Electronic Supplementary Material (ESI) for ChemComm.

Supporting Information

Dipicolinic acid: A strong anchoring group with tunable redox and spectral behavior for stable Dye-Sensitized Solar Cells.

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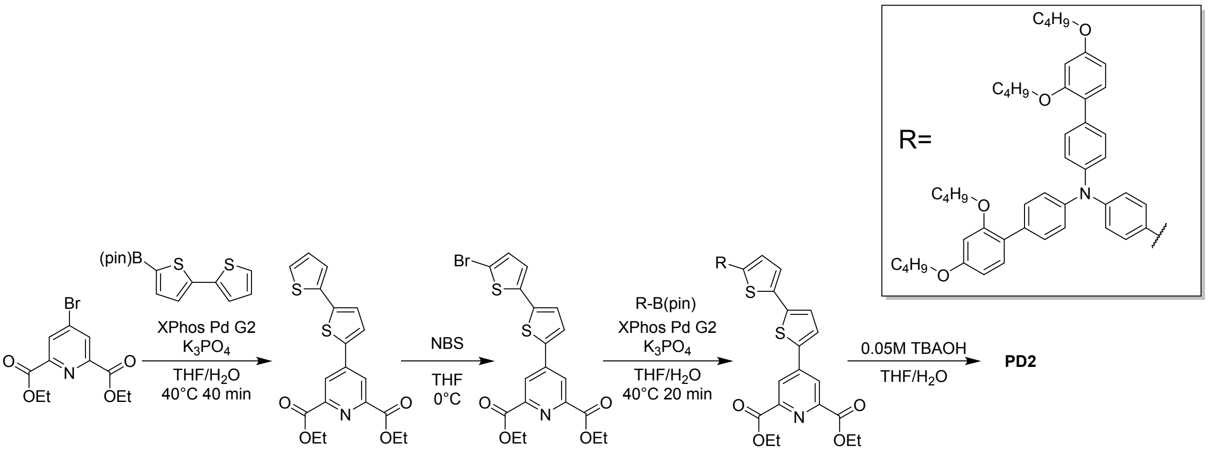
Synthesis of PD2

^{1}H and ^{13}C NMR spectra were recorded on Bruker 500 and 400 MHz instruments by using the residual signals δ=7.26 ppm and 77.0 ppm from $CDCl_3$, δ=2.50 and 39.4 ppm from [D$_6$]DMSO and δ =2.05, 29.84, and 206.26 ppm from [D$_6$]acetone, as internal references for ^{1}H and ^{13}C respectively. HRMS were performed using a Waters (USA) MALDI micro MX Matrix assisted laser desorption ionization-time of flight mass spectrometer. Tetrahydrofuran (THF) was dried by passing through a solvent column composed of activated alumina. N-Bromosuccinimide was purified by recrystallization from water. Chemicals were purchased from Sigma-Aldrich. Commercially available reactants were used without further purification unless otherwise noted.4-bromopyridine-2,6-dicarboxylate and 2-([2,2'-bithiophen]-5-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane were prepared according to the literature procedures.[1] Flash chromatography was performed using silica gel 60Å (35-63 µm).



Scheme S1. Synthetic route to **PD2**.

Diethyl 4-([2,2'-bithiophen]-5-yl)pyridine-2,6-dicarboxylate (1). To a solution of diethyl 4-bromopyridine-2,6-dicarboxylate (302 mg, 1.0 mmol), 2-([2,2'-bithiophen]-5-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (438 mg, 1.5 mmol) and chloro(2-dicyclohexylphosphino-2′,4′,6′-triisopropyl-1,1′-biphenyl)[2-(2′-amino-1,1′-biphenyl)]palladium(II) (79 mg, 0.1 mmol) in THF (3 ml) under N_2, a degassed aqueous solution of K_3PO_4 (0.5 M, 4 ml, 2 mmol) was added. The mixture was stirred for 40 min at 40°C. HPLC indicated 100% conversion of the bromide after 10 minutes. H_2O (20 ml) was added and the product was extracted with DCM (3x20 ml). The combined organic phases were dried over anhydrous $MgSO_4$. Solvent removal by rotary evaporation followed by flash chromatography (EtOAc/$CHCl_3$ 1:6) afforded **1** as a pale yellow solid (311 mg, 80%). ^{1}H NMR (500 MHz, Acetone) δ 8.41 (s, 2H), 7.93 (d, J = 3.9 Hz, 1H), 7.54 (d, J = 5.0 Hz, 1H), 7.46 (d, J = 3.2 Hz, 1H), 7.41 (d, J = 3.9 Hz, 1H), 7.15 (dd, J = 4.9, 3.8 Hz, 1H), 4.46 (q, J = 7.1 Hz, 4H), 1.42 (t, J = 7.1 Hz, 6H).^{13}C NMR (126 MHz, Acetone) δ 165.33, 150.82, 144.24, 141.38, 138.51, 137.07, 129.68, 129.43, 127.25, 126.38, 126.21, 123.45, 62.61, 14.72.HRMS (ESI) *m/z*: [M+H]$^+$calcd for $C_{19}H_{18}NO_4S_2$, 388.0672; found, 388.0657.

Diethyl 4-(5'-bromo-[2,2'-bithiophen]-5-yl)pyridine-2,6-dicarboxylate (2). To a stirred solution of **1** (214 mg, 553 µmol) in THF (20 ml) at 0°C, NBS (100 mg, 564 µmol) was added in one portion. The reaction was kept at 0°C for 40 min, after which it was allowed to warm to room temperature over a period of 120 min. H_2O (100 ml) was added, upon which the product precipitated. The precipitate was filtered and washed with H_2O. The residue was recrystallized from heptane (90 ml) from which **2** precipitated as yellow cotton-like needles (159 mg, 62%). ^{1}H NMR (500 MHz, Acetone) δ 8.39 (s, 2H), 7.93 (d, *J* = 3.3 Hz, 1H), 7.39 (d, *J* = 3.4 Hz, 1H), 7.27 (d, *J* = 3.3 Hz, 1H), 7.20 (d, *J* = 3.4 Hz, 1H), 4.45 (q, *J* = 6.9 Hz, 4H), 1.41 (t, *J* = 7.0 Hz, 6H).^{13}C NMR (126 MHz, Acetone) δ 165.28, 150.83, 144.02, 139.86, 139.19, 138.87, 132.71, 129.69, 126.90, 126.63, 123.53, 112.77, 62.63, 14.71.HRMS (ESI) *m*/*z*: [M+H]$^+$calcd for $C_{19}H_{18}BrNO_4S_2$, 467.9777; found, 467.9757

Diethyl 4-(5'-(4-(bis(2',4'-dibutoxy-[1,1'-biphenyl]-4-yl)amino)phenyl)-[2,2'-bithiophen]-5-yl)pyridine-2,6-dicarboxylate (Et_2PD2). To a solution of **2** (135 mg, 290 µmol),**3** (283 mg, 349 µmol) and chloro(2-dicyclohexylphosphino-2′,4′,6′-triisopropyl-1,1′-biphenyl)[2-(2′-amino-1,1′-biphenyl)]palladium(II) (22.8 mg, 29 µmol) in THF (2 ml) under N_2, a degassed aqueous solution of K_3PO_4 (0.5 M, 1160 µl, 580 µmol) was added. The mixture was stirred for 20 min at 40 °C. H_2O (20 ml) was added and the product was extracted with DCM (3x20 ml). The combined organic phases were dried over anhydrous Na_2SO_4 and the solvent removed by rotary evaporation. Flash chromatography (EtOAc/DCM 5:95) afforded **Et_2PD2** as an orange solid (161 mg, 52%). ^{1}H NMR (500 MHz, Acetone) δ 8.39 (s, 2H), 7.92 (d, *J* = 3.9 Hz, 1H), 7.60 (d, *J* = 8.6 Hz, 2H), 7.51 (d, *J* = 8.5 Hz, 4H), 7.40 (m, 3H), 7.26 (d, *J* = 8.4 Hz, 2H), 7.13 (dd, *J* = 13.9, 8.6 Hz, 6H), 6.64 (d, *J* = 2.0 Hz, 2H), 6.58 (dd, *J* = 8.4, 2.1 Hz, 2H), 4.45 (q, *J* = 7.1 Hz, 4H), 4.02 (td, *J* = 6.3, 2.2 Hz, 8H), 1.74 (m, 8H), 1.48 (m, 14H), 0.98 (t, *J* = 7.4 Hz, 6H), 0.93 (t, *J* = 7.4 Hz, 6H).^{13}C NMR (126 MHz, DMSO) δ 165.41, 159.29, 156.55, 149.28, 147.16, 144.76, 143.67, 142.93, 139.67, 136.70, 133.73, 133.29, 130.53, 130.17, 129.53, 126.76, 126.44, 125.44, 123.97, 123.69, 122.85, 122.02, 121.79, 105.87, 100.24, 67.65, 67.22, 30.84, 30.71, 18.85, 18.81, 13.75, 13.68.HRMS (ESI) *m*/*z*: [M]$^+$calcd for $C_{65}H_{70}N_2O_8S_2$, 1070.4574; found, 1070.4580.

4-(5'-(4-(bis(2',4'-dibutoxy-[1,1'-biphenyl]-4-yl)amino)phenyl)-[2,2'-bithiophen]-5-yl)pyridine-2,6-dicarboxylic acid (PD2). To a stirred solution of **Et_2PD2** (107 mg, 100 µmol) in a mixture of THF (15 ml) and H_2O (5 ml) under N_2, a solution of tetrabutylammonium hydroxide (1 M in MeOH) (1 ml, 1 mmol) was added. Shortly after the addition of the base, the color of the solution changed from orange to yellow. The reaction mixture was stirred for 3 hours at room temperature. The solution was then acidified by addition of HCl (200 ml, 0.1 M) upon which a fine brown precipitate formed. The suspension was filtered through a P4 glass filter and the residue was washed thoroughly with H_2O and MeOH. Drying the residue under high vacuum gave analytically pure **PD2** (86 mg, 85%). ^{1}H NMR (500 MHz, DMSO) δ 8.34 (s, 2H), 8.01 (s, 1H), 7.54 (d, *J* = 8.2 Hz, 2H), 7.42 (m, 7H), 7.17 (d, *J* = 8.3 Hz, 2H), 7.01 (m, 6H), 6.58 (s, 2H), 6.52 (d, *J* = 8.3 Hz, 2H), 3.94 (d, *J* = 4.9 Hz, 8H), 1.64 (m, 8H), 1.38 (ddd, *J* = 38.8, 14.7, 7.3 Hz, 8H), 0.92 (t, *J* = 7.3 Hz, 6H), 0.84 (t, *J* = 7.3 Hz, 6H).^{13}C NMR (126 MHz, DMSO) δ 165.41, 159.29, 156.55, 149.28, 147.16, 144.76, 143.67, 142.93, 139.67, 136.70, 133.73, 133.29, 130.53, 130.17, 129.53, 126.76, 126.44, 125.44, 123.97, 123.69, 122.85, 122.02, 121.79, 105.87, 100.24, 67.65, 67.22, 30.84, 30.71, 18.85, 18.81, 13.75, 13.68. UV–vis DCM: $\lambda_{max}(\varepsilon)$ = 456 nm (26000 M^{-1} cm^{-1}), PhMe: $\lambda_{max}(\varepsilon)$ = 460 nm (29000 M^{-1} cm^{-1}). HRMS (ESI) *m*/*z*: [M+H]$^+$calcd for $C_{61}H_{63}N_2O_8S_2$, 1015.4026; found, 1015.4034.

