Supporting Information for

The first thieno[3,4-b]pyrazine based small molecular acceptor with linear A_2-A_1-D-A_1-A_2 skeleton for fullerene-free organic solar cells with a high *V*oc of 1.05V

*Jianfeng Li[1,2#], Jing Yang[1,2#], Junyi Hu[1,2], You Chen[1,2], Bo Xiao[1,2], Erjun Zhou[*1]*

[1]CAS Key Laboratory of Nanosystem and Hierarchical Fabrication, CAS Center for Excellence in Nanoscience, National Center for Nanoscience and Technology, Beijing 100190, P. R. China.

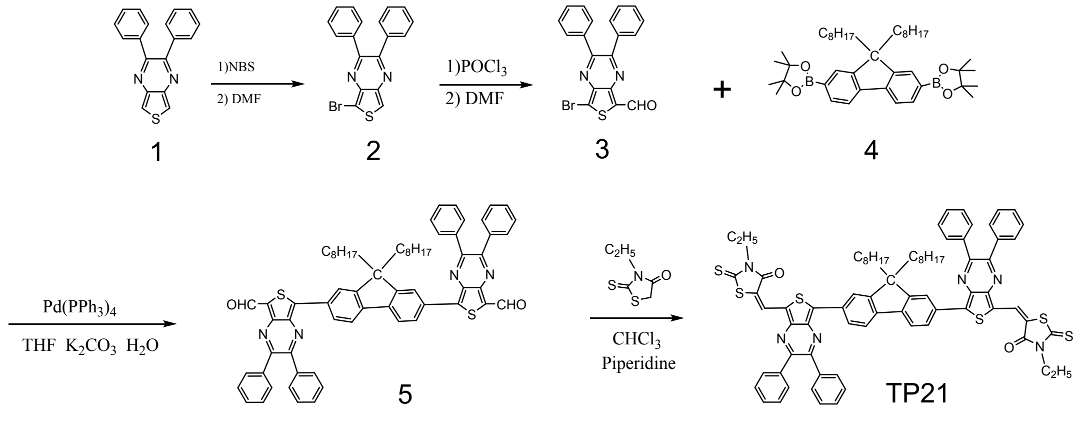
[2]University of Chinese Academy of Sciences, Beijing 100049, P. R. China.

 # This two authors contributed equally to this paper.

1: Materials and Methods

Materials. All Chemicals and solvents were reagent grades and purchased from Alfa, Aldrich, Beijing Chemical Plant or other chemical companies and used without further purification. The TP (monomer 1) compounds were synthesized according to the procedures in the literatures [1] and fluorene was purchase from Sigma Aldrich.

Synthetic Procedure:



~~Scheme 1,~~ Synthetic route of TP-based small molecule acceptor.

5-bromo-2,3-diphenylthieno[3,4-b] pyrazine (2): Compound 1 (10g, 34.7 mmol) was dissolved in 200 mL of dry DMF in a 500 mL flask. Then a solution of NBS (6.17 g, 34.7mmol) in DMF (30 mL) was added to a solution which was cooled in an ice bath. Then the reaction mixture was warmed to room temperature and stirred for overnight. The reaction mixture was poured into water and then extracted with chloroform. The organic layers were combined, washed with sodium chloride solution and dried with sodium sulfate. Further purification was performed using flash silica gel chromatography (chloroform) to generate 2 (8.1g,63%) as a green solid. 1HNMR (400 M, $CDCl_3$): δ(ppm) 8.08 (s, 1H), 7.47(d, 2H), 7.42 (4, 2H), 7.30 (m, 6H).

