thiophenyl-2-yl-phenylamine))-3’,4’-dibutyl-dithieno[3,2-b:2’,3’-d]thiophen-[2,2’,5’,5’’]-bithiophene-5-carbaldehyde (0.06 mmol), 15.3 mg cyanoacetic acid (0.18 mmol), 2.8 mg ammonium acetate were dissolved in 1 ml acetic acid and 1 ml THF. The reaction mixture was refluxed for 20 hours. The solution was then cooled to room temperature and after the removal of the solvent, the crude product was purified on column chromatography using chloroform/methanol=4:1 as eluent, when a dark red solid was obtained (47 mg, 87%).

$^1$H-NMR (500 MHz, DMSO-d6): 8.10 (s, 1H), 7.80 (d, $J = 4.2$ Hz, 1H), 7.71 (d, $J = 8.2$ Hz, 2H), 7.59 (d, $J = 8.6$ Hz, 2H), 7.42 (m, 2H), 7.35 (m, 4H), 7.09 (m, 6H), 7.01 (m, 2H), 2.78 (m, 4H), 1.48 (m, 8H), 0.95 (t, 6H)

$^{13}$C-NMR (125 MHz, DMSO-$d_6$) 162.8, 155.3, 151.5, 148.6, 147.3, 146.3, 145.8, 144.2, 142.5, 138.8, 136.5, 133.8, 129.8, 129.0, 128.2, 127.5, 125.8, 124.1, 123.9, 122.7, 121.6, 117.7, 95.1, 35.0, 27.3, 22.1, 14.3

IR (KBr, cm$^{-1}$) 2214 (C≡N), 1685 (C=O), 1585 (COOH)

HR-MS (TOF MS ESI) m/z: 893.1015 [$M^+$] calcd. for $C_{50}H_{40}N_2O_2S_6$ ($M^+$): 893.1020

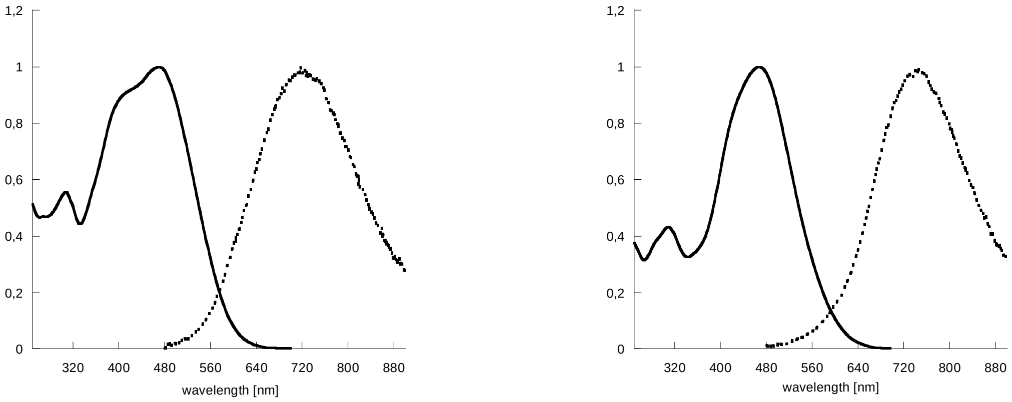

**Figure S2.** Normalized UV/Vis absorption (solid line) and emission (dashed line) spectra of DEK1 (left) and DEK2 (right) in chloroform