Device preparation and characterization

Fluorine-doped tin oxide (FTO) glass plates (Pilkington-TEC15) were cleaned in subsequent order of detergent solution, water and EtOH using an ultrasonic bath overnight. The conducting glass substrates were immersed into a 40 mM aqueous $TiCl_4$ solution at 70 ^oC for 30 min and washed with water and ethanol. The screen-printing procedure was used to prepare 9μmtransparent nanocrystallinefilm (Dyesol, 18 NR-T).Scattering layer (2μm) was also prepared by screen-printing method using Solaronix R/SP paste. The TiO_2 electrodes were gradually heated in an oven (Nabertherm Controller P330) in ambient air atmosphere. The temperature gradient program used included two stationary plateaus at 325 ^oC (10 min), and 450 ^oC (30 min). After sintering the electrodesas described above, a post-$TiCl_4$ treatment was performed using 40 mMaqueous $TiCl_4$ solution at 70 ^oC for 30 min and washed with water and ethanol. A second and final sintering, at 450 °C for 30 min, was performed. The prepared electrodes were immersed into 0.2 mMorganic dyesolutions in DCM with saturated CDCA and kept for 17 h in the dark at room temperature. After sensitization, the electrodes werefurther rinsed with the DCM and dried. The photo-electrodes were assembled with a platinized counter electrode using 25 μm thick hot-melt film (Surlyn, Solaronix). The electrolyteswere introduced through a hole drilled in the back of the counter electrode. Finally, the hole was also sealed with the Surlynfilm.

J-V characteristics were measured using a Keithley source/meter under simulated sunlight of 100 $mW\cdot cm^{-2}$ light intensity from a Newport 300 W solar simulator. A black mask (5 mm × 5 mm) was used in the subsequent photovoltaic studies to diminish refection light.The apparatus for Incident Photon to Current Conversion Efficiency (IPCE) consisted of a computer-controlled setup with a xenon light source (Spectral Products ASB-XE-175), a monochromator (Spectral Products CM 110), and a Keithley 2700 multimeter. Both systems were calibrated against a certified reference solar cell (IR-filtered silicon solar cell, Fraunhofer ISE, Freiburg, Germany). For each dye-electrolyte combination two devices were tested and the values presented in Table 2 are the mean values.

Electrolytes used for solar cells:

A: 0.5 M LiI, 0.05 M I_2 in acetonitrile

B: 0.5 M LiI, 0.05 M I_2, 0.5 M TBP in acetonitrile

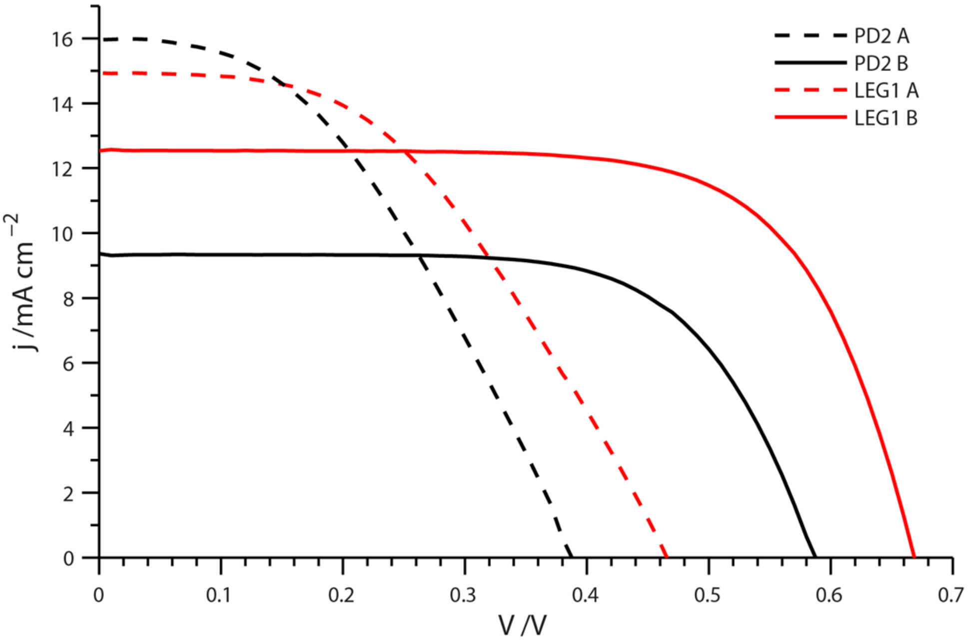


Figure S1. *I-V* curves of PD2 and LEG1 sensitized DSSCs using electrolytes A and B measured at 100 mW/cm².

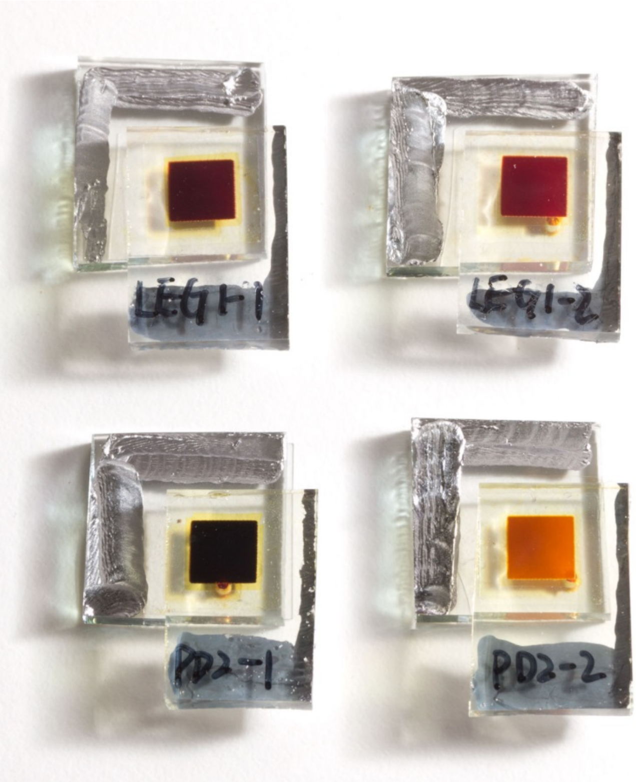


Figure S2. Photograph of DSCs sensitized with LEG1 (top) and PD2 (bottom) using electrolyte A (left) and B (right).

FT-IR Measurements

For the PD2 on TiO_2 nanoparticles FTIR measurement a 6 μmthickdoctor-bladed TiO_2film was sensitized in a 0.2 mM PD2 solution (DCM) for 17 h. The film was rinsed with ethanol and dried. Then the sensitized TiO_2 film was scraped off the glass substrate, mixed with KBr (~3 mg film to 300 mg dry KBr) and pressed into a pellet. The FTIR spectra shown in Figure 4 are manually baseline corrected and the raw data is shown in Figure S3.

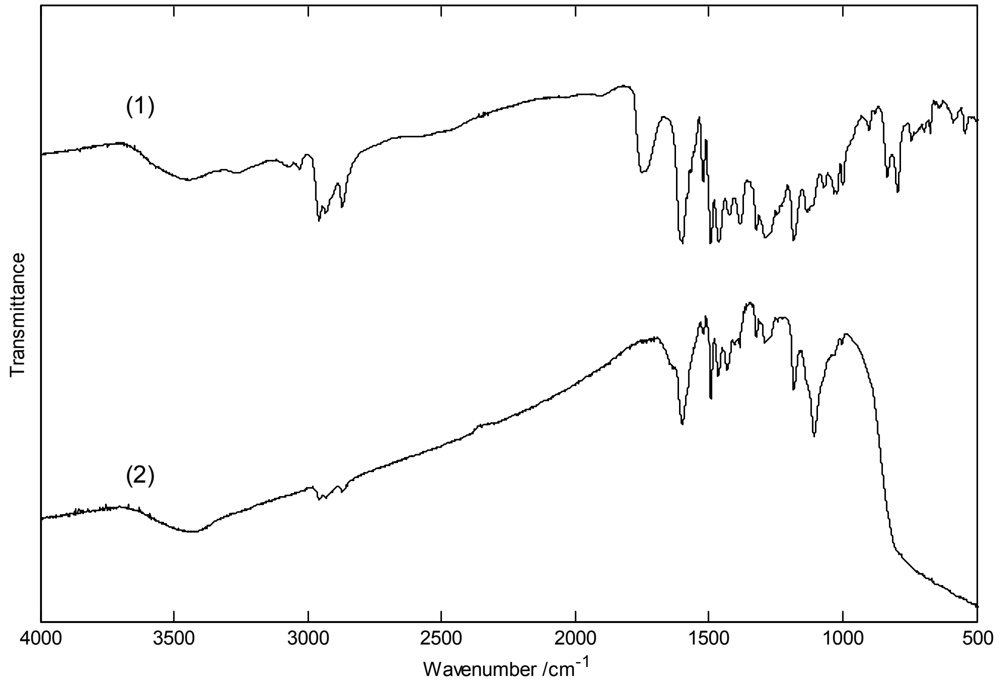


Figure S3. FT-IR spectra of PD2 (1) and TiO_2 sensitized with PD2 (2) in KBr.

Film absorbance pH-dependence

A 6 μmthick doctor-bladed TiO_2film was sensitized in a 0.2 mM PD2 solution (DCM)for 5 min. The film was then submerged in a 5% (v/v) Et_3N in DCM solution for 1 min and air-dried. The absorbance spectra were collected with the film at a 45° angle to the incident beam in a cuvette filled with buffer solution. Aqueous (potassium) phosphate buffers (ionic strength: 0.1 M) were used with the exception of at pH 1, where 0.1 M HCl was used in place of a buffer solution.