7-bromo-2,3-diphenylthieno[3,4-b] pyrazine-5-carbaldehyde (3): Compound 1 (5g, 13.6 mmol) was dissolved in 40 mL anhydrous 1,2-dichloroethane and anhydrous DMF (4.2mL,54.4mmol) was cooled down to 0°C under nitrogen atmosphere. $POCl_3$ (2.5mL, 27.2mmol) was added drop wise into the solution. The mixture was stirred at 0 °C for 30min and room temperature for 1 hour respectively. Then it was heated to 60°C for 16 hours. The solution was cooled down to room temperature and sodium bicarbonate solution (1 M in water) was added to neutralize rest $POCl_3$. Then it was poured into water, extracted with dichloromethane, dried with $MgSO_4$ and concentrated under reduced pressure. The crude product was purified by silica gel chromatography with dichloromethane/petroleum ether (1:1) as eluent, affording 3 as yellow solid (2.6 g, 43% yield). 1HNMR (400 M, $CDCl_3$): δ(ppm) 10.68 (s, 1H), 7.50(m, 4H), 7.41 (t, 2H), 7.34(m, 4H)

7,7'-(9,9-dioctyl-9H-fluorene-2,7-diyl) bis(2,3-diphenylthieno[3,4-b] pyrazine-5-carbaldehyde) (5): A solution of 6 (660mg, 1.04 mmol) and 6 (940 mg, 2.38 mmol) in THF (30 ml) was degassed before addition of $Pd(PPh_3)_4$ (60 mg, 0.05 eq) and subsequent degassing for 1 h. K_2CO_3 solution (1M, 5 ml) was then added and the reaction was heated under argon at 80 °C for 20h. After cooling to room temperature, the reaction was quenched with water and extracted with CH_2Cl_2. Flash column chromatography on silica gel with

$CHCl_3$ as the eluent, afforded 7 as a red solid (960 mg, 90%). ^{1}HNMR (400 M, $CDCl_3$): δ(ppm) 10.80(s, 1H), 8.54(s, 1H), 8.38(d, 1H), 7.94(d, 1H), 7.61(m, 4H), 7.41(m, 6H), 2.14(m, 2H), 1.05(m, 10H), 0.76(m, 5H).

TP21: Compound 5 (400 mg, 0.26 mmol), 3-ethylrhodanine (318 mg, 1.97 mmol), chloroform (30 mL) and piperidine (0.2 mL) were added to a two-necked round-bottom flask. The mixture was deoxygenated with nitrogen for 10 minutes, and then refluxed for 30 minutes. After cooling to room temperature, the mixture was poured into methanol (100 mL) and stirred for 10 minutes, then filtered. The residue was purified by column chromatography on silica gel with $CHCl_3$ as an eluent yielding a green solid (280mg, 52% yield). ^{1}HNMR (400 M, $CDCl_3$): δ(ppm) 8.91(s, 1H), 8.55(s, 1H), 8.40 (d, 1H), 7.91(d, 1H), 7.64(m, 4H), 7.41(m, 6H), 4.29(m, 2H), 2.20(t, 2H), 1.37(t, 3H), 1.05(m, 10H), 0.74(m, 5H). MALDI-TOF MS (m/z) calcd:1304.4, found:1305.9 $(M+H)^+$

