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Supporting Information

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Bis-isoindigos: New Electron-Deficient Building Blocks for Constructing Conjugated Polymers with Extended Electron Delocalization

Xuyi Luo, Dung T. Tran, Hong Sun, Tianxiong Mi, Natalie M. Kadlubowski, Yan Zhao, Kejie Zhao, and Jianguo Mei*This manuscript is part of a special issue on Organic Materials. .

Supporting Information

Bis-isoindigos: new electron-deficient building blocks for conjugated polymers with extended conjugation length

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I. General Information

All reagents purchased from suppliers were used without further purification. ^1H - and ^{13}C -NMR spectra were recorded using Varian Inova 300 in deuterated chloroform at 293 K. GPC was performed by high-temperature gel permeation chromatography at 150 °C using 1,2,4-trichlorobenzene (TCB) as eluent. Differential scanning calorimetry (DSC) measurements were acquired using a TA Q1000 calorimeter at a heating rate of 10 °C min⁻¹ with nitrogen as purge gas. UV-vis-NIR spectra were measured with an Agilent Technologies Cary 6000i UV-Vis-NIR spectrophotometer (350-1800 nm). All the electrochemistry related experiments (CV, DPV) were performed using BioLogic SP-150. FET device characterization was carried out using Keithley 4200.

II. Synthetic Procedures

Scheme S1. Possible strategies to synthesize the A-A building block, taking Bis-TII as an example.

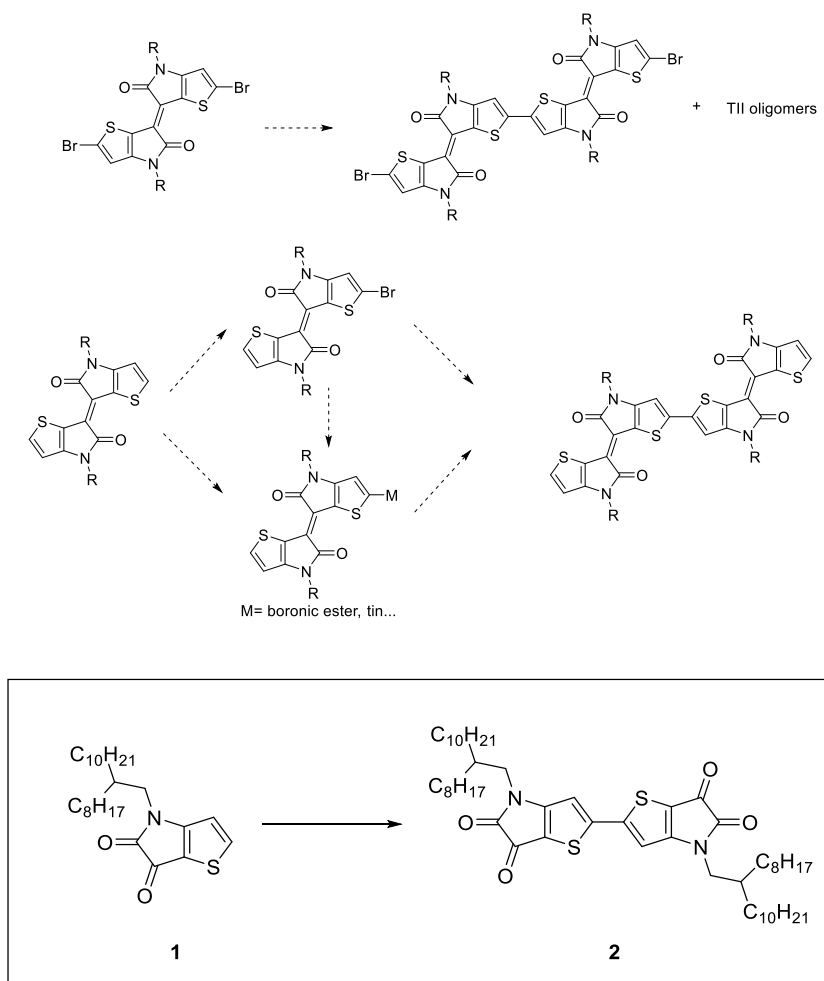
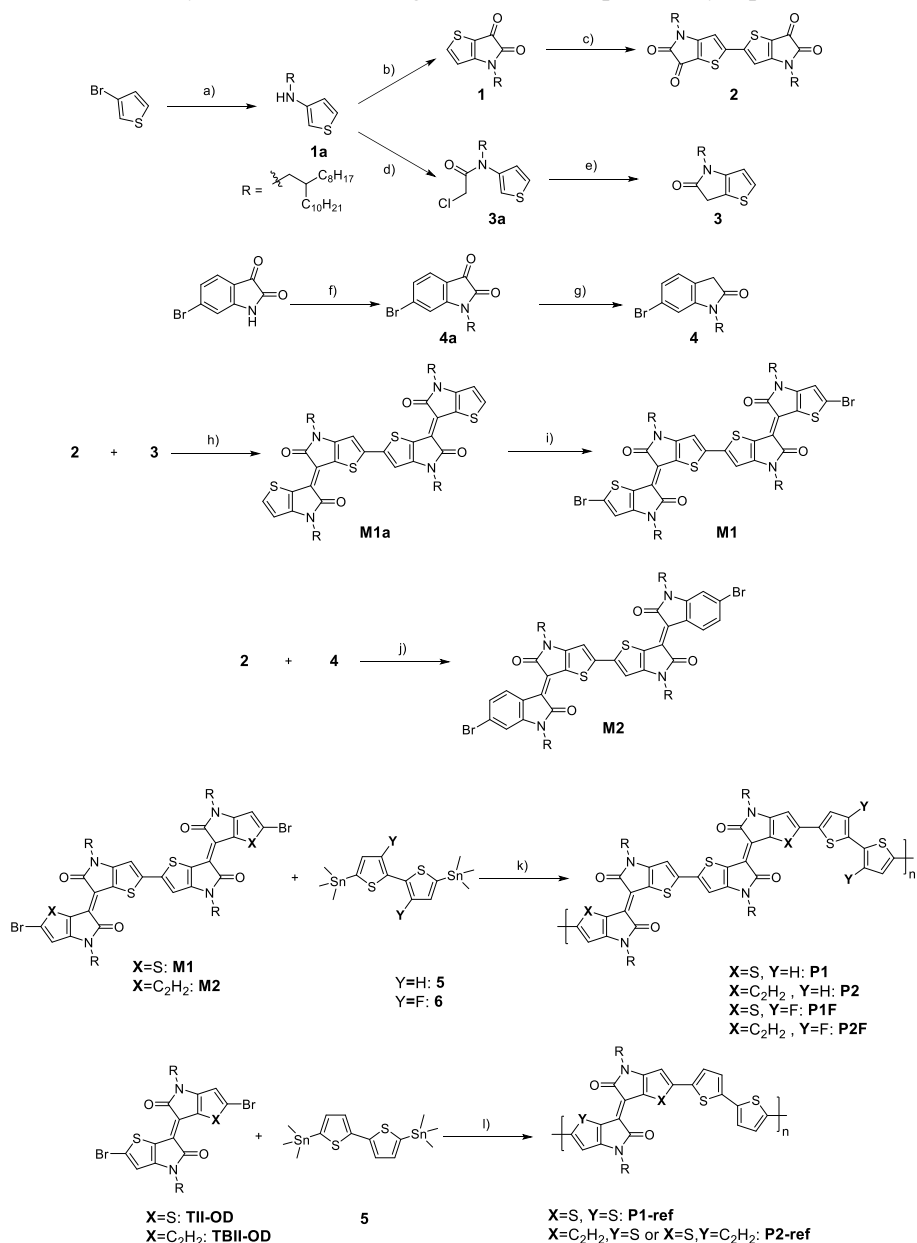