Desorption studies

Films were sensitized according to the procedure described in device preparation.Two films were used for each measurement. Desorption was initially attempted using a solution of 0.1 M TBAOH in MeOH, but proceeded slowly for PD2 (incomplete after 36 days). A solution of 0.1 M TBAOH in DCM/MeOH (~9:1 v/v) was used to achieve complete desorption in 3 days. 0.02 mM PD2 in the same basic solution was used to determine dye loading on TiO_2.

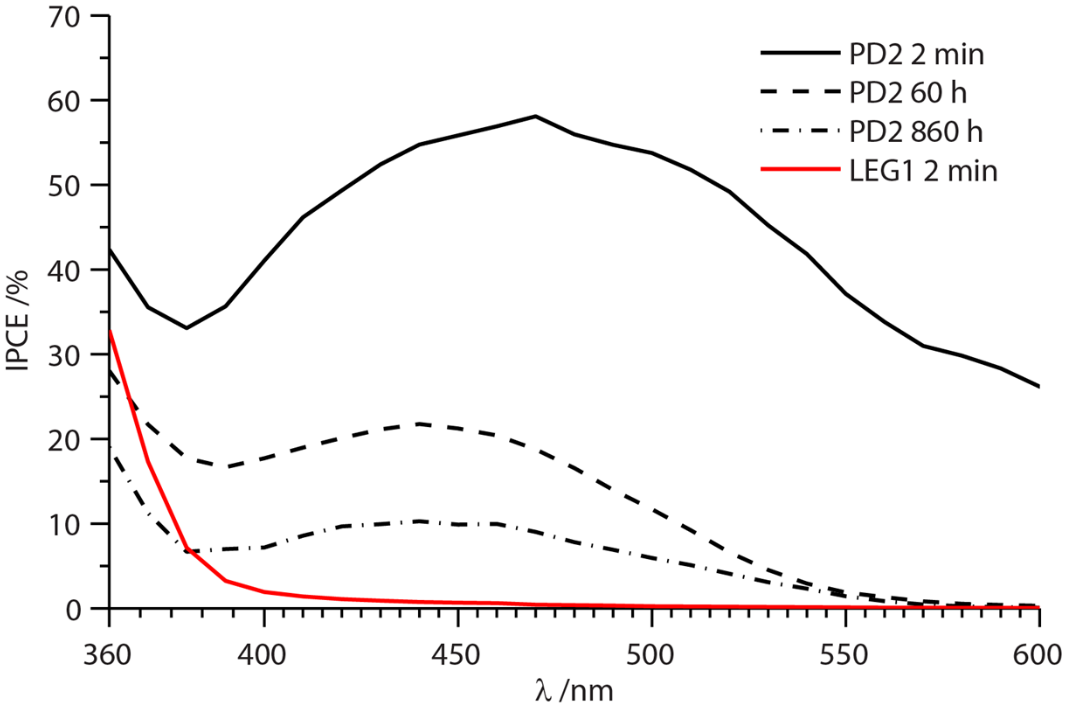


Figure S4. IPCE spectra for devices constructed using PD2 and LEG1-sensitized TiO_2 films treated in a desorption bath consisting of 0.1 M TBAOH in EtOH. Electrolyte A was used for the devices. The IPCE spectra after the desorption treatment are notably different from those before, likely due to electrolyte A being insufficiently acidic to fully restore the protonation of the adsorbed dyes.

Absorption and emission spectra in solution

The absorption spectra were recorded in DCM at near 1 AU peak absorbance on a Perkin-Elmer Lambda 750 UV/Vis/NIR spectrophotometer. The LEG1 absorption spectrum was reproduced from the literature.[1b] The emission spectra were recorded in DCM around 0.1 AU absorbance on a Horiba FluoroLogspectrofluorometer and are corrected.

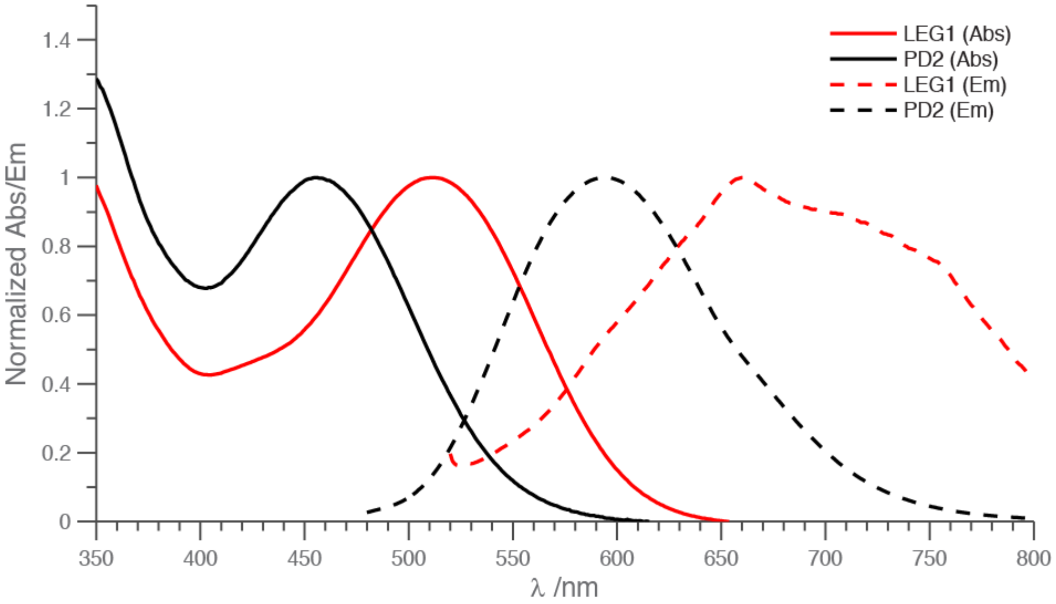


Figure S5. Normalized absorption and emission spectra of PD2 and LEG1.

PES & NEXAFS

The PES and NEXAFS measurements were conducted at the undulatorbeamline I411 at the national research facility MAX IV in Lund. The kinetic energy of the photoelectrons was measured using a Scienta R4000 WAL analyser. The N1s-NEXAFS spectra were measured by detecting the secondary electrons in partial yield mode. The NEXAFS spectra were photon energy calibrated by measuring Ti3p peak with first and second order light and normalized versus the resonance at 402 eV. The PES spectra were calibrated using the Ti2p signal set to 458. 56 eV[2]. The N1s-Nexafs spectra were smoothed by using a binomial function to reduce the noise level.

Sensitized electrodes were prepared accordning to the following: thin (2um) TiO_2 electrodes were sensitized in DCM solutions with 0.2 mM of PD2 or LEG1 with cheno-deoxicholic acid (2 mM) for 16-17 hours. Some PD2 electrodes were post-treated with TBP/MeCN (0.5 M), KOt-Bu/MeOH (0.1 M), HCOOH/MeCN(0.5 M)or TBAOH/MeOH (0.1 M) for ten minutes and then rinsed with ethanol. Also a multilayer of PD2 on conductive glass was prepared by dripping dye solution on the glass and evaporates the solvent.

The intensities of the S2p peaks were normalized vs. the corresponding Ti3p signal thus giving information of the amount of dye on the surface. The Ti3p peak was detected just before the S2p signal eliminating effects due to different light intensities. The relative amounts of LEG1 and PD2 with different treatments are summarized in Table S1.

Table S1. Relative adsorbed amounts of PD2 and LEG1 determined by PES.

PD2	PD2+CDCA	PD2+CDCA+tBP treatment	PD2+CDCA+TBAOH treatment	LEG1+CDCA
2.1	1.7	1.7	1	1

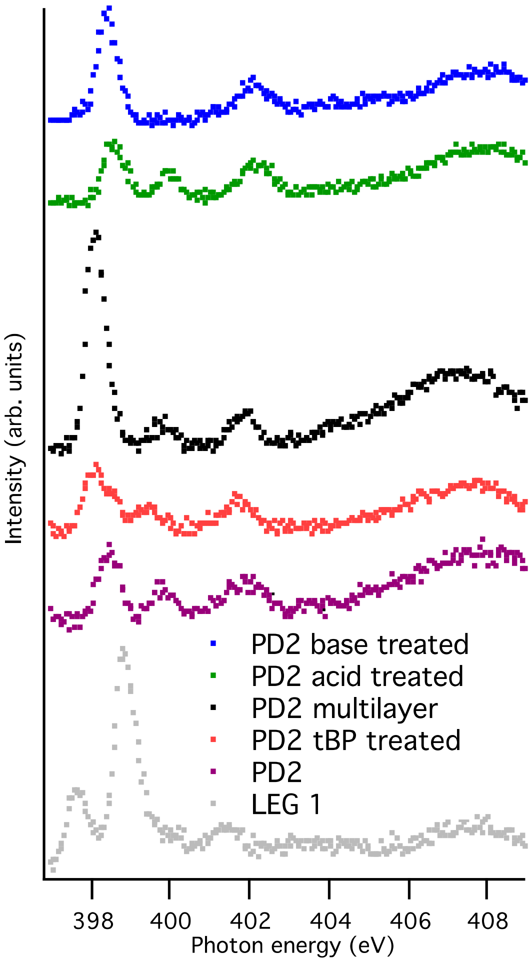


Figure S6. N1s-NEXAFS spectra of LEG1 and PD2. The peak near 400 eV in the TBP sample is likely caused by residual protonated TBP. All spectra except PD2 multilayer are of dye adsorbed to TiO_2.

Stability test

The cells were prepared in a similar way as described in device preparation, but using a 6 µm thick transparent layer of TiO_2. The electrolyte used was 0.3 M/0.15 M $Co(bpy)_3[B(CN)_4]_{2/3}$ and 0.2 M TBP in acetonitrile.

The light soaking treatment was 100 mW/cm² simulated solar irradiation at 60 °C.

Table S2. Device efficiency after various periods of light soaking.

PD2	Voc / V	Jsc / mA cm-2	ff	η
Initial	0.64	3.6	0.43	1.0
192 h	0.71	7.6	0.66	3.6
360 h	0.71	9.7	0.61	4.2
552 h	0.71	9.6	0.69	4.6
1000 h	0.69	9.7	0.57	3.8

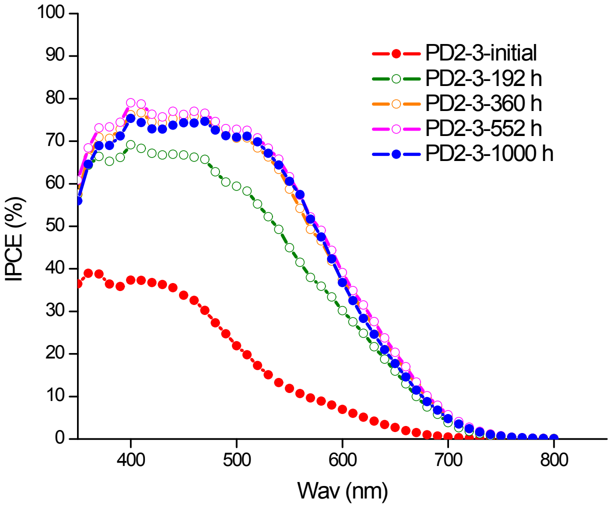


Figure S7. IPCE after various periods of light soaking.