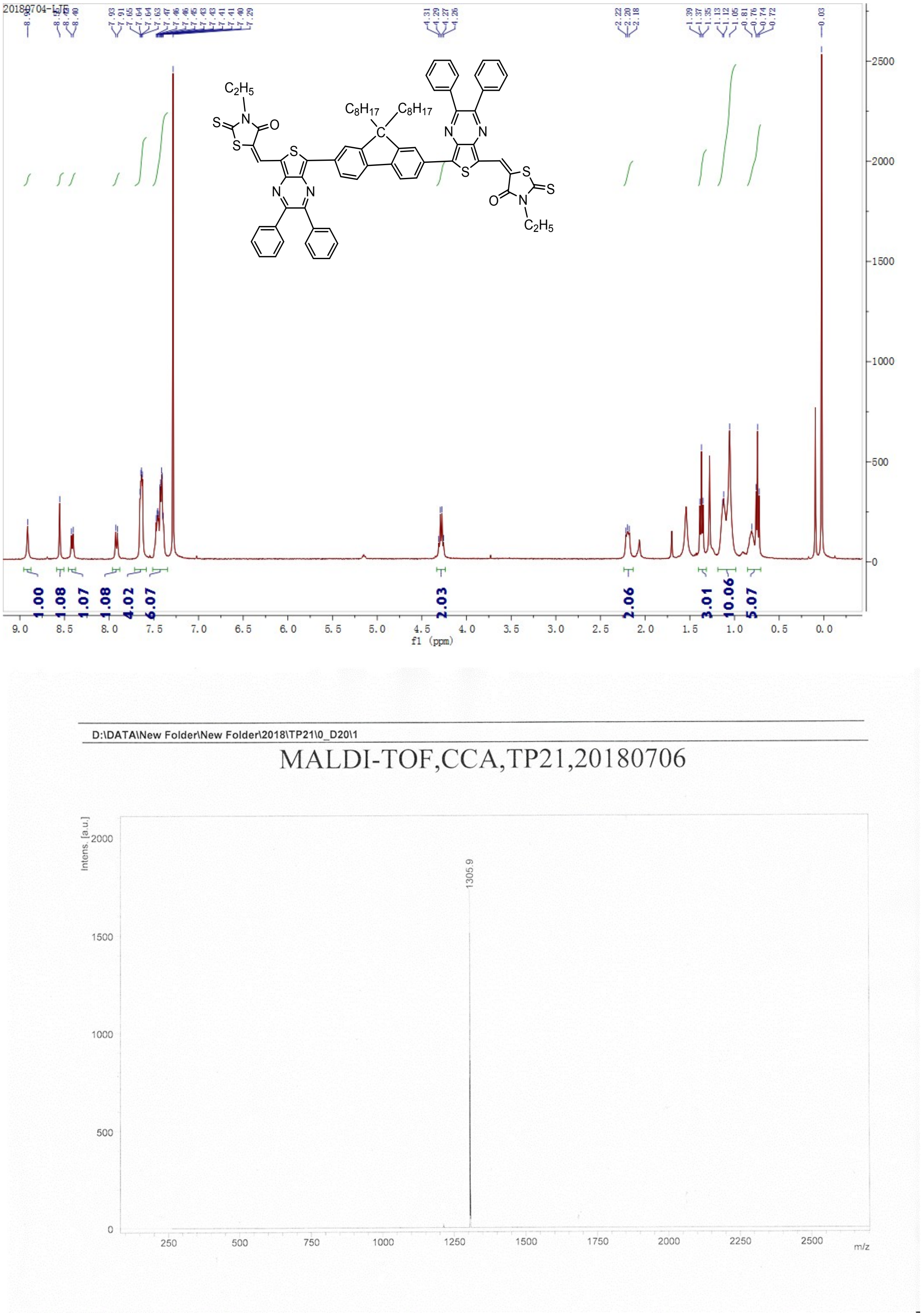
Methods. ^{1}H NMR spectra were obtained using an Avance III 400 (Bruker, Billerica, MA; 400 MHz) NMR spectrometer. UV-vis absorption spectra were acquired on a Lambda 950 spectrophotometer (PerkinElmer, Waltham, MA). Thermogravimetric analysis (TGA) was recorded on Diamond TG/DTA under the protection of nitrogen at a heating rate of 10℃ · min^{-1}. Cyclic voltammetry (CV) was performed on a CHI-600E electrochemical workstation (Shanghai Chenhua Instruments Co., Ltd., Shanghai, China) using a platinum plate coated with a thin blend film, a platinum wire, and an Ag/AgCl electrode as the working electrode, counter electrode, and reference electrode, respectively. The CV system was calibrated using the ferrocene–ferrocenium (Fc/Fc+) redox couple in a 0.1 mol L^{-1} tetrabutylammonium hexafluorophosphate (Bu_4NPF_6) solution in acetonitrile. Atomic force microscopy (AFM) images of the blend films were obtained on a MultiMode 8 scanning probe microscope (Bruker).

