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Supporting information for

Adjusting Energy Levels and Bandgaps of Conjugated Polymers via Lewis Acid-Base Reactions

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1. Experimental Section

1.1. Measurements and Characterizations

The ^{1}H NMR, ^{11}B NMR, ^{13}C NMR and ^{19}F NMR spectra were measured on a Bruker AVANCE 500 MHz spectrometer using tetramethylsilane (TMS; δ = 0 ppm) as an internal standard and $CDCl_3$ as solvent. The ^{11}B NMR spectra were tested in the quartz NMR tube with boron content lower than 0.1 ppm. Polymer molecular weights were demonstrated by Wate/Waters using tetrahydrofuran (THF) as solvent at room temperature. Single crystal of 2,5-bis(5-bromo-4-hexylthiophen-2-yl)pyrazine using for X-ray diffraction analysis was prepared by slow growth from hexane solvent at room temperature. Single crystal X-ray data collection was carried out on a Rigaku R-AXIS RAPID Image Plate single-crystal diffractometer at room temperature using Mo K_α radiation (λ = 0.71073 Å), monochromatised by a graphite crystal. Crystallographic data for the structure of compound **3** has been deposited with the Cambridge Crystallographic Data Center as supplementary publications CCDC 1864601. UV-vis absorption was recorded on a Hitachi UV-2450 spectrometer spectrophotometer (300–1100 nm) in glovebox. The electrochemical measurements were carried out in a deoxygenated solution of tetra-n-butylammonium hexafluorophosphate (Bu_4NPF_6, 0.1 M) in acetonitrile with a computer-controlled CHI760E electrochemical workstation. A glassy carbon electrode, a Pt wire, and saturated calomel electrode (SCE) electrode were used as the working, counter, and reference electrodes, respectively. The thermal analysis, Thermogravimetric (TGA) and Differential scanning calorimetry (DSC) analysis, was recorded on DTG-60H and DSC 200, respectively. AFM images were tested using a Nanoscope V AFM (Digital Instruments) in tapping mode. AFM samples were prepared by spin-coating the **P1** and **P1**/BCF solutions in glass substrates. For titration experiments, the concentration of 10^{-4} M for pristine polymer solution and 10^{-3} M for BCF solution were prepared. During the titration tests, after adding suitable volume of BCF solution to 0.1 mL polymer solution and diluted to 1 mL, the UV-vis absorption spectra of blends were tested. The commercialized BCF was treated with toluene/Et_3SiH for 5 minutes followed by volatile removal and sublimation at 120 ºC under vacuum.

1.2 Gaussian calculations

Density functional theory (DFT) calculations were performed using the Gaussian 09 program with the B3LYP exchange-correlation functional.[1-3] All-electron triple-ξ valence basis sets with polarization functions (6-31G) are used for all atoms. Geometry optimizations were performed with full relaxation of all atoms. All alkyl chains were reduced to methyl groups for avoiding computational load. For each molecule, various conformations with different dihedral angles were optimized, and the data for the one with the lowest energy are reported.

1.3 Materials synthesis

Synthesis routes toward **P1** and **P2** are shown in **Scheme 2**. The palladium catalyst and BCF were purchased from TCI and two monomers, i.e., compounds **1** and **2** were purchased from Derthon Co Ltd. Synthesis of compound **3** was reported in our former work.[4] Toluene was purchased from Acros and distilled from Na before use.