Table S1. optimization of oxidative coupling from **1** to **2**. All conductions shown in the table were conducted with 200 mg compound **1** and 20 mL solvent, unless there is a special note.

Catalyst	Catalyst loading	AgF (eq.)	solvent	T (°C)	Time (h)	%Yield
Pd ₂ (dba) ₃	3%	2.0	DMSO	65	12	25% ^a
Pd ₂ (dba) ₃	3%	2.0	DMSO	90	20	49%
Pd ₂ (dba) ₃	3%	4.0	DMSO	110	48	21%
Pd(OAc) ₂	5%	0.75 ^b	DMSO	90	24	40% ^c
Pd(OAc) ₂	10%	2.1	DMSO	90	24	54%
Pd ₂ (dba) ₃	3%	2.0	DMF ^d	90	20	36% ^e
Pd(dppf)Cl ₂	6%	2.0	DMSO	90	20	39%

^aMost starting material remained unreacted. ^bAg₂O was used in this condition instead of AgF, and 0.75 equivalent of benzoic acid was also added. ^cThe reaction was conducted with 40 mg of compound **1**. ^d20 mL DMF with several drops of DMSO was applied. ^eIn this condition, the 2-octyldodecyl side chain of compound **1** was replaced with an n-octyl alkyl chain. Thieno-isatins (backbone of compound **1**) with Linear alkyl chains dissolve better than those with branched alkyl chains in DMF.

Scheme S2. Synthetic routes to **P1**, **P2**, **P1F** and **P2F**. Compound **1a**, **1**, **3a**, **3**, **4a**, **THI-OD**, **TBII-OD**, **P1-ref**, **P2-ref** are synthesized according to the methods previously reported.¹

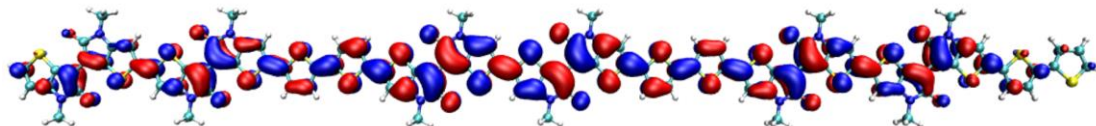


a) 2-octyldodecan-1-amine, CuI, K₃PO₄, DMEA, 80 °C, 48 h, 56%; b) Oxalyl chloride, NEt₃, DCM, 0 °C, overnight, 61%; c) AgF, Pd (OAc)₂, DMSO, 90 °C, 24 h, 54%; d) Chloroacetyl chloride, DCM, 0 °C, overnight, 77%; e) Pd(OAc)₂, JohnPhos, NEt₃, Toluene, 100 °C, 3 h, 79%; f) K₂CO₃, 9-(bromomethyl)nonadecane, DMF, 100 °C, overnight, 70%; g) Hydrazine hydrate, DMSO, 130 °C, 24 h, 66%; h) PTSA, Toluene, 110 °C, 12 h, 88%; i) NBS, CHCl₃, 0 °C, 30 min, 87%; j) PTSA, Toluene, 110 °C, 12 h, 89%; k) Pd₂(dba)₃, P(*o*-tol)₃, Toluene, 110 °C, 16 h, 63%-95%. l) Pd₂(dba)₃, P(*o*-tol)₃, Toluene, 110 °C, 24 h, 70%-81%.

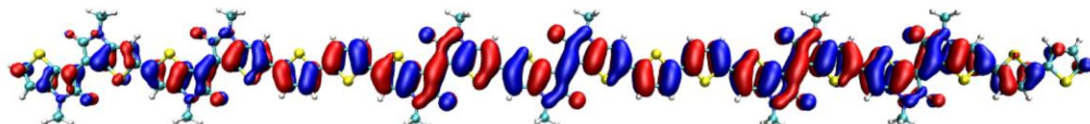
P1-ref and **P2-ref** were obtained with 70% and 81% yield respectively. The batch of **P2-ref** we synthesized has a Mn of 39.2 KDa and a PDI of 4.37.