2: Fabrication and characterization of photovoltaic cells

A patterned ITO was pre-cleaned by detergent, deionized water, acetone and 2-propanol for 15 min, respectively, under ultrasonic condition. The cleaned ITO was then treated by ultraviolet ozone cleaner (Jelight Company, USA) to form the hydrophilic surface. The PEDOT:PSS solution was spin-coated on the ITO at 3500 rpm for 30s and dried over 150℃ for 15 min under air. The J61: TP21 solution (optimized weight ratio of 1:1) in chlorobenzene was then spin-coated above PEDOT:PSS layer at a total concentration of 20 mg/mL within a nitrogen-filled glove box. Then the active layer was used CB as solvent and spin speed of 3000 rpm for the active layer, the D/A weight ratio of 1:1 and annealing temperature of 140 °C for 10 min. The Ca (20 nm) and Al (80 nm) cathode were evaporated onto the active layer under a pressure of below 3×10^{-6}mbar with an active area of 4 mm^2. The current density-voltage curves were collected by a Keithley 2420 under Oriel Newport 150W solar simulator (AM 1.5G). The thicknesses of the active layer were detected by Alpha-atepD-120stylus profilometer, Kla-Tencor.

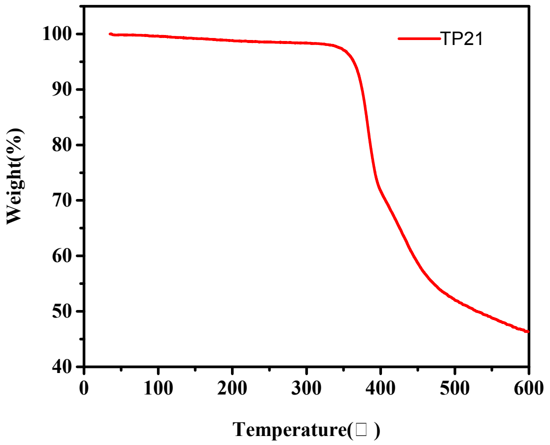
The EQEs were measured by an Oriel Newport System. All above measurements were done at room temperature in air. The mobility of hole-only or electron-only of the PSCs device was achieved by fabricated the architecture ITO/PEDOT:PSS/active layer/Au for holes or ITO/TiOx/active layer/Al for electrons, where TiOx layer was fabricated by sol-gel method from titanium (diisopropoxide) bis (2,4-pentanedionate), 75% in isopropanol liquid (TIPD). The mobility was extracted by fitting the current density-voltage curves using the Mott-Gurney relationship (SCLC). The active layer and electrodes were prepared the same as the solar cells condition. Au (80 nm) and Al (80 nm) cathodes were thermal evaporated in glove box at a chamber pressure of ~ 3.0×10^{-6} torr.

3: ^{1}H NMR Spectra and MALDI-TOF MS of the Monomers



~~**Figure S1.**~~ ^{1}H NMR and MALDI-TOF MS of **TP21**.

4: Thermogravimetric analysis; UV-vis absorption spectra and Cyclic voltammogram



~~**Figure S2.**~~ Thermogravimetric analysis (10℃min^{-1} at N_2 atmosphere) of TP21.