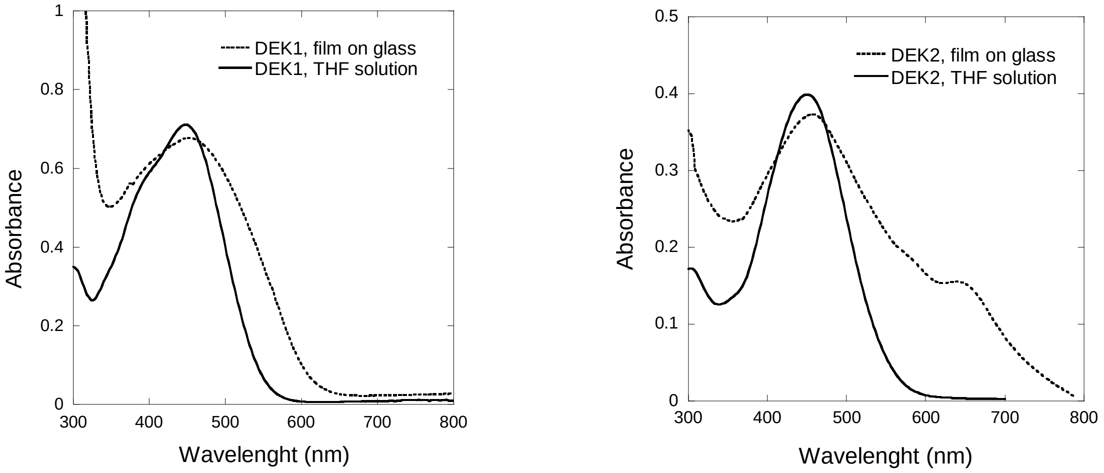

**Figure S3.** Normalized UV/Vis absorption in solution (solid line) and film (dashed line) spectra of DEK1 (left) and DEK2 (right)

**Table S1.** Optical properties and Energy Levels of DEK1 and DEK2 dyes

| Dye | $\lambda_{abs}^{max}$ (nm)[a] | $\varepsilon_{abs}^{max}$ ($10^3M^{-1}m^{-1}$ )[a] | $\lambda_{pl}^{max}$ (nm)[a] | $E_{(S+/S)}$ (V)[b] | $E_{(0-0)}$ (eV)[c] | $E_{(S+/S*)}$ (V)[d] | HOMO (eV)[e] | LUMO (eV)[e] |
|---|---|---|---|---|---|---|---|---|
| DEK1 | 477 | 53.5 | 718 | 1.09 | 2.11 | -1.02 | 5.59 | 3.55 |
| DEK2 | 465 | 57.6 | 743 | 1.09 | 2.03 | -1.02 | 5.53 | 3.50 |

[a] The absorption maximum wavelength ($\lambda_{abs}^{max}$), maximum molar extinction coefficient ($\varepsilon_{abs}^{max}$) and photoluminescence maximum wavelength ($\lambda_{pl}^{max}$) were derived from the absorption and photoluminescence spectra of the dyes dissolved in chloroform

[b] The oxidation potential derived from cyclic voltammetry (converted to NHE)

[c] The 0-0 transition energy ($E_{0-0}$) was estimated from the crossing point of normalized absorption and photoluminescence spectra (see Figure 1)

[d] The excited state oxidation potentials were derived from the equation: $E_{(S+/S*)}=E_{(S+/S)}-E_{(0-0)}$

[e] The HOMO was calculated from the onset oxidation potential (cyclic voltammetry) and LUMO from HOMO and optical band gap

## DEK1 and DEK2 loading evaluation by UV-Vis spectrophotometry

Optical absorption spectra were collected at room temperature on a PGINSTRUMENTS T80 spectrophotometer using 1-cm quartz cuvettes. Dye loading on $TiO_2$ substrates was evaluated by detaching the anchored dyes by means of a solution of triethylamine/chloroform (9/1, V/V), after calibration.