III. Characterizations and DFT Calculations

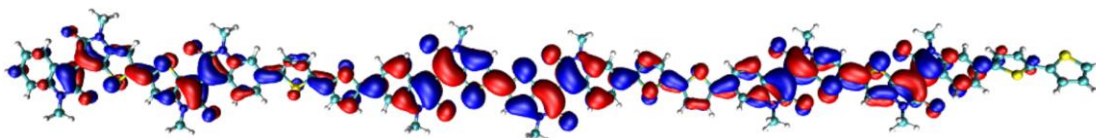
a) LUMO of **P1**



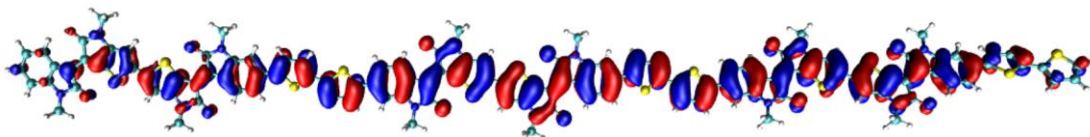
HOMO of **P1**



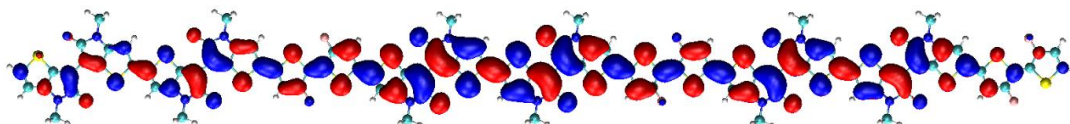
b) LUMO of **P2**



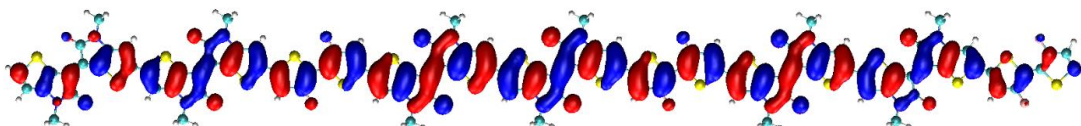
HOMO of **P2**



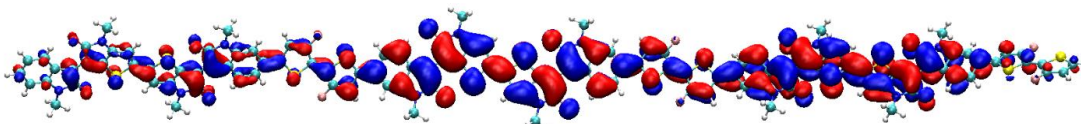
c) LUMO of **P1F**



HOMO of **P1F**



d) LUMO of **P2F**



HOMO of **P2F**

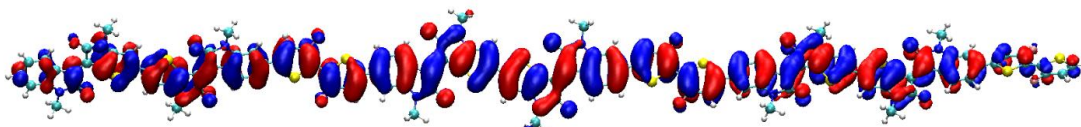


Figure S1. FMO electron distribution diagrams of Bis-IID trimers with density functional theory

calculations (B3LYP/6–31G(d)). HOMO/LUMO plots of a) **P1**, b) **P2**, c) **P1F** and d) **P2F**.

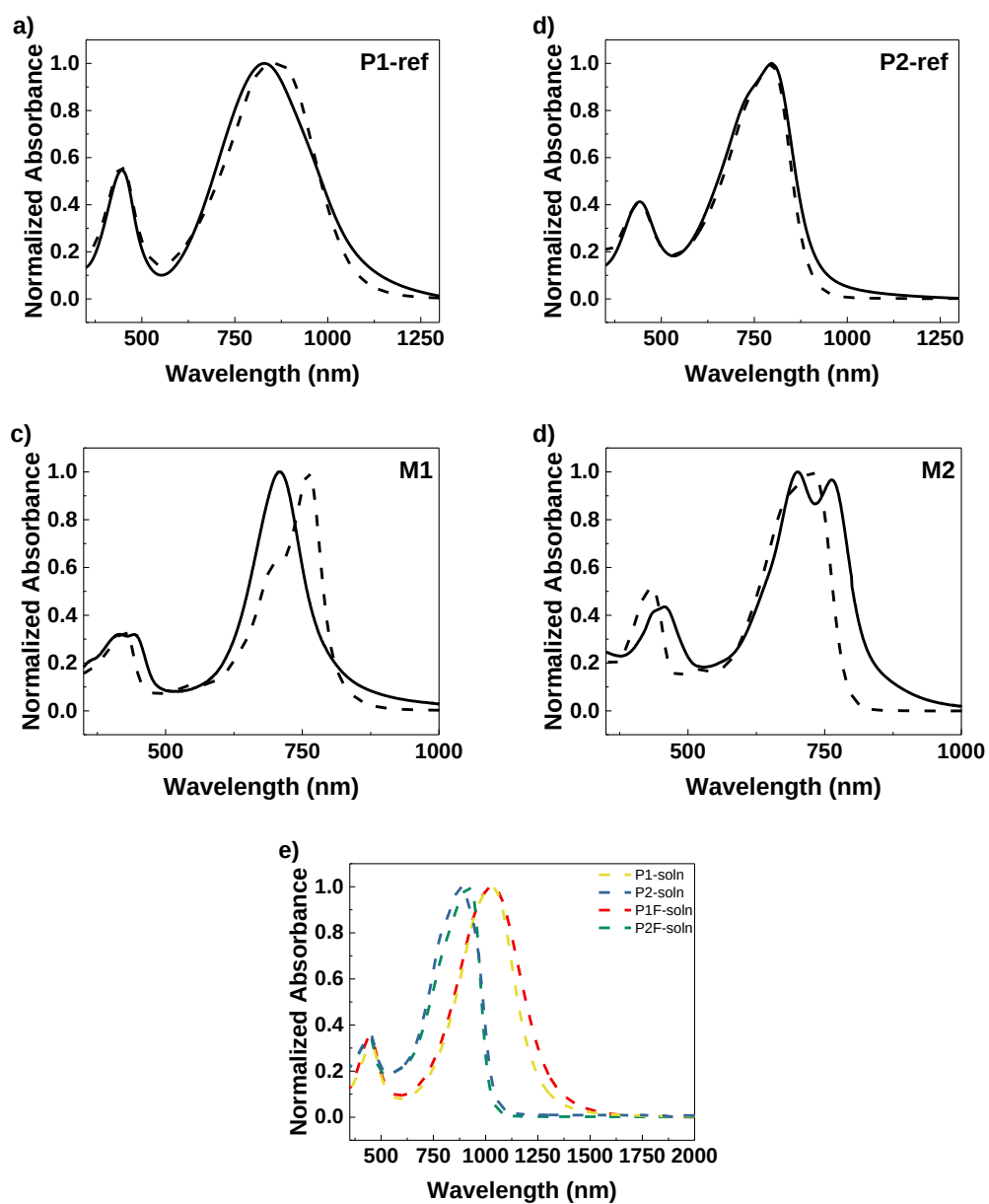


Figure S2. Normalized absorption spectra of a) **P1-ref**, b) **P2-ref** c) **M1** and d) **M2** in solution (dashed line) and as films (solid line); e) **P1**, **P2**, **P1F** and **P2F** in *o*-dichlorobenzene.

