

Electronic supplementary information for

Conjugated linker correlated energetics and kinetics in dithienopyrrole dye-sensitized solar cells

Jing Zhang, Zhaoyang Yao, Yanchun Cai, Lin Yang, Mingfei Xu, Renzhi Li,* Min Zhang,* Xiandui Dong and Peng Wang*

State Key Laboratory of Polymer Physics and Chemistry, Changchun Institute of Applied Chemistry, Chinese Academy of Sciences, Changchun 130022, China

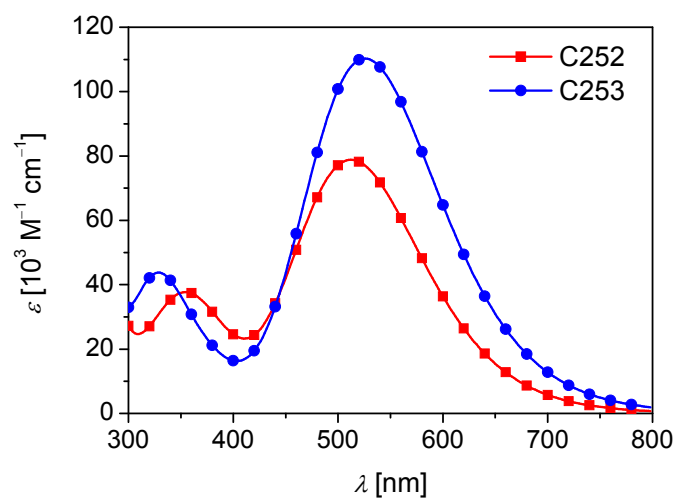


Fig. S2 Simulated electronic absorption spectra of **C252** and **C253** in THF at the CAM-B3LYP/6-31G(d,p) level.

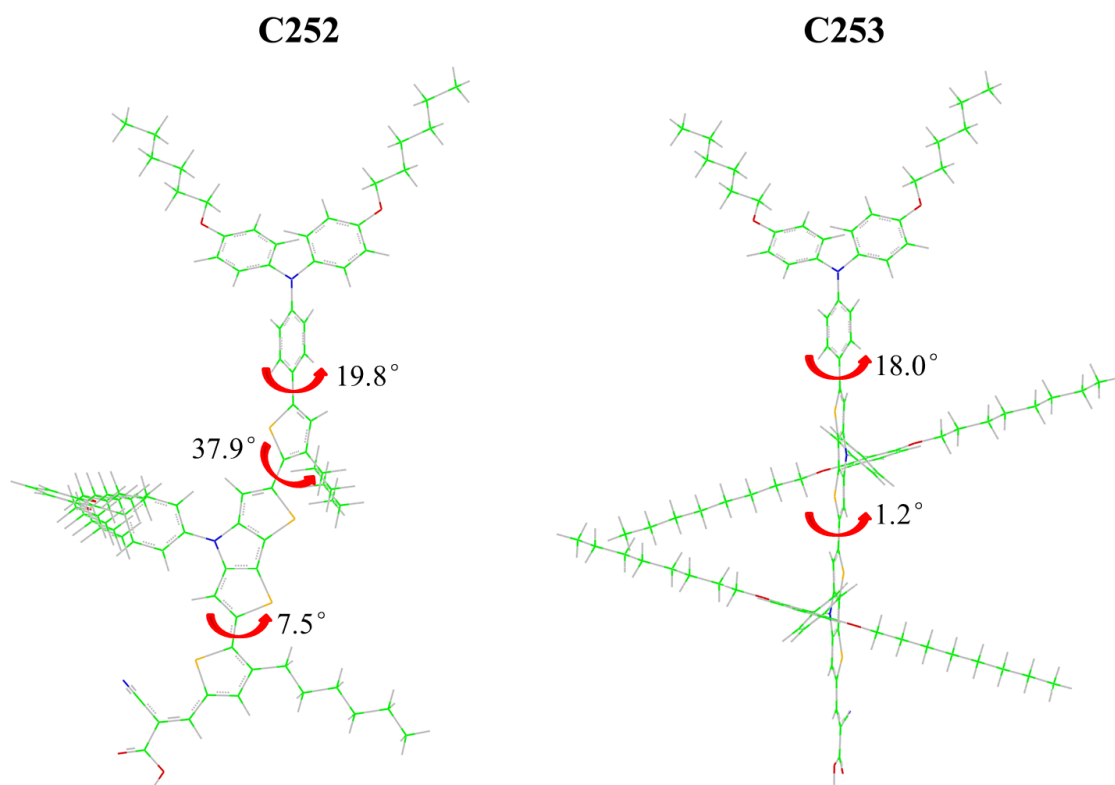


Fig. S3 Optimized geometries of C252 and C253.