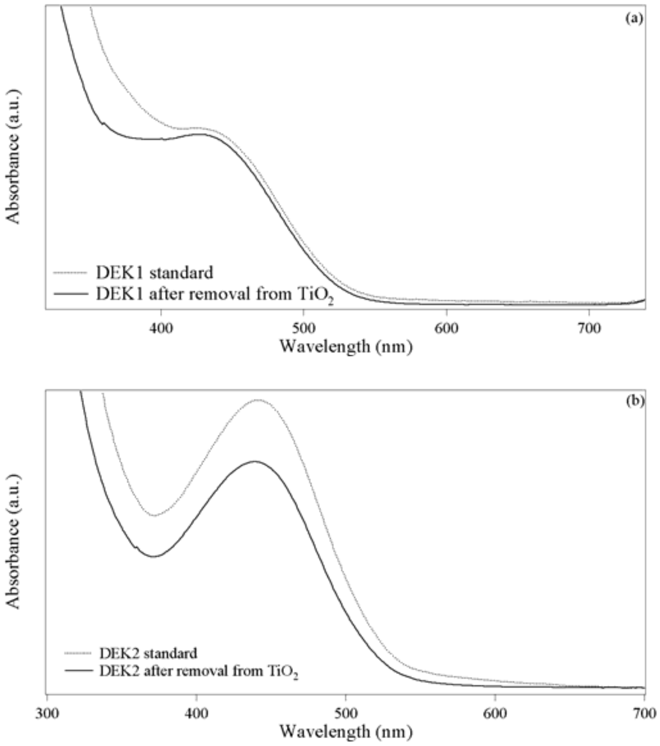

**Figure S4.** UV-Vis features of DEK1 (a) and DEK2 (b) in standard solution (dotted line) and after the removal from TiO2 surface (solid line).

## Diffuse reflectance infrared Fourier transform analyses

Diffuse reflectance infrared Fourier Transform spectra were recorded in a Bruker VERTEX 70v spectrometer (accumulating 64 scans at 4 cm$^{-1}$ resolution) and displayed in the Kubelka-Munk unit[5,6]. Sample chamber was evacuated in order to polish the spectra from the spectral contributions of $CO_2$ and humidity; a MCT detector cooled by liquid nitrogen was employed. KBr powder was used as a background. A layer of KBr was deposited by tape casting onto a FTO glass and used as a background for direct measurements on solar cells.

Interaction between DEK1 and DEK2 and $TiO_2$ was evaluated by directly analyzing the sensitized photoanode. DEK1 and DEK1 loaded onto titania spectra are reported as example in Figure S 1 (similar results are obtained for DEK2 and related cells). Region below 1000 cm$^{-1}$ is not considered for discussion since it is completely masked by TiO2 vibrations in loaded dyes.

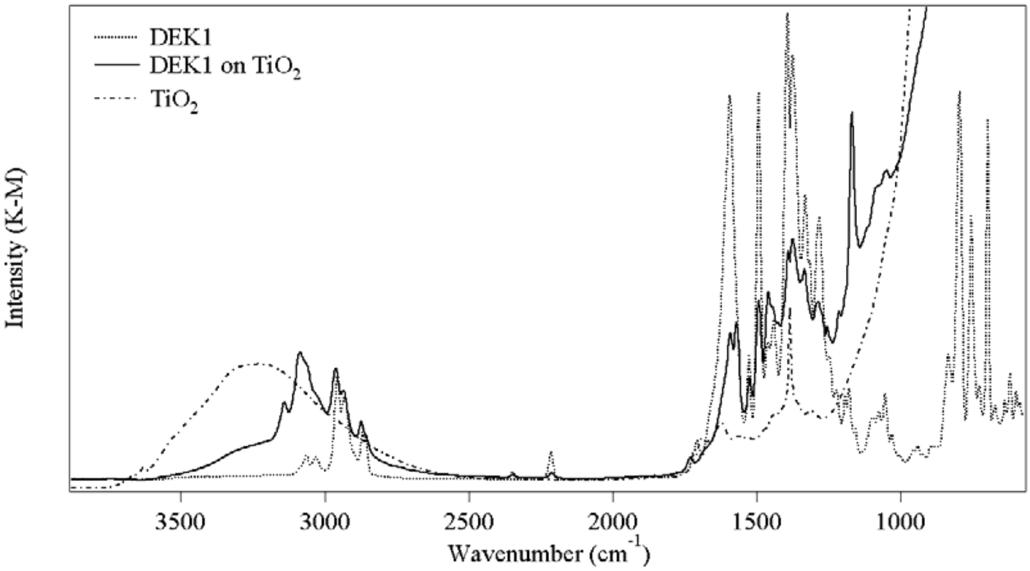

**Figure S5**: Infrared spectra of DEK1 (dotted line), DEK1 loaded onto $TiO_2$ surface (solid line) and $TiO_2$ (dashed line).