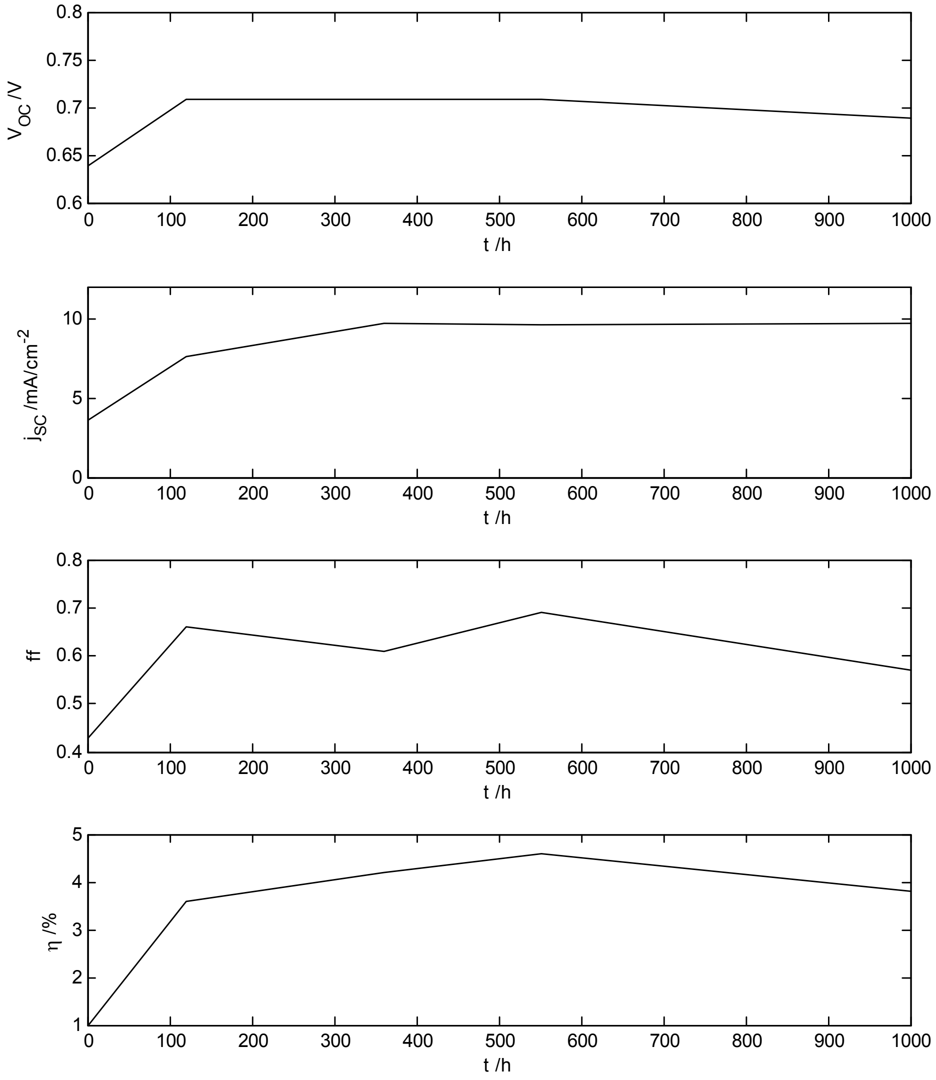


Figure S8. Device performance characteristics after various periods of light soaking.

Single crystal diffraction

Single crystal X-ray diffraction data were collected from a plate like crystal on a Rigaku Saturn 724+ diffractometer at 100(2) K using a synchrotron radiation (λ =0.6889 Å) at beamline I19, Diamond Light Source, UK. Data reduction and multi-scan correction were applied usingCrystalAlis software[3]. The structure was solved and refined by SHELX[4]. All the no-hydrogen atoms were refined anisotropically and all the hydrogen atoms were refined isotropically as rigid body in calculated position.

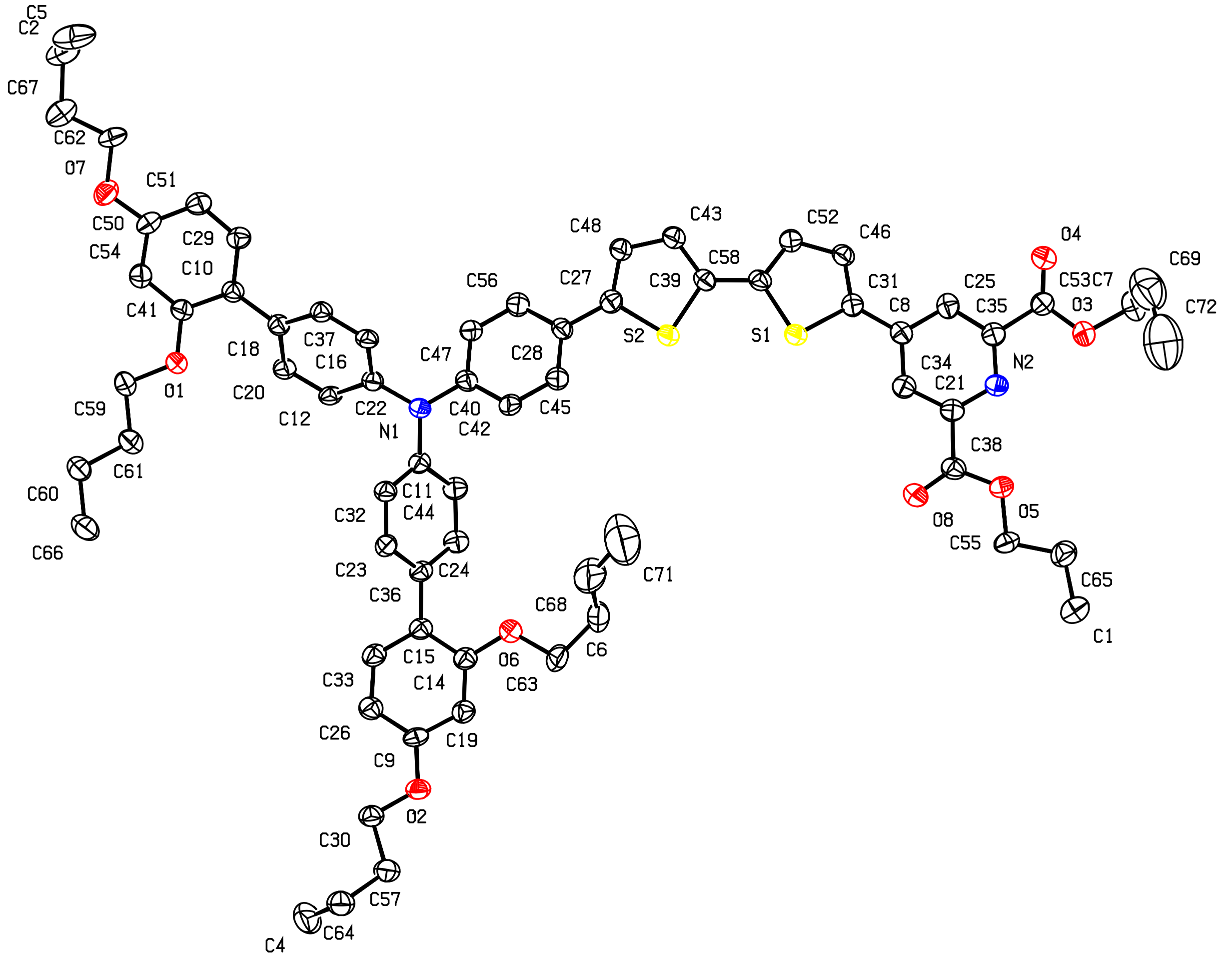


Figure S9. ORTEP drawing of *n*-Pr$_2$PD2 generated from SCD data.