Synthesis of **P1**. Compound **1** (100 mg, 0.081 mmol), compound **3** (46 mg, 0.081 mmol), and P(*o*-tolyl)$_3$ (15% mol) were dissolved in dry toluene (10 mL) and degassed with N_2 for 8 min. Then $Pd_2(dba)_3$ (5% mol) was added and degassed with N_2 for another 8 min. The reaction mixture was sealed quickly and heated to 110 ºC for 12 hours under N_2 atmosphere. After cooling to room temperature, the solution was added dropwise into methanol (200 mL). The precipitate was filtrated and collected. The collected solid was successively extracted with methanol, acetone, and hexane in a Soxhlet extractor to remove the monomers, oligomers, and other soluble organics. Finally, $CHCl_3$ was used to extract and the solution was condensed to 5 mL, which was added dropwise to 200 mL methanol. Precipitate was filtrated and dried under vacuum to obtain **P1** (90 mg, 85%) as a red solid (M_n = 21.2 kDa, PDI = 1.77). ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.77 (s, 1H), 7.46 (s, 2H), 7.23–7.14 (m, 5H), 7.09 (d, *J* = 7.4 Hz, 4H), 2.81 (s, 2H), 2.57 (s, 4H), 1.65 (d, *J* = 50.8 Hz, 8H), 1.31 (m, 18H), 0.88 (s, 9H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 156.49, 156.25, 153.32, 145.38, 145.32, 141.79, 141.72, 141.61, 140.70, 140.61, 139.95, 139.28, 138.25, 135.23, 128.41, 127.90, 122.20, 117.47, 63.07, 35.61, 31.75, 31.66, 31.36, 30.45, 30.26, 29.79, 29.73, 29.33, 29.17, 22.67, 22.62, 14.12. Anal. calcd for $(C_{88}H_{104}N_2S_4)$n: C, 80.19%, H, 7.95%, N, 2.13%. Found: C, 80.58%, H, 7.71%, N, 1.82%

P2 was obtained via the same procedures by using compound **2** and **3** as monomers (yield 80%, M_n = 19.2 kDa, PDI = 2.76). ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.79 (s, 1H), 7.51 (d, *J* = 23.6 Hz, 2H), 7.39 (s, 1H), 7.21 (d, *J* = 7.6 Hz, 4H), 7.11 (d, *J* = 7.8 Hz, 4H), 2.69 (d, *J* = 11.5 Hz, 6H), 1.65 (d, *J* = 51.8 Hz, 8H), 1.35–1.25 (m, 18H), 0.91–0.85 (m, 9H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 153.50, 146.27, 145.42, 143.45, 142.04, 141.89, 141.07, 140.17, 139.32, 138.86, 136.96, 136.10, 134.70, 133.87, 128.54, 128.07, 118.99, 117.02, 63.00, 35.64, 31.73, 31.65, 31.29, 30.52, 29.73, 29.64, 29.29, 29.22, 22.66, 22.62, 14.11. Anal. calcd for $(C_{92}H_{104}N_2S_6)$n: C, 77.26%, H, 7.33%, N, 1.96%. Found: C, 77.61%, H, 6.93%, N, 1.87%.

2. Supporting figures

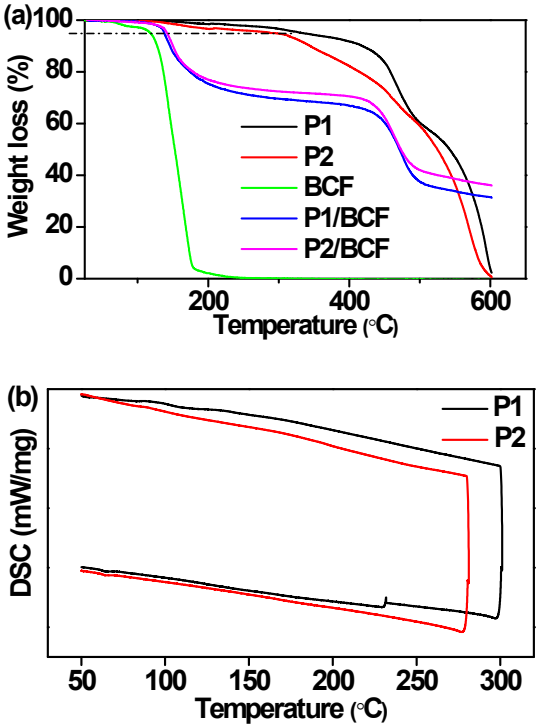
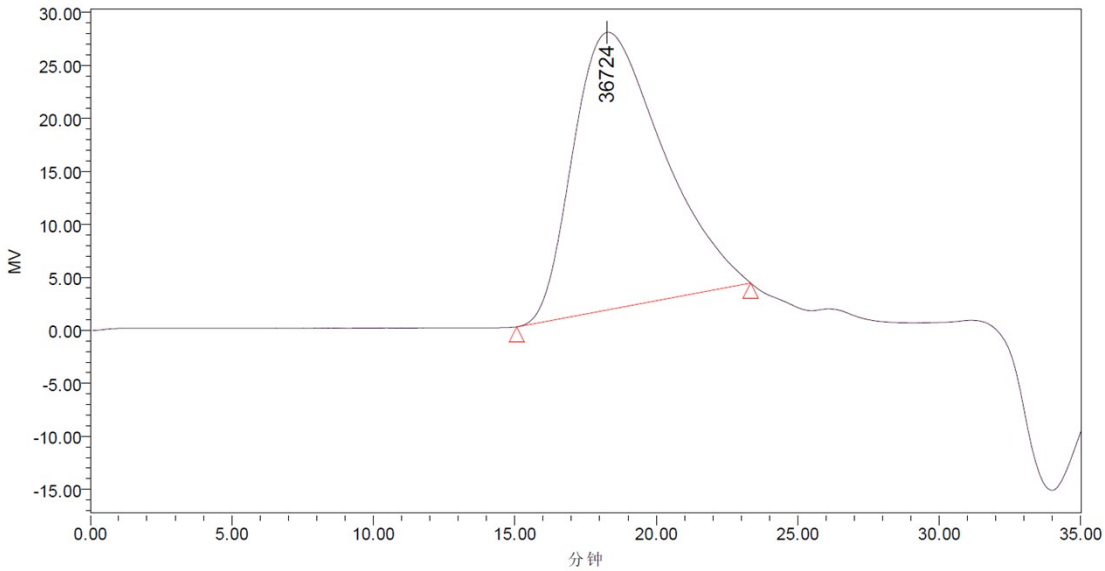