**Table S2:** Infrared correlation table for DEK1, $TiO_2$ and related photoanodes. Abbreviation list: ν (stretching); δ (bending); s (strong), w (weak), b (broad), sh (shoulder), v (very), asym (asymmetric), sym (symmetric).

| **Vibration mode** | **DEK1 ($cm^{-1}$)** | **$TiO_2$ ($cm^{-1}$)** | **DEK1 on $TiO_2$ ($cm^{-1}$)** |
|---|---|---|---|
| ν O-H | ---- | 3313-3172 (s, vb) | 3269 (sh) |
| ν C-H (aromatic) | 3068, 3030 (w) | --- | 3140,3084 |
| ν C-H (aliphatic) | 2962, 2869 | --- | 2961, 2873 |
| ν CN | 2212 | --- | 2212 |
| ν C=O | 1724 (sh), 1705 (w) | --- | |
| Bithiophene ring vibration modes | 1612 (sh), 1593, 1526, 1493, 1441, 1221, 1332, 1179, 1078, 1053, 834, 754, 697 | --- | 1612 (sh), 1592, 1524, 1493, 1440, 1330, 1221 |
| $\nu_{asym}$ C02 | --- | --- | 1571 |
| δasym (C-H) methyl | 1460 | --- | 1460 |
| δsym (C-H) methyl | 1393, 1376 (doublet) | | 1393, 1375 (doublet) |
| Methylene twisting and wagging | 1330-1150 (w) | | 1330-1150 (w) |
| $\nu_{sym}$ C02 | ---- | | 1375 (broader) |
| ν C-0 | 1244 | | 1255 |

Infrared profiles of DEK1 is especially dominated by the contribution of aromatic vibrations, due to both the phenyl groups present on the acceptor side of the molecule and thiophene rings. These vibrations keep rather intense also in the spectra of dye loaded $TiO_2$, as expected.

The most interesting bands are those of cyanide and carboxylic groups. The first one in completely preserved as for both shape and position (2212 $cm^{-1}$) in dye loaded $TiO_2$, thus indicating that –CN is not involved in anchoring the dye to the metal oxide surface.

The situation of carboxylic group is more complicated. In DEK 1, indeed, the C=O stretching can be found as a weak peak at 1705 $cm^{-1}$, with a shoulder centred at 1724 $cm^{-1}$. This receded position is expected in the case of α,β -unsaturated carboxylic compounds.

In the spectrum of DEK1-$TiO_2$ the peak is disappeared, thus suggesting that COOH is the binding arm of DEK1 molecule. A new vibrational contribution centred at 1571 $cm^{-1}$, due to the asymmetric stretching of carboxylate, appears in the spectrum of loaded DEK1. The corresponding symmetric stretching is partially masked by the asymmetric bending of C-H groups. However, in the spectrum of loaded DEK1 the peak presents a tail toward lower wavenumbers and appears much broader than the corresponding one in unloaded DEK1 spectrum, thus evidencing the presence of a new contribution.

## Photovoltaic measurements of the solar cells

The short-circuit current density ($J_{SC}$) linearly increases with light power density, while a logarithmic behavior has been found for the open-circuit voltage ($V_{OC}$), as expected for a well operating DSC.