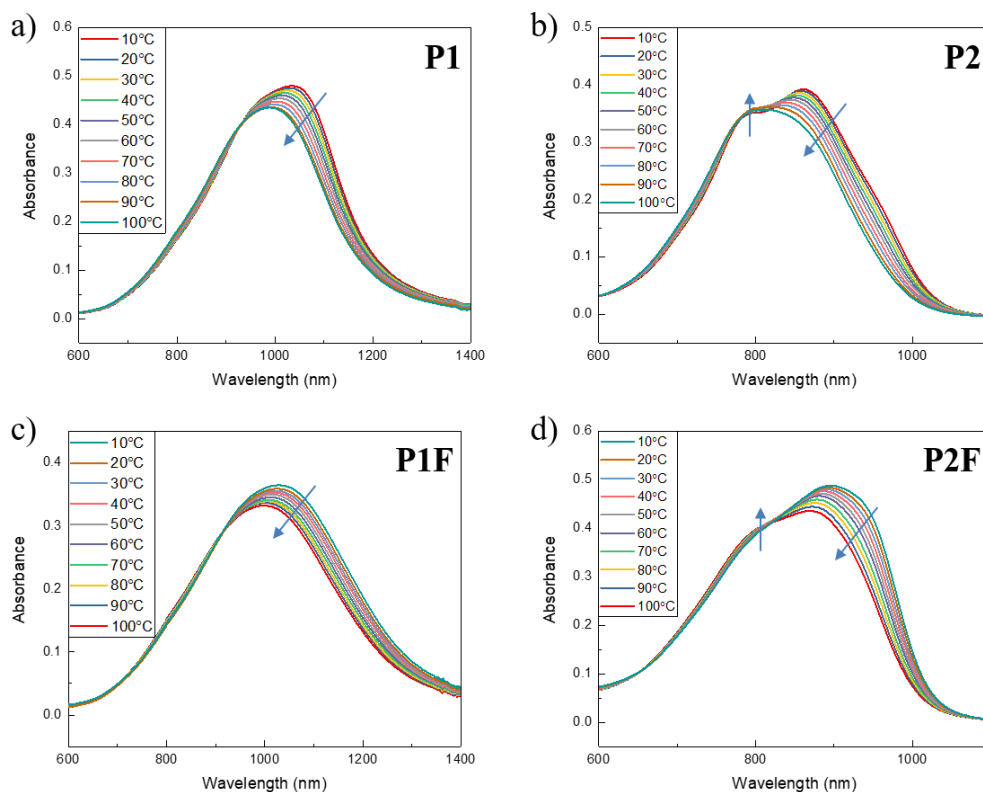


Figure S3. Temperature-dependent absorption spectra of **a) P1**, **b) P2**, **c) P1F** and **d) P2F** in *o*-dichlorobenzene.

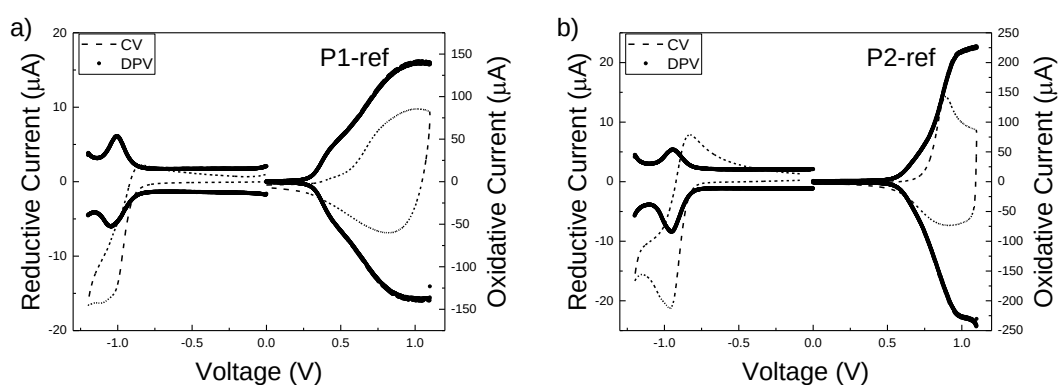
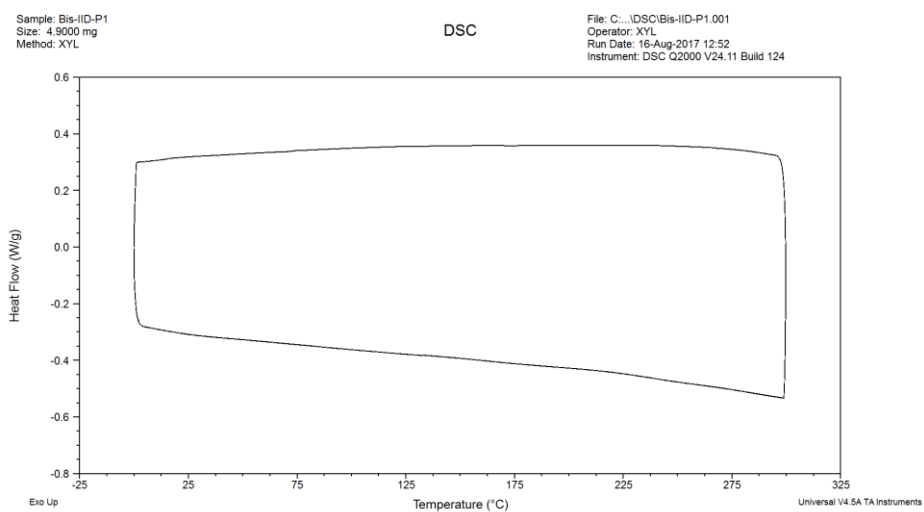
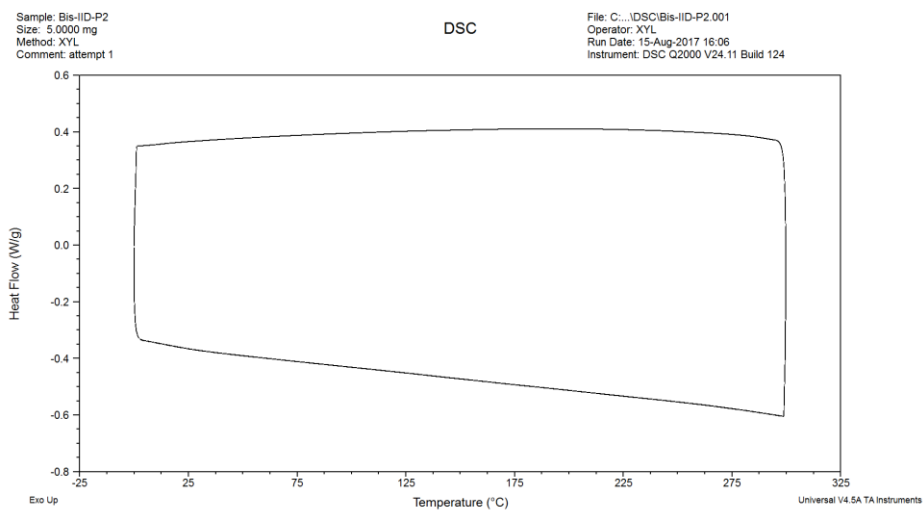


Figure S4. Cyclic Voltammograms (dashed lines) and differential pulse voltammograms (solid dots) of **a) P1-ref** film and **b) P2-ref** film in acetonitrile with 0.2 M *n*-Bu₄NPF₆ as supporting electrolyte (scan rate: 40 mV s⁻¹).