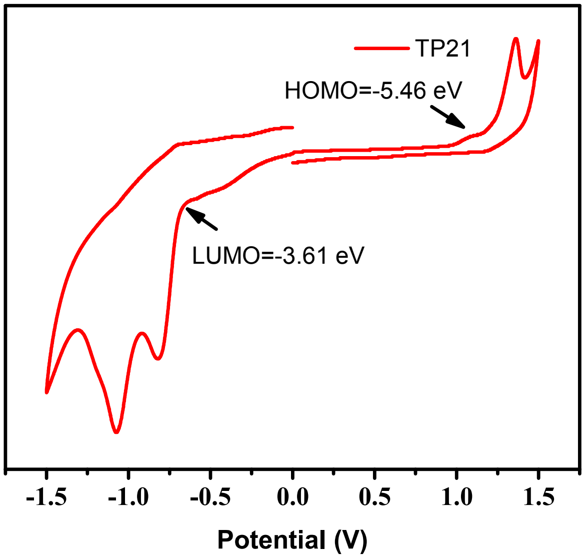


Figure S4. Cyclic voltammogram of TP21 films on a platinum plate in acetonitrile solution of 0.1 mol・L^{-1} Bu_4NPF_6 (Bu = butyl) at scan rate of 50 mV・s^{-1}.

5: Density Functional Theory calculation and Morphology of J61:TP21 films

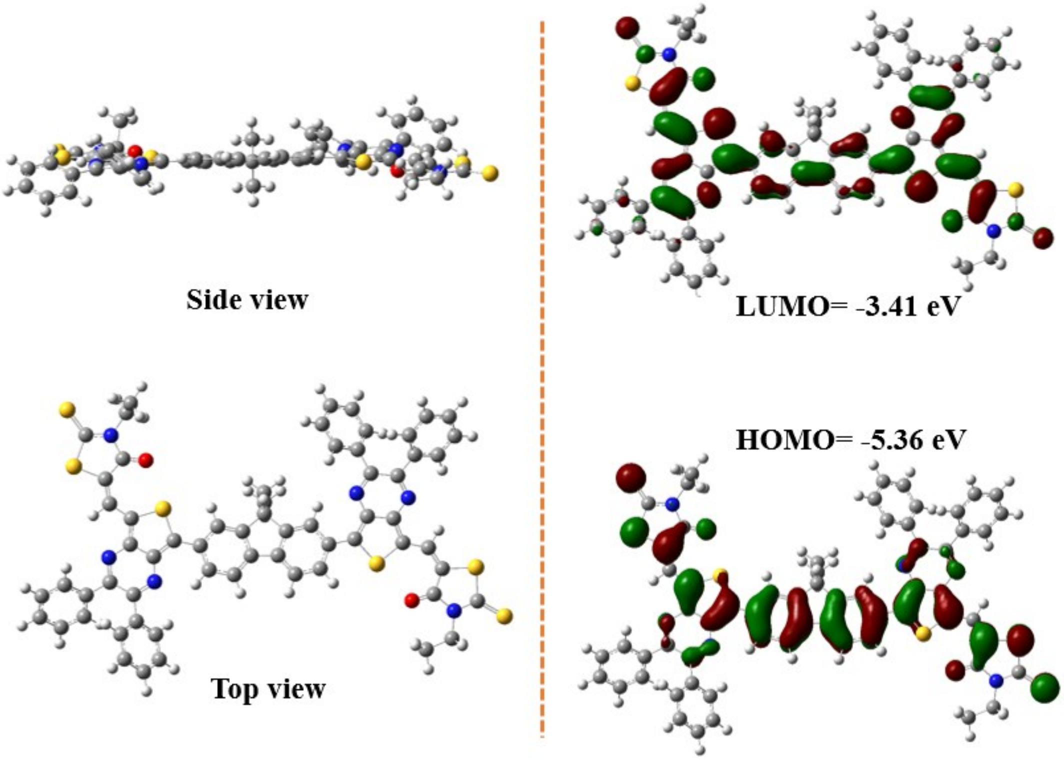


Figure S5. (a) Side view and top view for the optimized geometries; (b) the HOMO and LUMO of TP21.