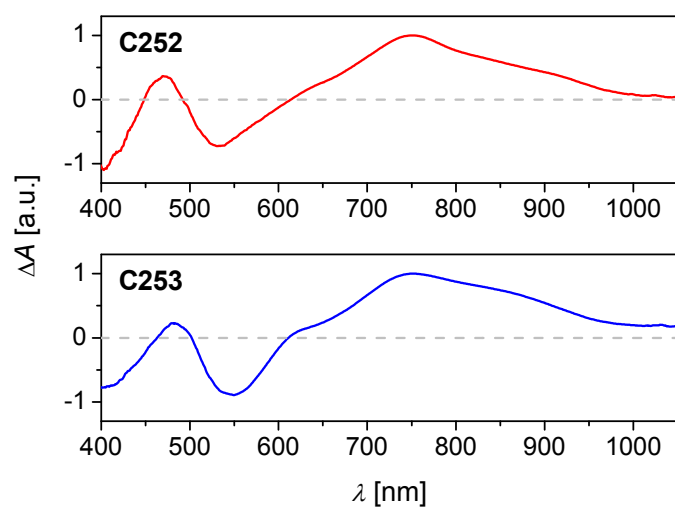
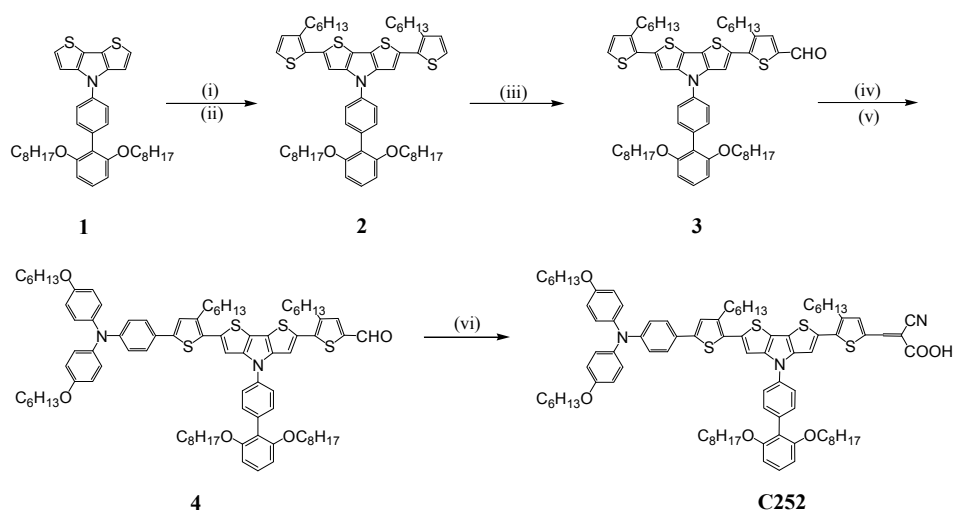


Fig. S4 Absorption change as a function of wavelength, upon applying a small positive potential to 2- μm -thick, dye-coated titania films dipped in EMITFSI.

Table S1 Intensities of the Ti2p_{3/2} signals and mean thicknesses of the dye coatings on titania calculated *via* empirical equations and parameters