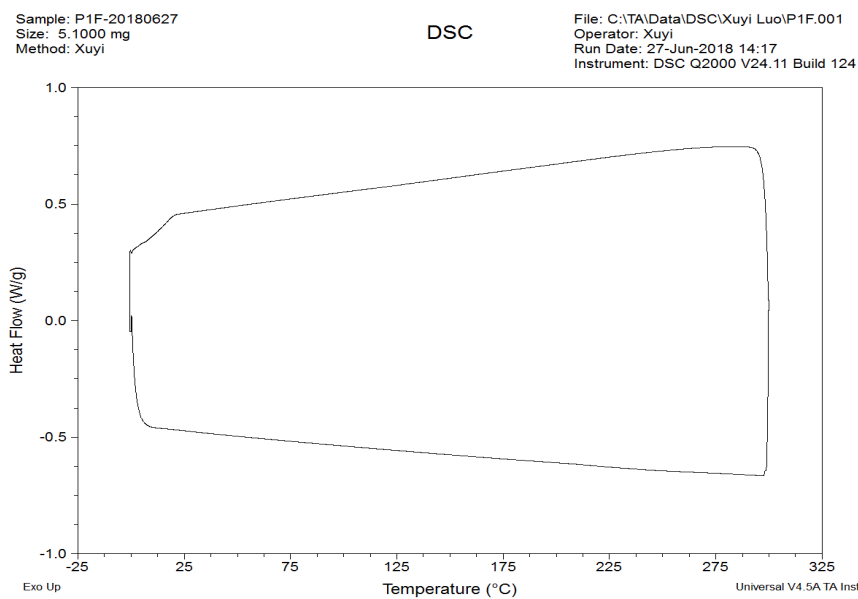
a)



b)



c)



d)

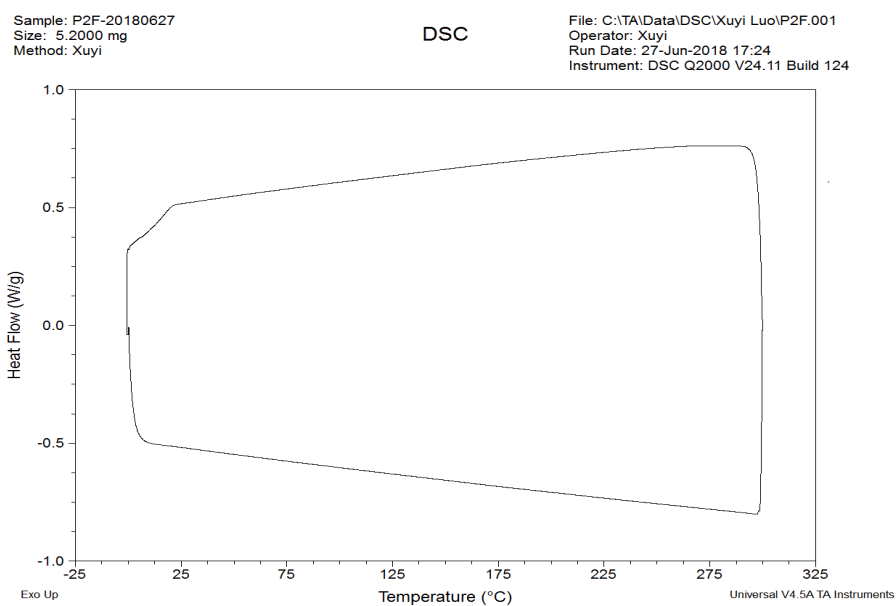
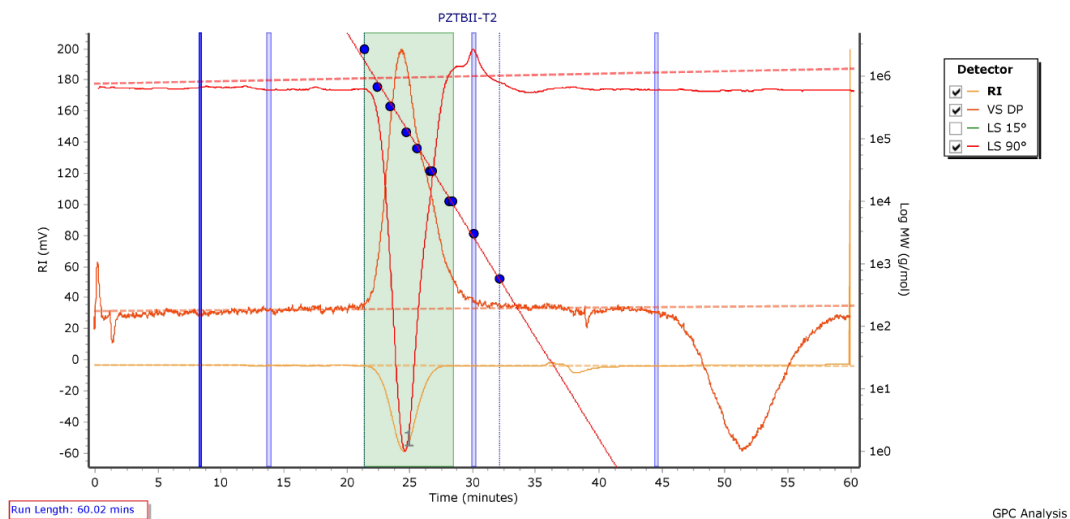


Figure S5. Differential scanning calorimetry (DSC) plots of **a) P1**, **b) P2**, **c) P1F** and **d) P2F**. No obvious peak was observed.