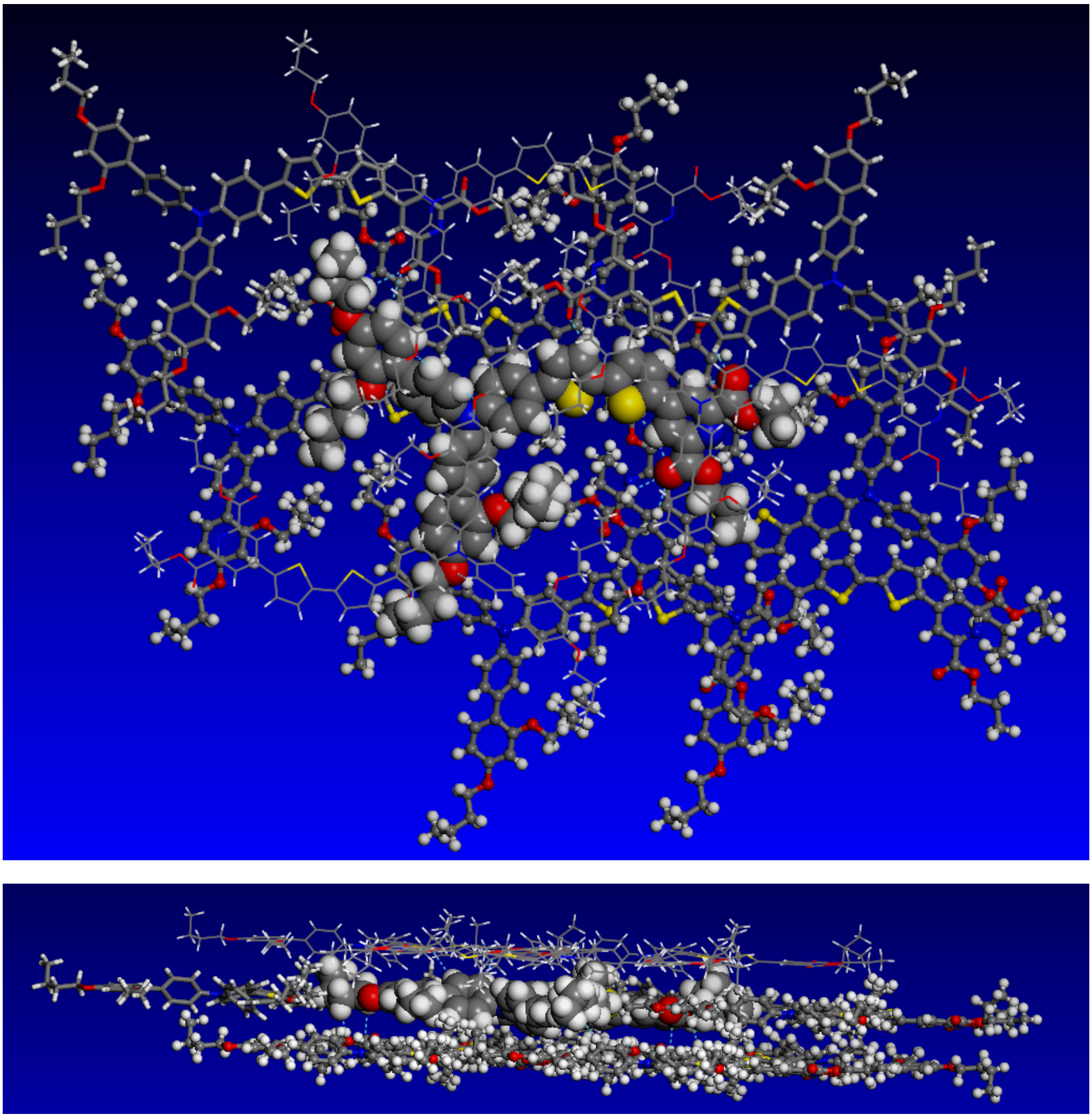


Figure S10. Local environment of *n*-Pr_2PD2 in the crystal structure.

NMR Spectra

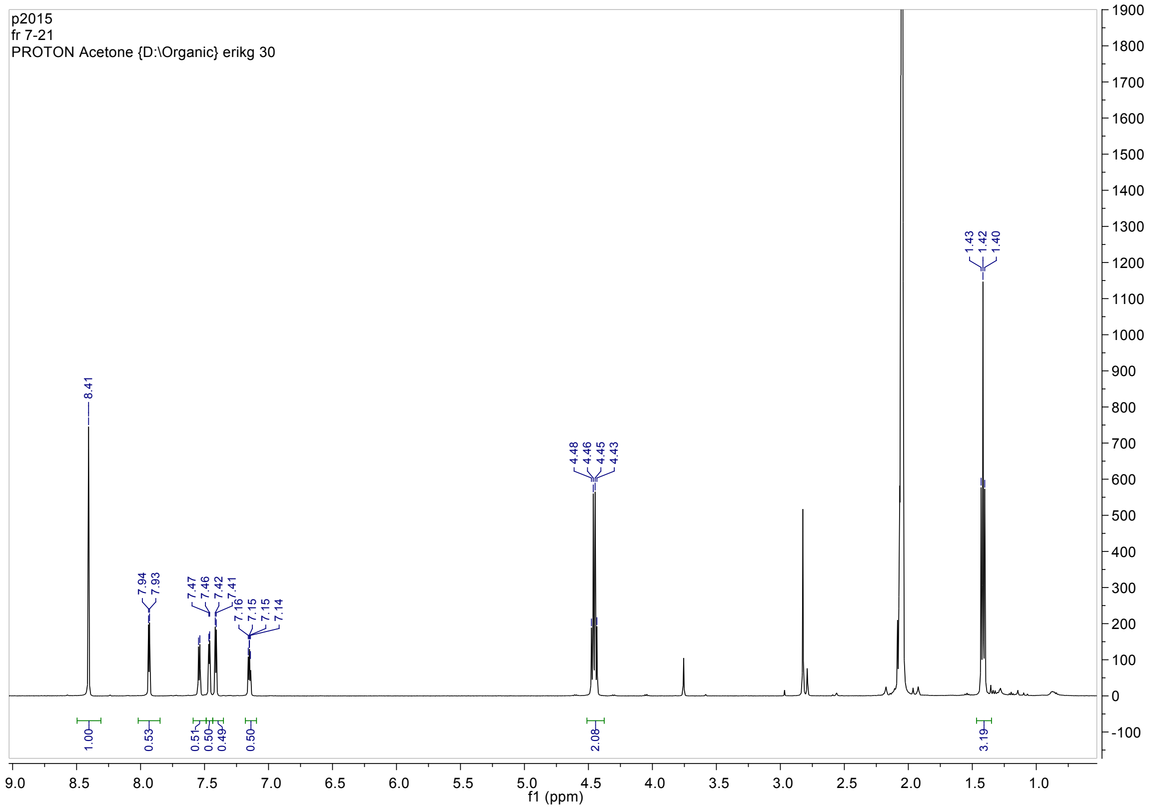


Figure S11. ^{1}H-NMR of **1** in d$_6$-acetone.

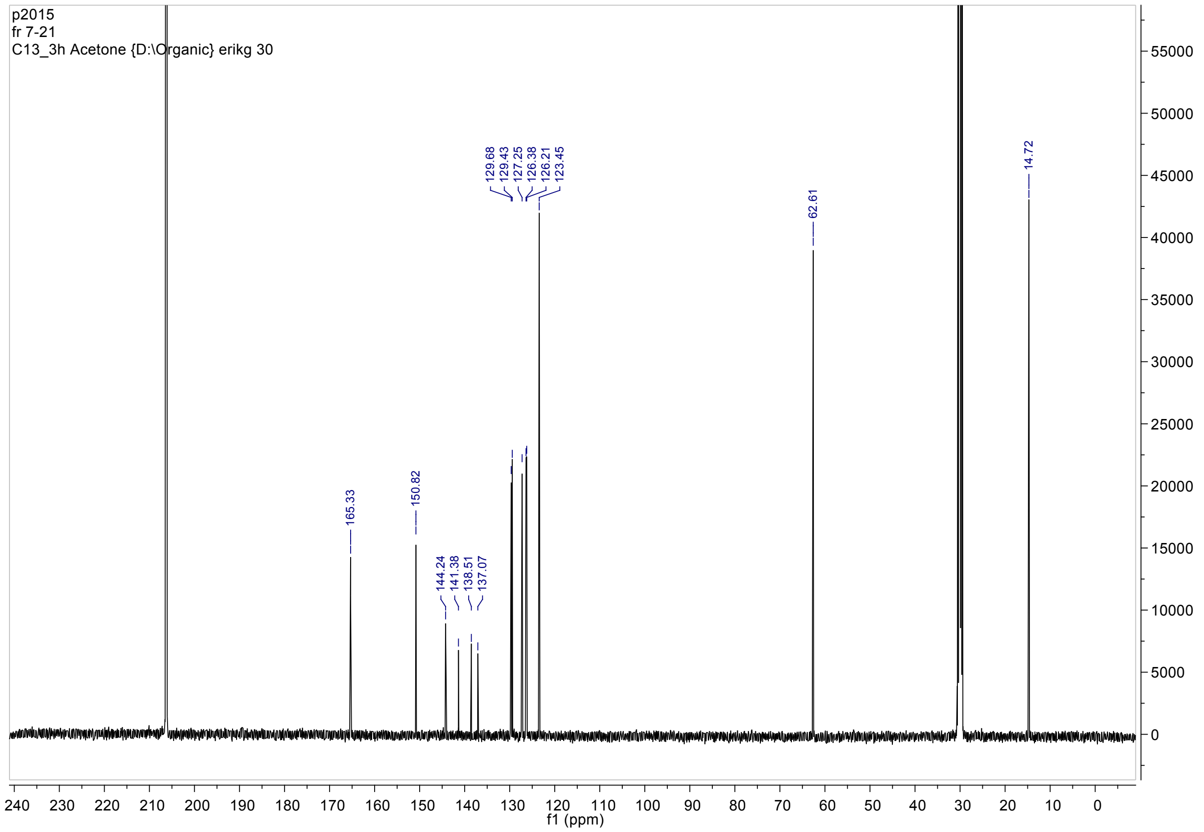


Figure S12. ^{13}C-NMR of **1** in d$_6$-acetone.

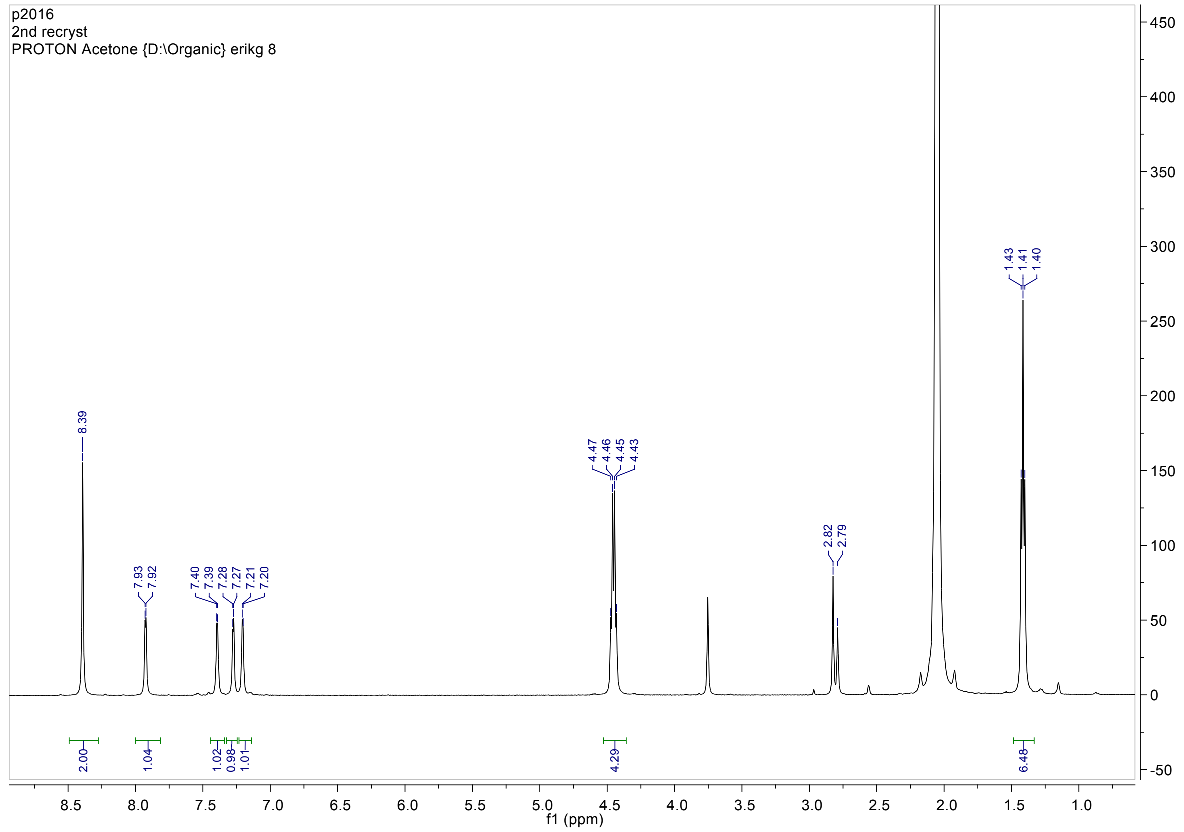


Figure S13. ^{1}H-NMR of **2** in d_6-acetone.