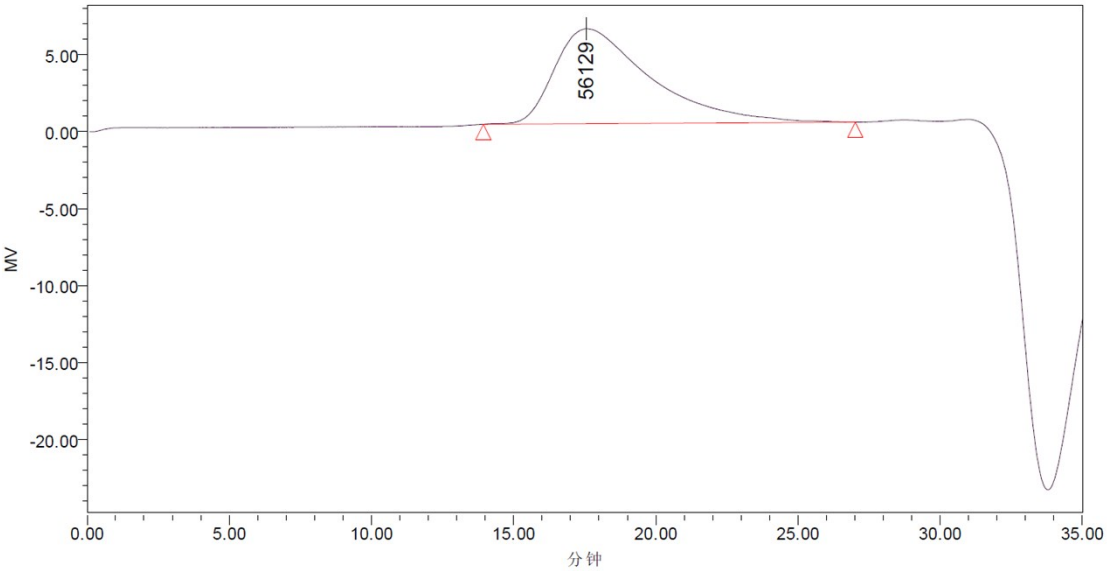
Fig. S1. TGA measurement of **P1**, **P2**, BCF, **P1**/BCF, and **P2**/BCF (a); DSC curves of copolymers with heating rate of 10 °C/min under argon atmosphere (b). Note: The 5% weight loss temperatures (T_d) are 336, 302, 121, 138, and 143 ºC, respectively, for **P1**, **P2**, BCF, **P1**/BCF, and **P2**/BCF.