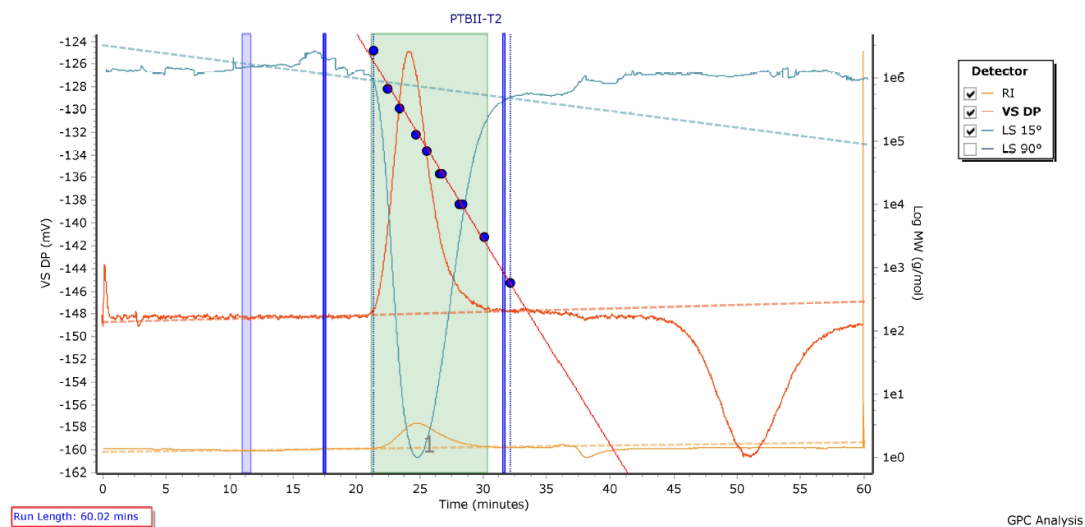
a)

Chromatogram Plot



b)

Chromatogram Plot



c)

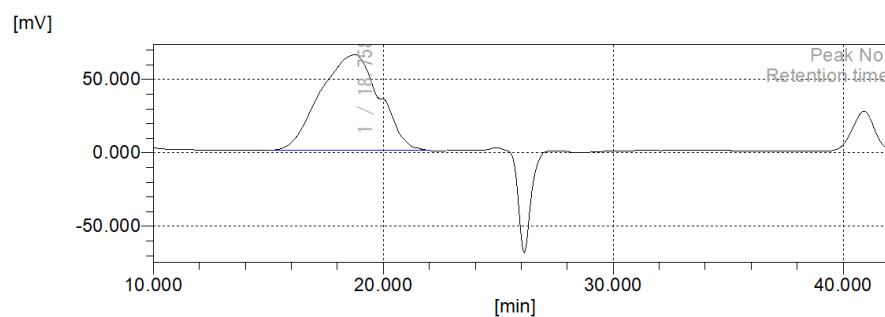


Figure S6. Chromatogram plot of a) P2 b) P2-ref and c) P2F by high-temperature gel permeation chromatography at 150 °C using 1,2,4-trichlorobenzene (TCB) as eluent.

IV. OFET Device Properties

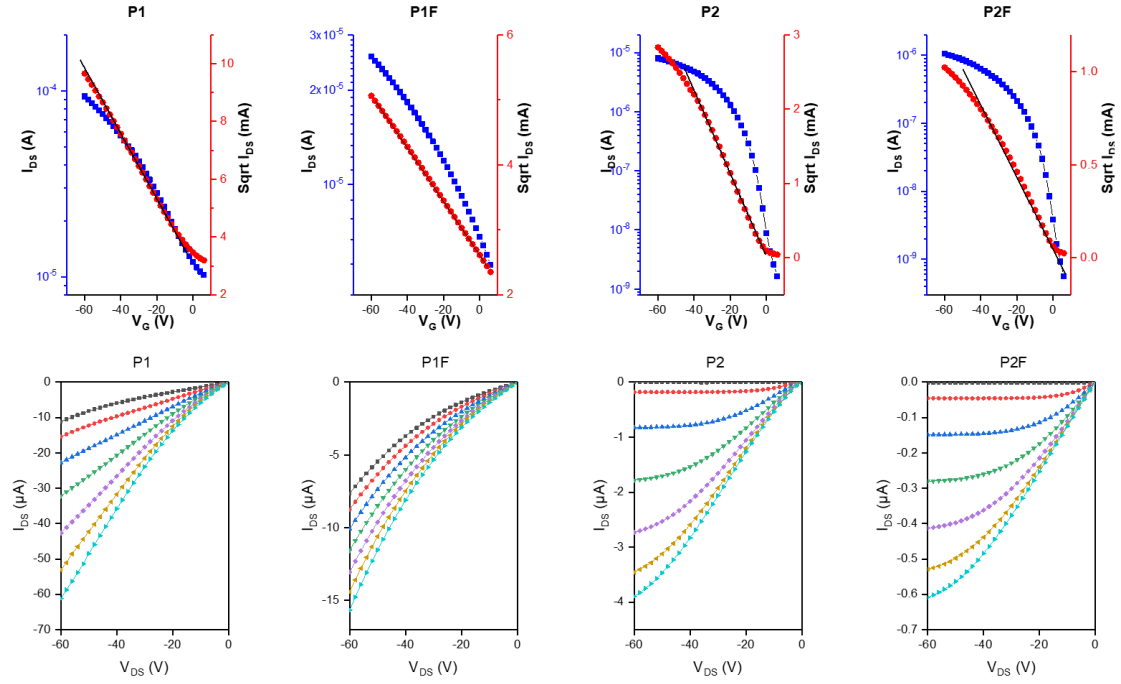


Figure S7. Typical transfer and output characteristics of FETs based on **P1**, **P2**, **P1F** and **P2F** with BGBC architecture and Au electrodes in ambient air.

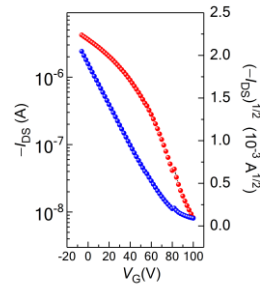


Figure S8. Transfer characteristics of the FET based on **P1** with BGBC architecture and Au electrodes in ambient air. A very high positive gate voltage was applied to turn off the device.

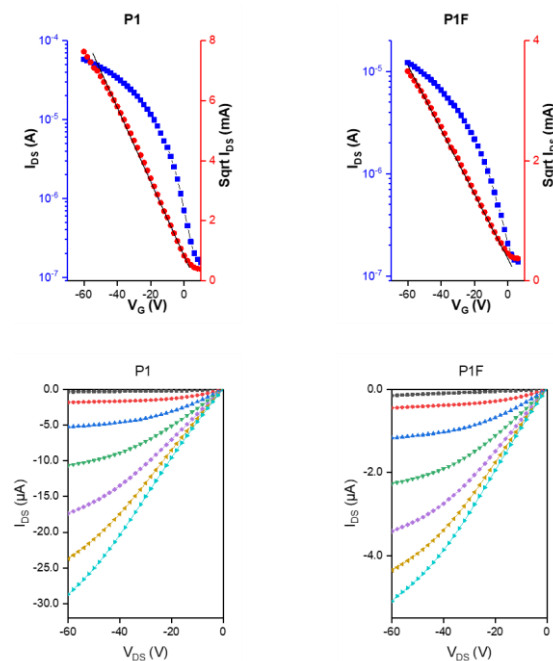


Figure S9. Transfer characteristics of the FET based on **P1** and **P1F** with BGBC architecture and Au electrodes under vacuum.