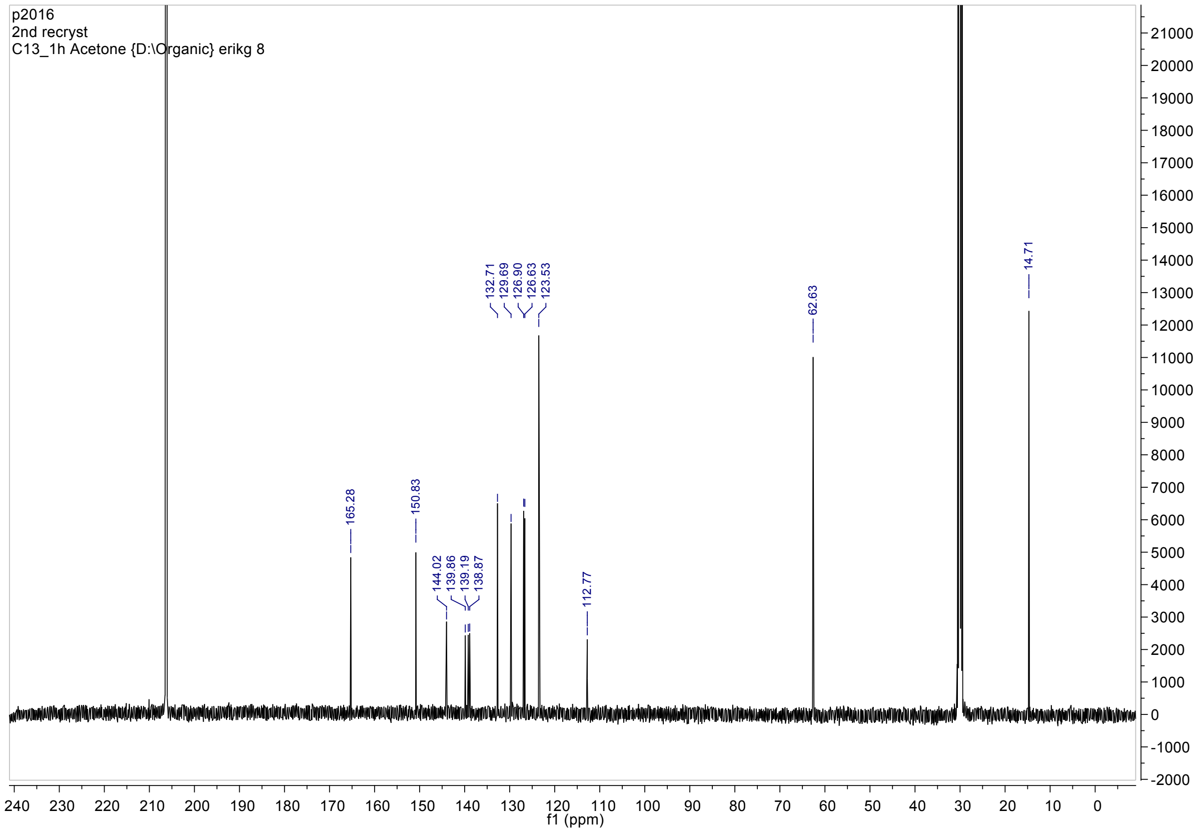


Figure S14. ^{13}C-NMR of **2** in d_6-acetone.

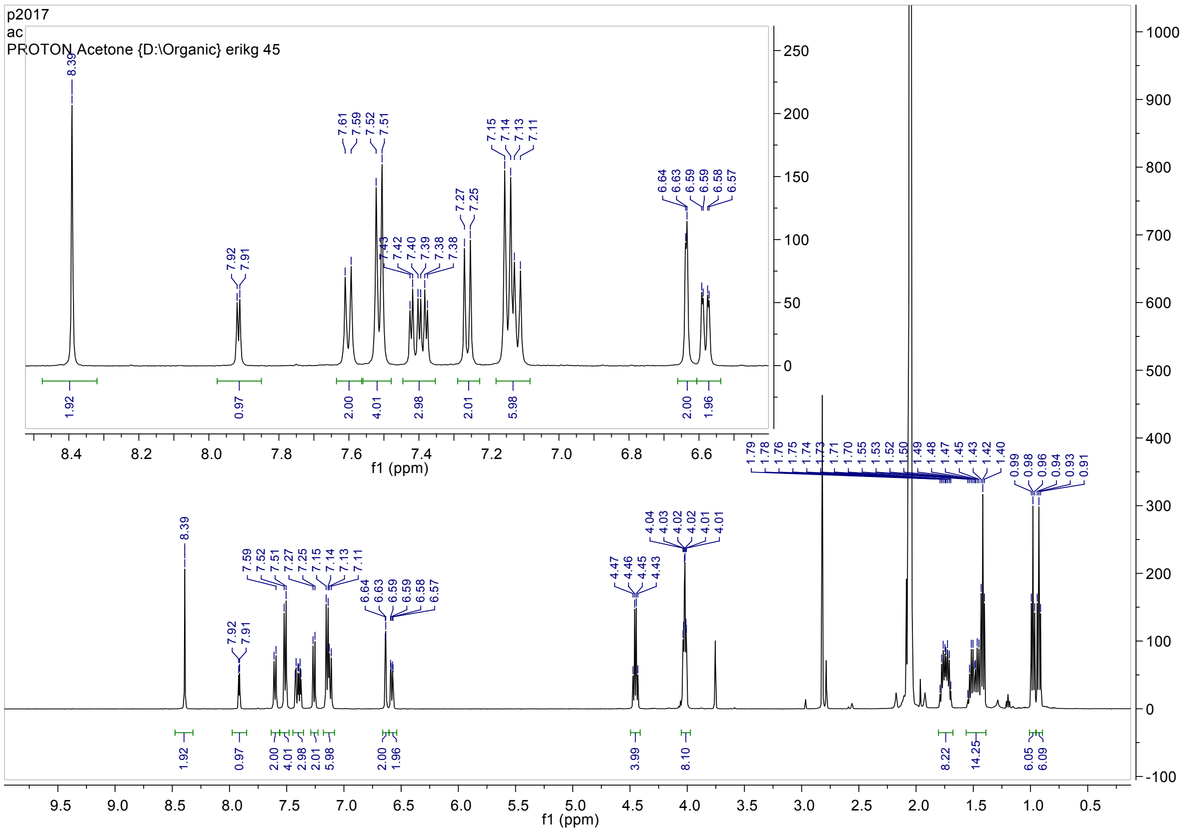


Figure S15. ^{1}H-NMR of **Et$_2$PD2** in d$_6$-acetone.

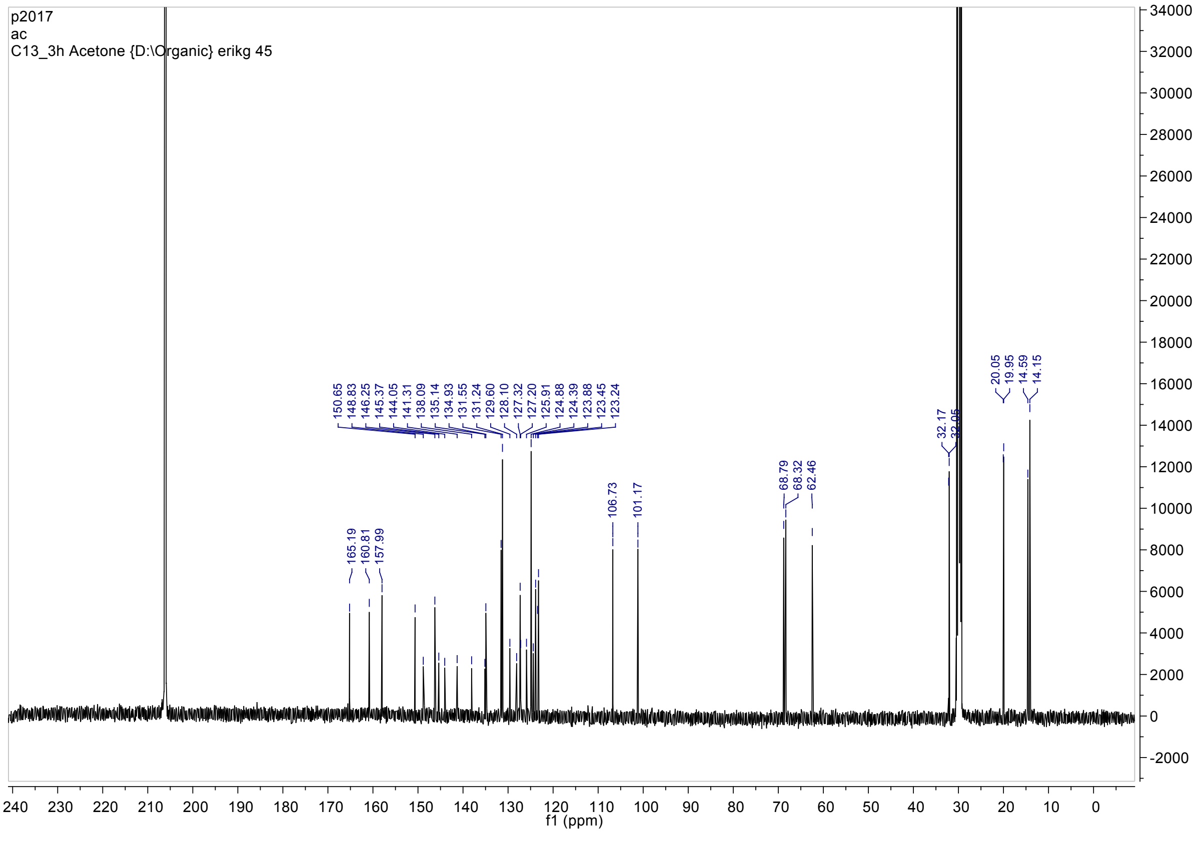


Figure S16. ^{13}C-NMR of **Et$_2$PD2** in d$_6$-acetone.