GPC Results

	Dist Name	Elution Volume (ml)	Retention Time (min)	Adjusted RT (min)	Mn	Mw	MP	Mz	Mz+1	Mz/Mw
1		18.267	18.267	18.267	21213	37545	36724	63078	95433	1.680085

Fig. S2. GPC curves and results for **P1**.



GPC Results

	Dist Name	Elution Volume (ml)	Retention Time (min)	Adjusted RT (min)	Mn	Mw	MP	Mz	Mz+1	Mz/Mw
1		17.564	17.564	17.564	19203	52931	56129	117201	279914	2.214206

Fig. S3. GPC curves and results for **P2.**

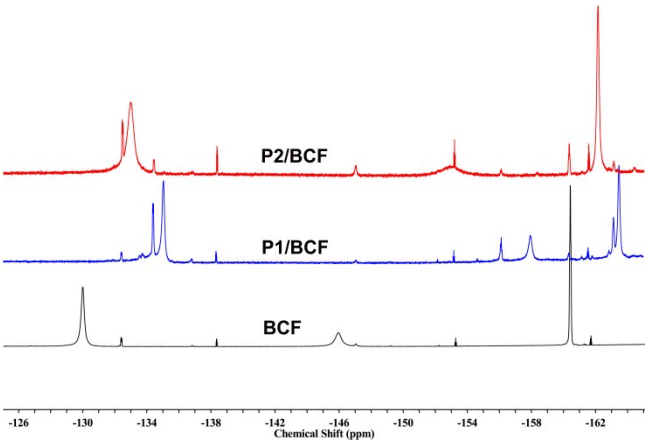