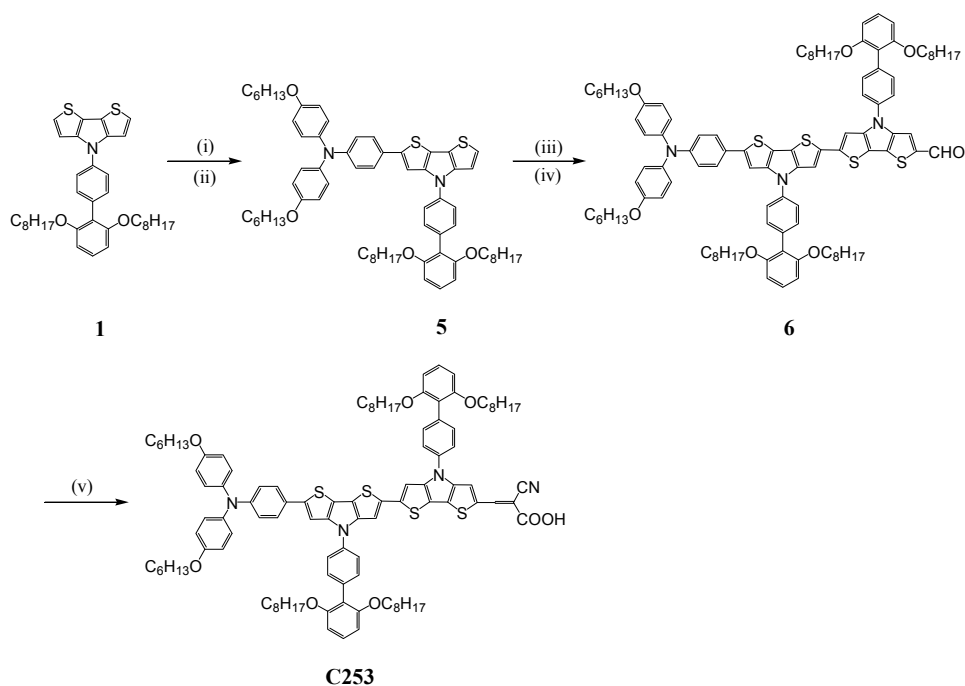
Sample	Intensity [cps]	<i>d</i> [Å]
TiO ₂	74047	—
C252 /TiO ₂	26288	33.1
C253 /TiO ₂	34151	24.5

Scheme S1 Synthetic route for **C252**^a



^a Reagents and conditions: (i) 2.0 equiv *t*-BuLi, THF, -78 °C, 3 h; 2.0 equiv Me₃SnCl, -78 °C to RT, overnight; (ii) 3.0 equiv 2-bromo-3-hexylthiophene, 12% P(*t*-Bu)₃, 3% Pd₂(dba)₃, 4.4 equiv CsF, dioxane, reflux, 4 h; (iii) 5.0 equiv DMF, 1.2 equiv POCl₃, DCE, 0 °C to RT, 24 h; (iv) 1.0 equiv NBS, THF, 0 °C, overnight; (v) 1.1 equiv 4,4,5,5-tetramethyl-2-{4-[*N,N*-bis(4-hexyloxyphenyl)amino]phenyl}-1,3,2-dioxaborolane, 2% Pd(OAc)₂, 2% SPhos, 5.0 equiv K₃PO₄, dioxane/H₂O (v/v, 5/1), RT, overnight; (vi) 3.0 equiv cyanoacetic acid, 7.0 equiv piperidine, CHCl₃, reflux, 12 h.

Scheme S2 Synthetic route for **C253**^b



^b Reagents and conditions: (i) 1.0 equiv *t*-BuLi, THF, $-78\text{ }^{\circ}\text{C}$, 4 h; 1.0 equiv Me_3SnCl , $-78\text{ }^{\circ}\text{C}$ to RT, overnight; (ii) 1.1 equiv *N,N*-bis(4-hexyloxyphenyl)-4-bromoaniline, 12% $\text{P}(t\text{-Bu})_3$, 3% $\text{Pd}_2(\text{dba})_3$, 2.2 equiv CsF, dioxane, reflux, 4 h; (iii) 1.5 equiv *t*-BuLi, THF, $-78\text{ }^{\circ}\text{C}$ to RT, 3 h; 1.5 equiv Me_3SnCl , $-78\text{ }^{\circ}\text{C}$ to RT, overnight; (iv) 0.9 equiv 4-(2',6'-bis(octyloxy)biphenyl-4-yl)-6-bromo-4*H*-dithieno[3,2-*b*:2',3'-*d*]pyrrole-2-carbaldehyde, 12% $\text{P}(t\text{-Bu})_3$, 3% $\text{Pd}_2(\text{dba})_3$, 2.2 equiv CsF, dioxane, reflux, 4 h; (v) 3.0 equiv cyanoacetic acid, 7.0 equiv piperidine, CHCl_3 , reflux, 12 h.