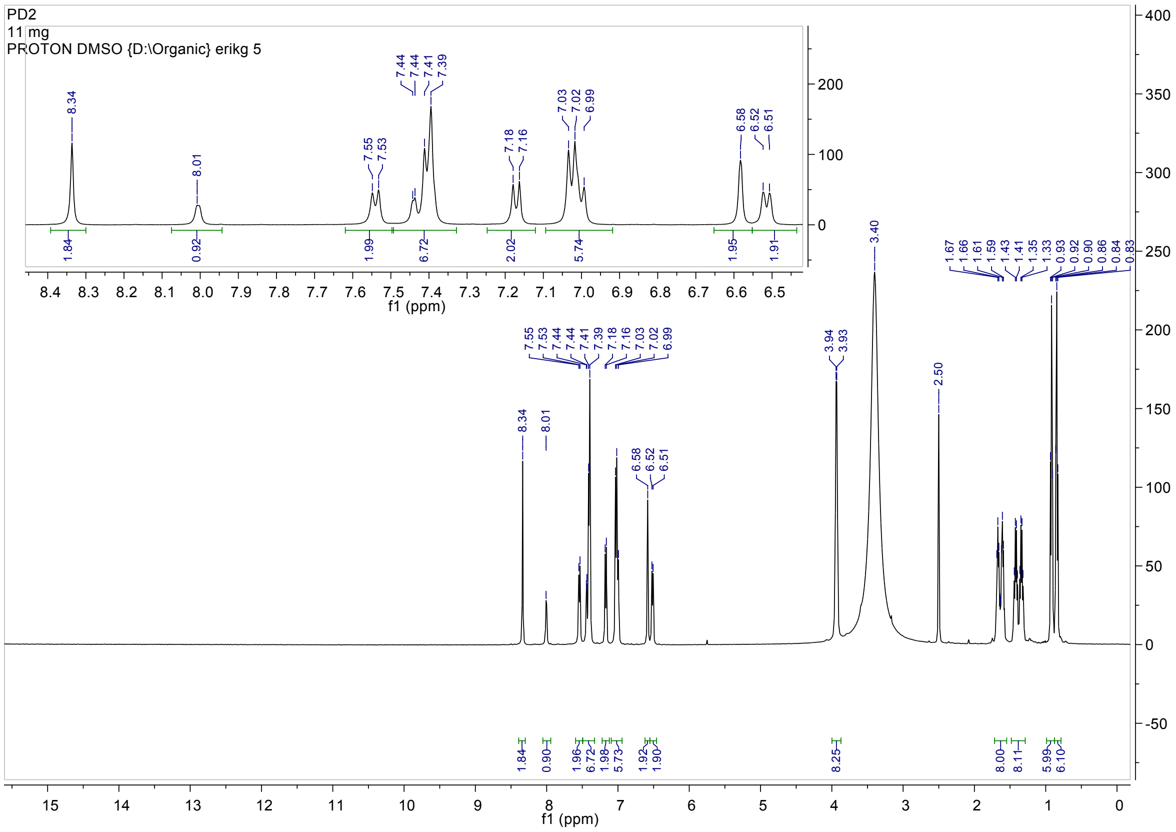


Figure S17. ^{1}H-NMR of **PD2** in d$_6$-DMSO.

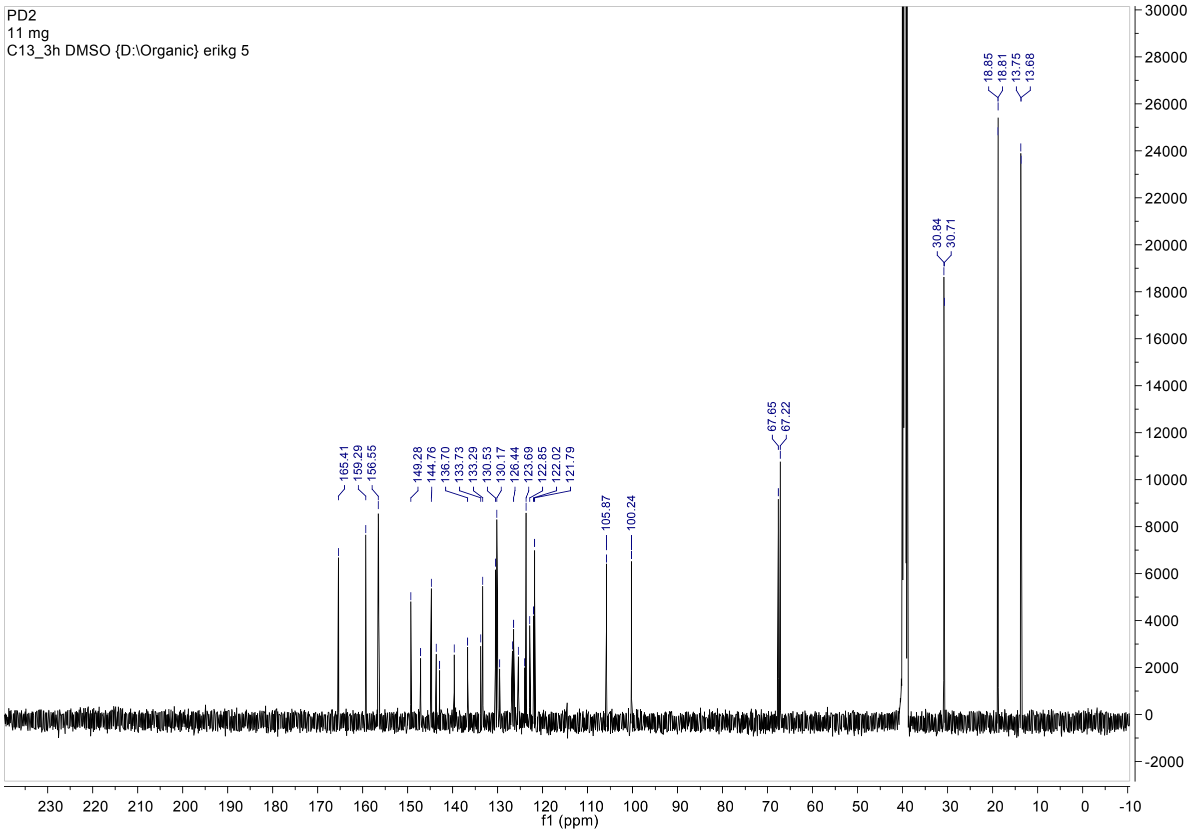
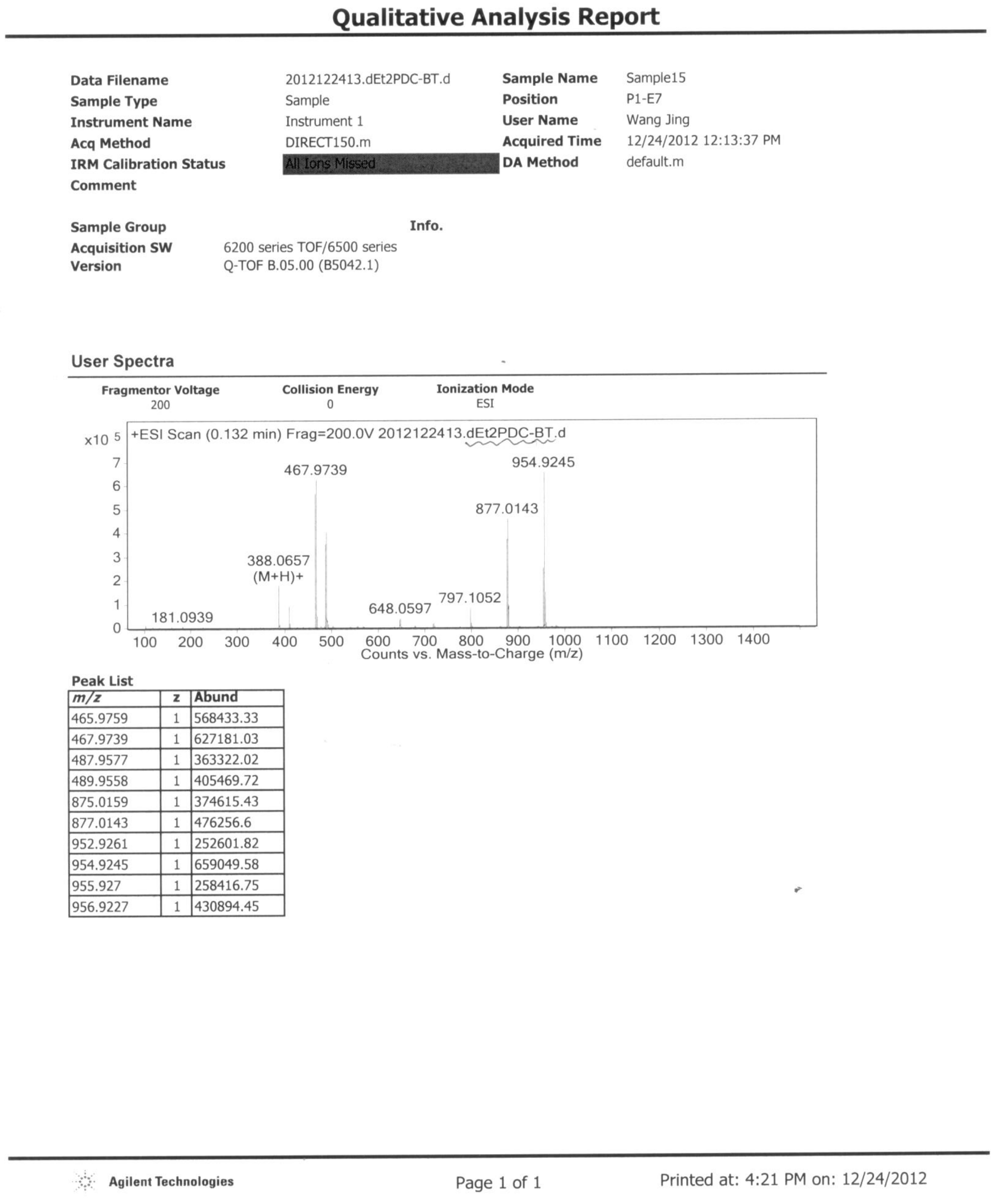


Figure S18. ^{13}C-NMR of **PD2** in d$_6$-DMSO.