Table S2. Summary of Bis-IID OFET devices with BGTC architecture and Au electrodes.

Polymers	μ_h , average ($\text{cm}^2\text{V}^{-1}\text{s}^{-1}$) ^a	μ_h , max ($\text{cm}^2\text{V}^{-1}\text{s}^{-1}$) ^a	$I_{\text{on/off}}$ ^a	μ_h , average ($\text{cm}^2\text{V}^{-1}\text{s}^{-1}$) ^b	μ_h , max ($\text{cm}^2\text{V}^{-1}\text{s}^{-1}$) ^b	$I_{\text{on/off}}$ ^b
P1	0.004	0.007	~10	0.013	0.017	10^2
P1F	0.002	0.004	~10	0.009	0.013	10^2
P2	0.019	0.024	10^3	N/A	N/A	N/A
P2F	0.021	0.03	10^3	N/A	N/A	N/A

^a Devices were tested in ambient air. ^b Devices were tested under vacuum.

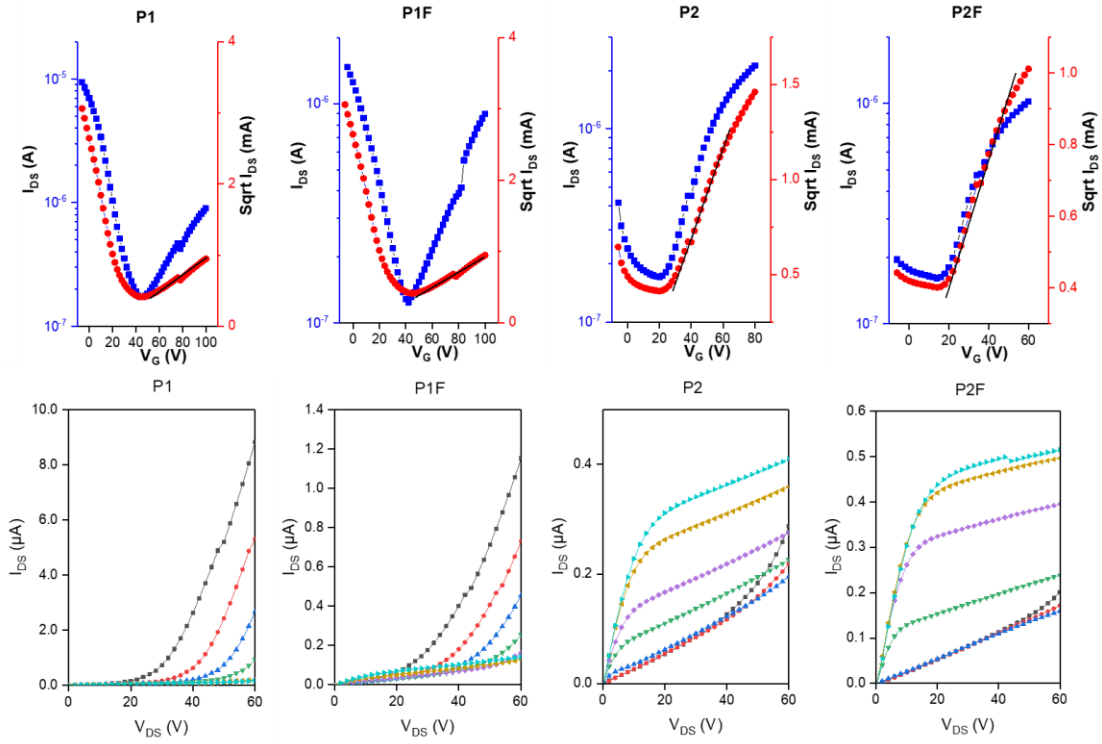


Figure S10. Typical n-type transfer and output characteristics of FETs based on **P1**, **P2**, **P1F** and **P2F** with BGTC architecture and Al contacts under vacuum.