Fig. S4. ^{19}F NMR spectrum of BCF, **P1**/BCF and **P2**/BCF in $CDCl_3$

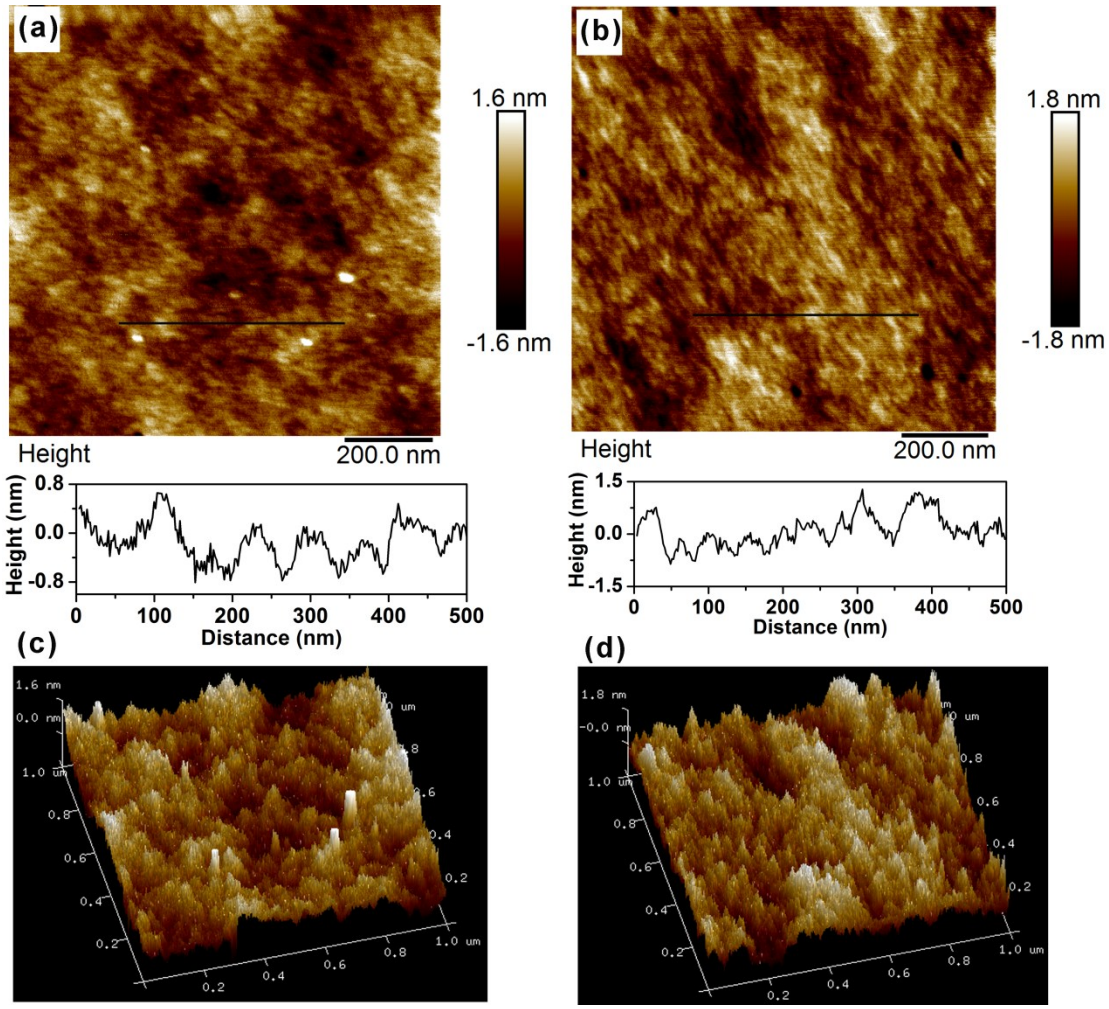


Fig. S5. Tapping mode AFM images of **P1** (a, R_q roughness = 0.5 nm) and **P1**/BCF (b, R_q roughness = 0.6 nm) and 3D images of **P1** (c) and **P1**/BCF (d). Note: scan area: 1×1 μm.

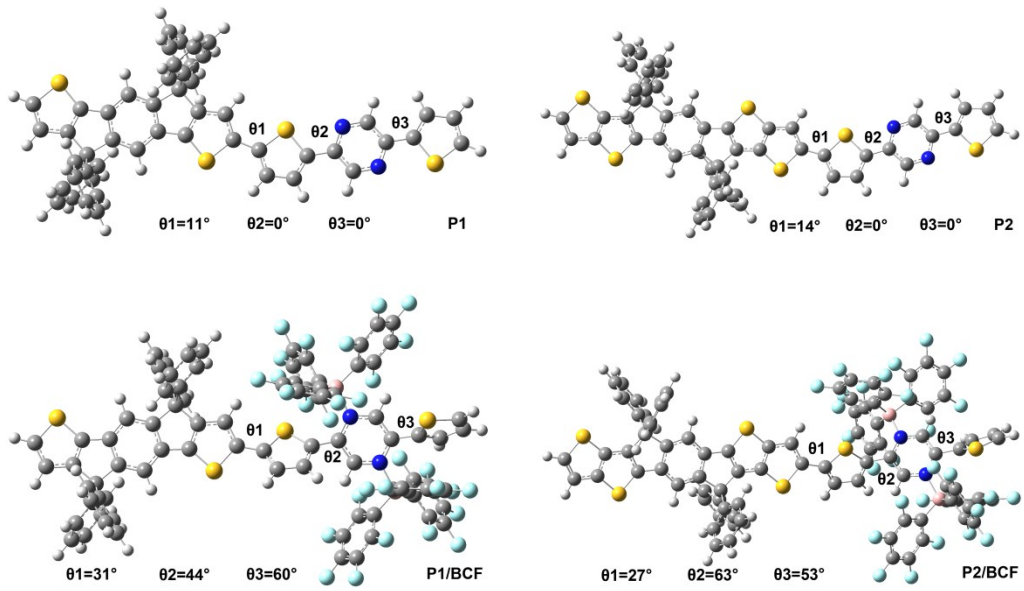


Fig. S6. Optimized molecular conformation calculated from Gaussian 09 in the level

of B3LYP/6-31G (d, p). The alkyl chains were omitted to simplify the calculations.