HRMS Spectra



Qualitative Analysis Report

Data Filename	2012122413.dEt2PDC-BT.d	**Sample Name**	Sample15
Sample Type	Sample	**Position**	P1-E7
Instrument Name	Instrument 1	**User Name**	Wang Jing
Acq Method	DIRECT150.m	**Acquired Time**	12/24/2012 12:13:37 PM
IRM Calibration Status	All Ions Missed	**DA Method**	default.m
Comment			

Sample Group **Info.**
Acquisition SW 6200 series TOF/6500 series
Version Q-TOF B.05.00 (B5042.1)

User Spectra

Fragmentor Voltage	**Collision Energy**	**Ionization Mode**
200	0	ESI

Peak List

m/z	z	Abund
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467.9739	1	627181.03
487.9577	1	363322.02
489.9558	1	405469.72
875.0159	1	374615.43
877.0143	1	476256.6
952.9261	1	252601.82
954.9245	1	659049.58
955.927	1	258416.75
956.9227	1	430894.45

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Figure S19. HR-MS of compound **1**.

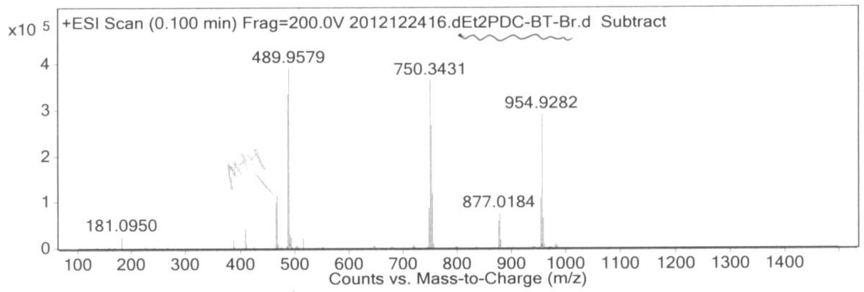
Qualitative Analysis Report

Data Filename	2012122416.dEt2PDC-BT-Br.d	**Sample Name**	Sample18
Sample Type	Sample	**Position**	P1-F1
Instrument Name	Instrument 1	**User Name**	Wang Jing
Acq Method	DIRECT150.m	**Acquired Time**	12/24/2012 2:40:23 PM
IRM Calibration Status	All Ions Missed	**DA Method**	default.m
Comment			

Sample Group		**Info.**
Acquisition SW Version	6200 series TOF/6500 series Q-TOF B.05.00 (B5042.1)	

User Spectra

Fragmentor Voltage	Collision Energy	Ionization Mode
200	0	ESI



Peak List

m/z	z	Abund	Formula	Ion
467.9757	1	115133.61	C19 H17 Br N O4 S2	(M+H)+
487.96	1	345572.74		
489.9579	1	391810.96		
749.3439		246079.04		
750.3431	1	364994.11		
751.3457	1	137016.21		
752.343	1	267992.09		
754.3442	1	118459.36		
954.9282	1	291031.22		
956.9271	1	191506.6		

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Figure S20. HR-MS of compound **2**.

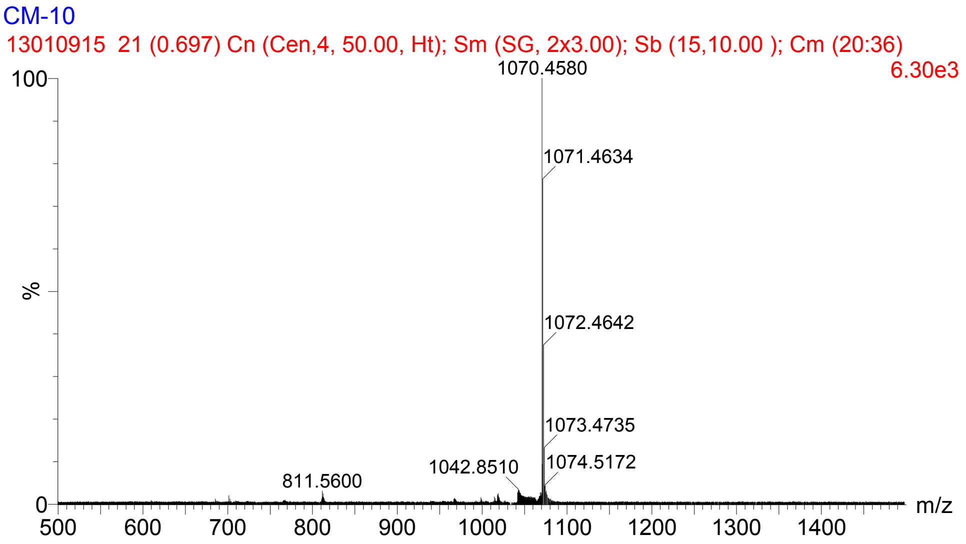

Figure S21. HR-MS of **Et$_2$PD2**.

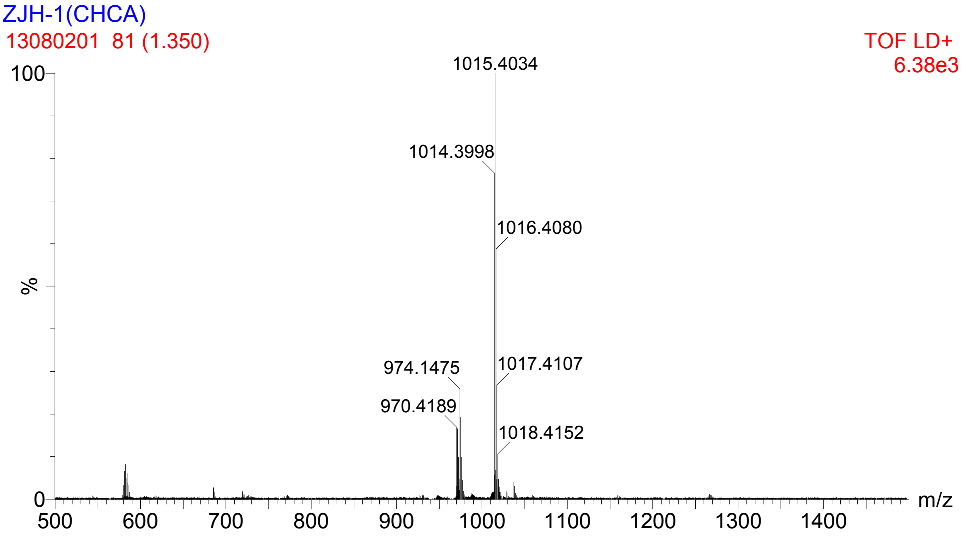

Figure S22. HR-MS of **PD2**.

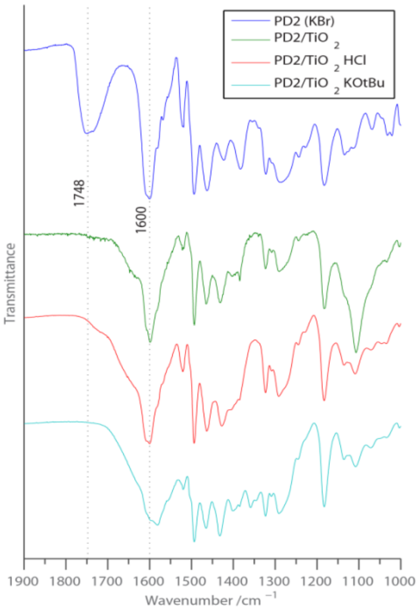

Figure S23. IR spectra of different samples

We are disinclined to assign the shoulder at ~1640 cm-1 to pyridinium, because this peak could also be from water; which typically appears around 1632 cm^{-1} (*Infrared and Raman Spectroscopydoi:10.1016/B978-0-12-386984-5.10003-5*). The samples used to collect the IR spectra of the dyes on TiO2 are quite dilute compared to that of the pure dye, thus making it difficult to avoid the water peak (see figure S3). Additionally, the proximity to two carboxylic acid groups and the TiO2 surface likely shifts the N-H stretch frequency due to hydrogen bonding. After carefully analysis the IR data shown in the figure, we can see a shoulder around 1725 cm-1 after HCl acid treatment, this shoulder could be assigned to –COOH group. A simple explanation to why the carbonyl peak is weak in the acid treated sample is that the HCl solution (0.1 M) used to treat the sample was not acidic enough to protonate the carboxylate, the pKa of for H-PDC+ is <0.5) (*J. Phys. Chem. A*, 2011, *115* (27), pp 7912–7920). In fact, we did notice an additional color change (to black) when a stronger acid was used. We did not study this state though, as it is not relevant for the DSSC. It is reasonable that the wavenumber of -COOH in PD2/TiO2 HCl sample (1725 cm-1) should be a little different from that (1750 cm-1) in pure dye (PD2/KBr), because the latter is not adsorbed to TiO2

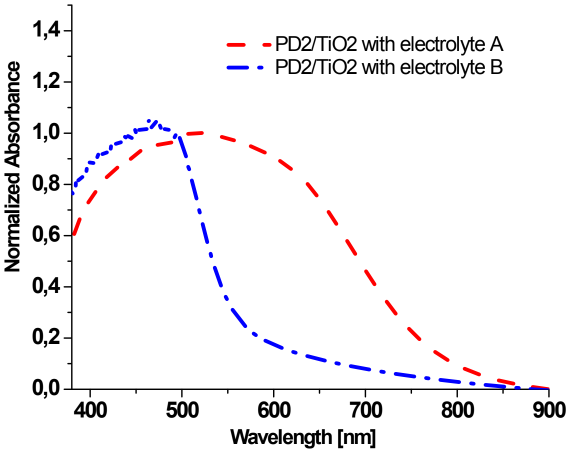

Figure S23. Absorption Spectra of PD2/TiO2 with different electrolyte

References

1. (a) Schmidt, B.; Ehlert, D. K., Preparation of N-Boc-(2,6-bis-(ethoxycarbonyl)pyridin-4-yl)-L-alanines as tridentate ligands. *Tetrahedron Lett.* **1998,***39* (23), 3999-4002;(b) E. Gabrielsson, H. E., Dr. Sandra M. Feldt, Dr. H. Tian, Dr. Gerrit Boschloo, Prof. A. Hagfeldt, Prof. L. Sun, Convergent/divergent synthesis of a linker-varied series of dyes for Dye-Sensitized Solar Cells based on the D35 donor. *Adv. Energy Mater.* **2013**.

2. Johansson, E. M. J.; Hedlund, M.; Siegbahn, H.; Rensmo, H., Electronic and molecular surface structure of Ru(tcterpy)(NCS)(3) and Ru(dcbpy)(2)(NCS)(2) adsorbed from solution onto nanostructured TiO2: A photoelectron spectroscopy study. *Journal of Physical Chemistry B* **2005,***109* (47), 22256-22263.

3. Crysalis Sofware system Version 171.35.19, Xcalibur CCD System, Oxford Diffraction Ltd., 2011.

4. Sheldrick, G., Acta Crystallogr. 2008, A64, 112-122.