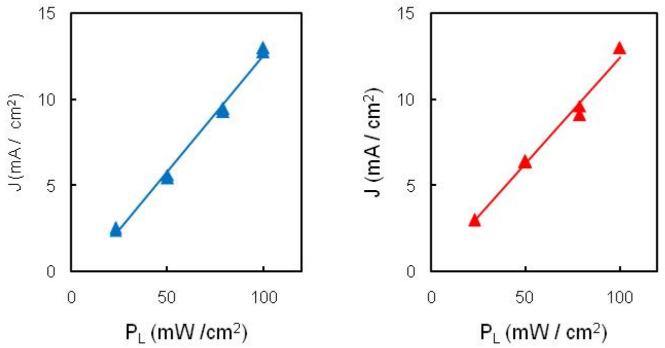

**Figure S6.** Short-circuit current density ($J_{SC}$) of typical DSCs sensitized with DEK1 (left) and DEK2 (right) molecules as a function of the light power density. The straight lines are linear fits of the experimental data.

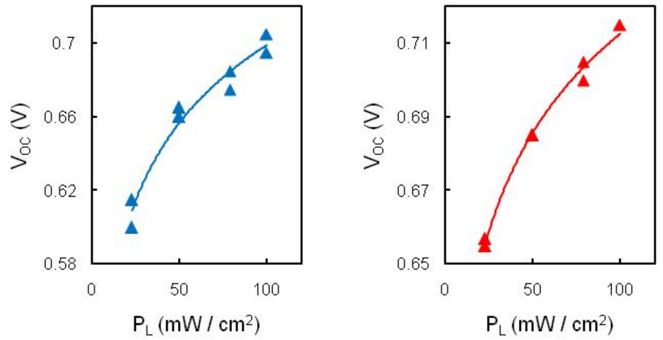

**Figure S7.** Open-circuit voltage ($V_{OC}$) of typical DSCs sensitized with DEK1 (left) and DEK2 (right) molecules as a function of the light power density. The curved lines are logarithmic fits of the experimental data.

The constant behavior of PCE and FF as a function of light power density is a sign that the recombination processes inside the cell are almost independent from the concentration of photoexcited electrons, which is one further proof of the good functional properties of the cell.

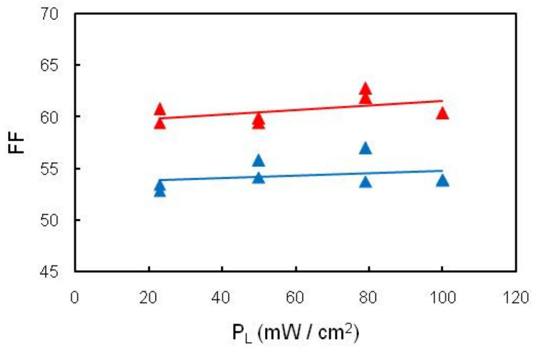

**Figure S8.** Fill factor (FF) of typical DSCs sensitized with DEK1 (blue) and DEK2 (red) molecules as a function of the light power density. The straight lines are linear fits of the experimental data.

## References

[1] K. Tamao, S. Komada, I. Nakajima, M. Kumada, *Tetrahedron*, **1982**, 38, 3347

[2] Soo-Jin Moon, Jun-Ho Yum, Robin Humphry-Baker, Karl Martin Karlsson, Daniel P. Hagberg, Tannia Marinado, Anders Hagfeldt, Licheng Sun, Michael Grätzel, Md K. Nazeeruddin, *J.Phys.Chem.C*, **2009**, 113, 16816

[3] K.R. Justin Thomas, Ying-Chan Hsu, J.T. Lin, Kun-Mu Lee, Kuo-Chuan Ho, Chin-Hung Lai, Yi-Ming Cheng, Pi-Tai Chou, *Chem.Mater.*, **2008**, 20, 1830

[4] H.Y. Yang, Y.S. Yen, Y.C. Hsu, H.H. Chou, J.T. Lin, *Org.Lett.*, **2010**, 12, 16

[5] P. Kubelka, F. Munk, *Z. Technol. Phys.*, **1931**, 12 593

[6] G. Kortum, *Reflectance Spectroscopy*, Springer, New York, **1969**