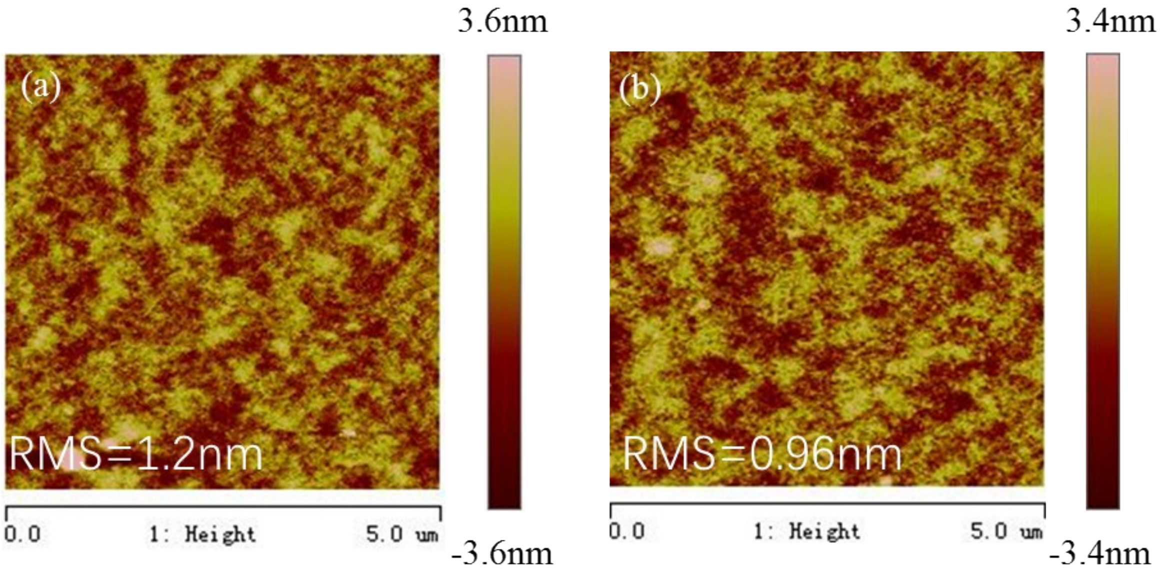


Figure S6. AFM height images (5μm × 5μm) of (a)(b) active layers based on **J61**:**TP21** without and with thermal annealing (TA) treatment.

6: Photovoltaic Data

Table S1. Photovoltaic performance parameters of the PSCs based on J61: TP21 with various solvents and blend weight ratios, under the annealing temperature of 100℃.

Solvent	D/A	V_{OC} (V)	J_{SC} (mA cm^{-2})	FF	PCE (%)
CF	1:1	0.98	5.53	0.35	1.91
DCB	1:1	1.04	8.89	0.45	4.18
CB	1.5:1	1.04	8.88	0.42	3.84
	1:1	**1.04**	**9.09**	**0.45**	**4.27**
	1:1.5	1.04	8.45	0.47	4.09

Table S2. Photovoltaic performance parameters of the PSCs based on J61: TP21 with different additives and the annealing temperatures.

Additives	T(℃)	V_{OC} (V)	J_{SC} (mA cm^{-2})	FF	PCE (%)
No	No	1.03	8.31	0.42	3.63
	80	1.04	8.84	0.44	4.03
	100	1.04	9.09	0.45	4.27
	120	1.04	9.75	0.47	4.75
	130	1.06	9.84	0.51	5.34
	140	**1.05**	**10.93**	**0.51**	**5.81**
	150	1.05	9.30	0.53	5.20
	160	1.02	8.71	0.48	4.30
	180	0.98	6.55	0.42	2.72
	200	0.97	5.12	0.40	1.97
1%DPE	130	1.05	9.73	0.54	5.49
	140	1.05	10.62	0.51	5.74
	150	1.05	10.39	0.51	5.52
1%CN	130	1.06	10.59	0.51	5.74
	140	1.05	9.83	0.54	5.54
	150	1.04	9.59	0.54	5.35

References

1. ~~Liyanage, N.P., et al., *Thieno[3,4-b]pyrazine as an Electron Deficient pi-Bridge in D-A-pi-A DSCs.* ACS Appl Mater Interfaces, 2016. **8**(8): p. 5376-84.~~