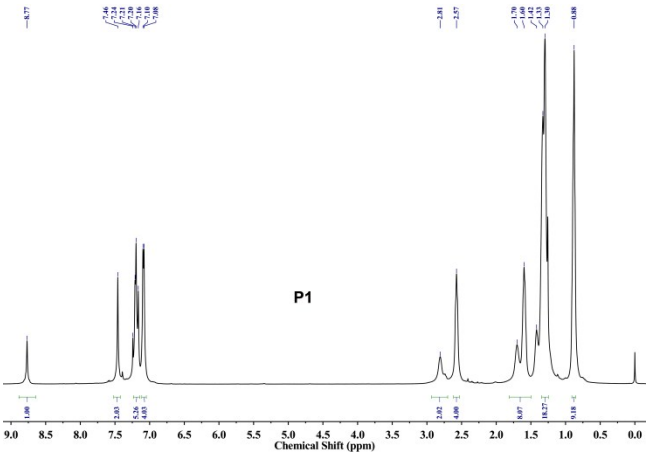


Fig. S7. ^{1}H NMR spectrum of **P1** in $CDCl_3$

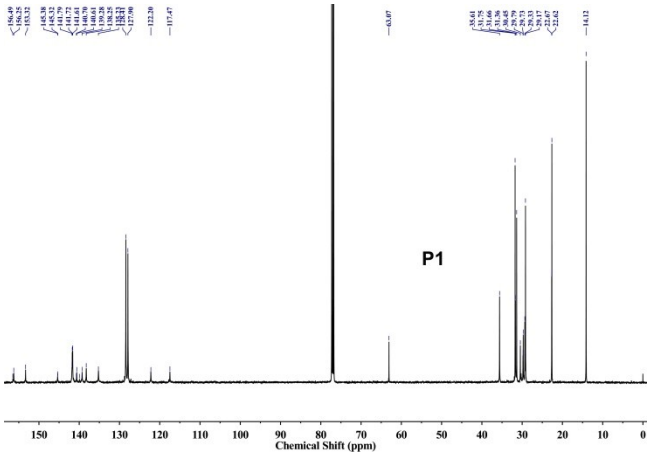


Fig. S8. ^{13}C NMR spectrum of **P1** in $CDCl_3$

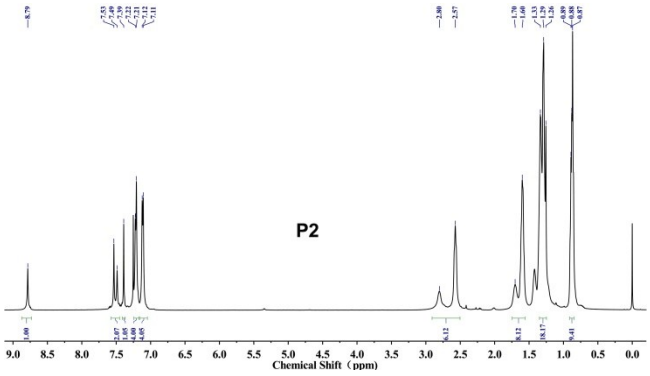


Fig. S9. ^{1}H NMR spectrum of **P2** in $CDCl_3$

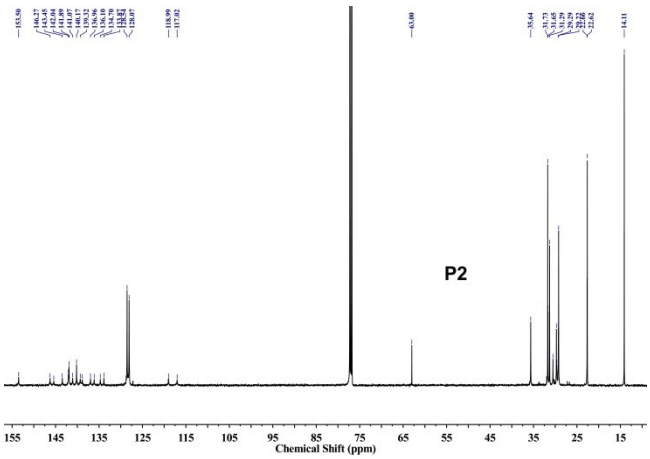


Fig. S10. ^{13}C NMR spectrum of **P2** in $CDCl_3$

3. References

1. A. D. Becke, *The Journal of Chemical Physics*, 1993, **98**, 5648-5652.
2. A. D. Becke, *Physical Review A*, 1988, **38**, 3098-3100.
3. C. Lee, W. Yang and R. G. Parr, *Physical Review B*, 1988, **37**, 785-789.
4. Y. Li, H. Meng, D. Yan, Y. Li, B. Pang, K. Zhang, G. Luo, J. Huang and C. Zhan, *Tetrahedron*, 2018, **74**, 4308-4314.