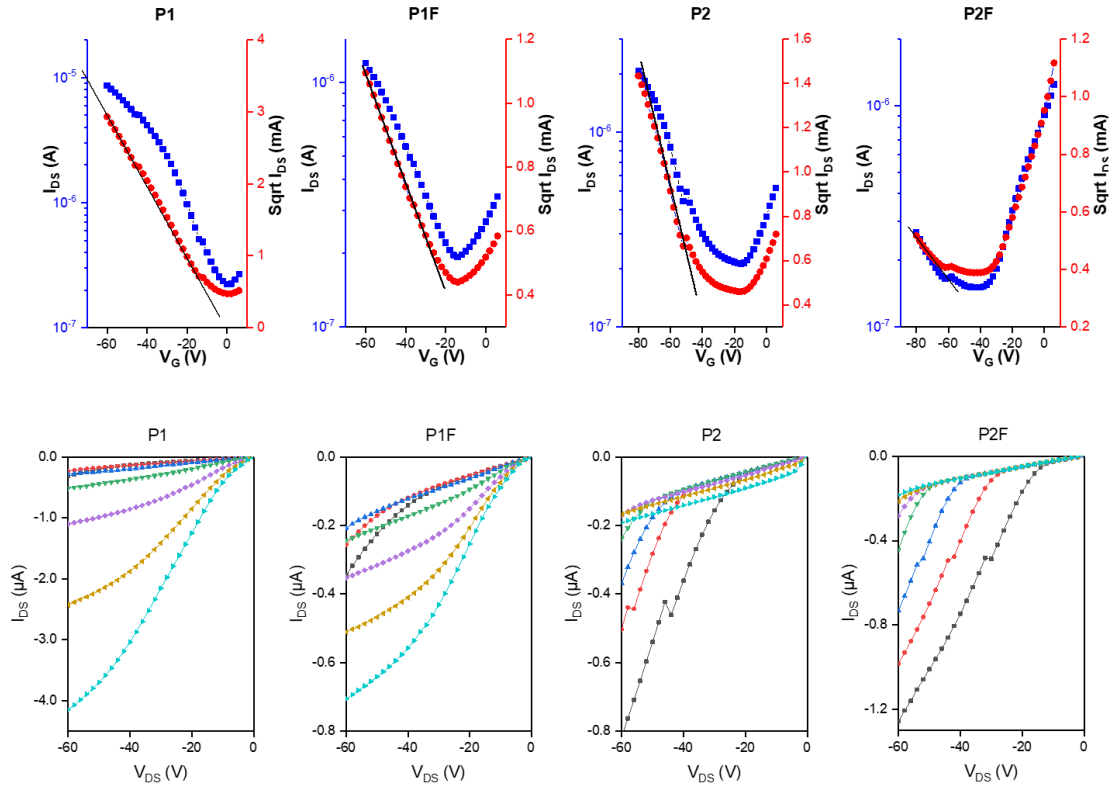


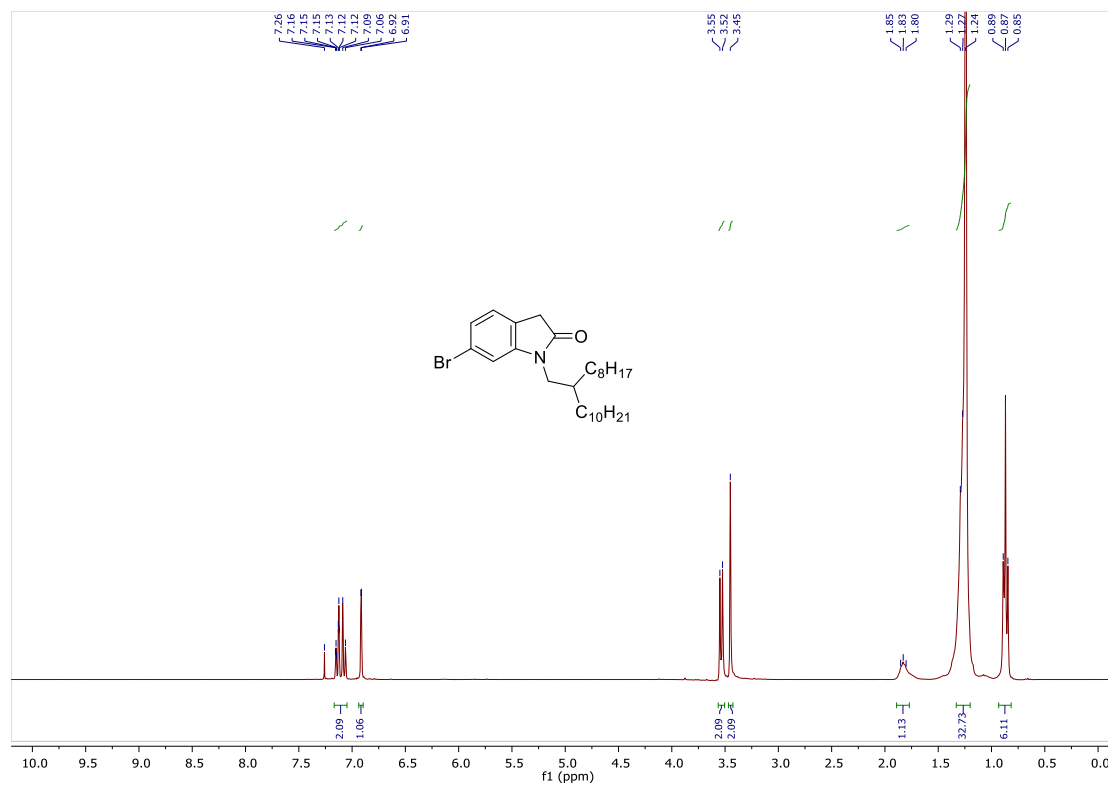
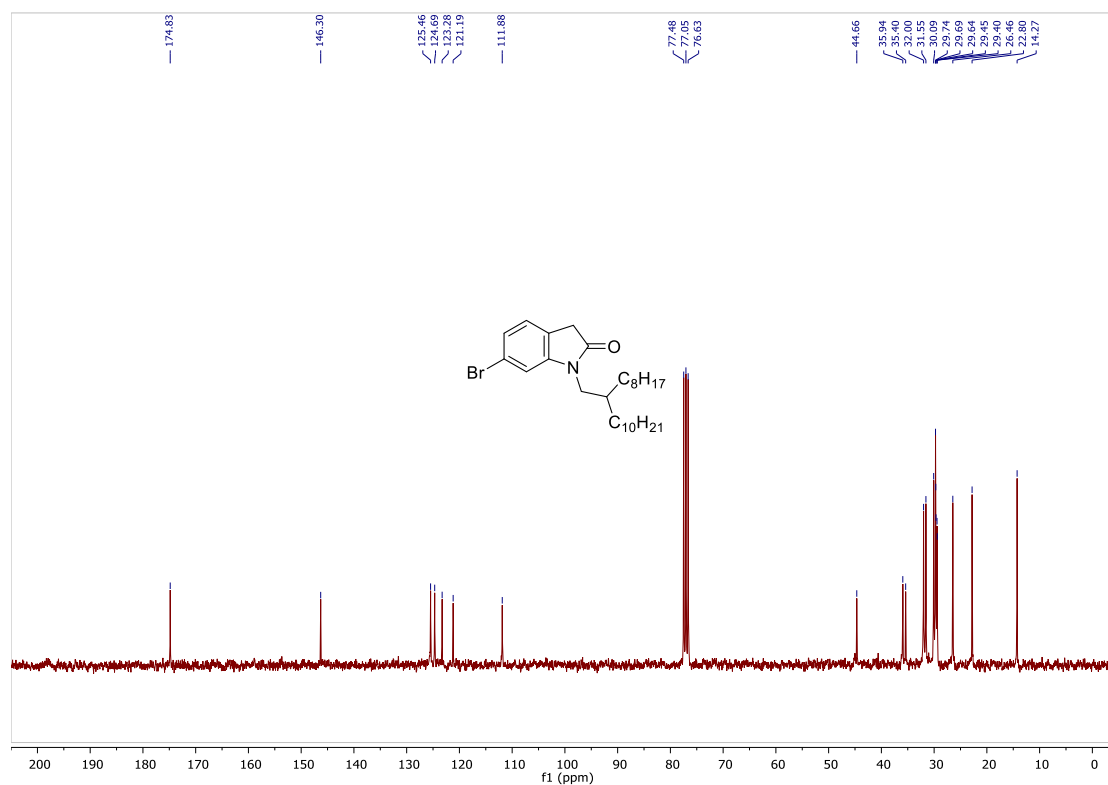
Figure S11. Typical p-type transfer and output characteristics of FETs based on **P1**, **P2**, **P1F** and **P2F** with BGTC architecture and Al contacts under vacuum.

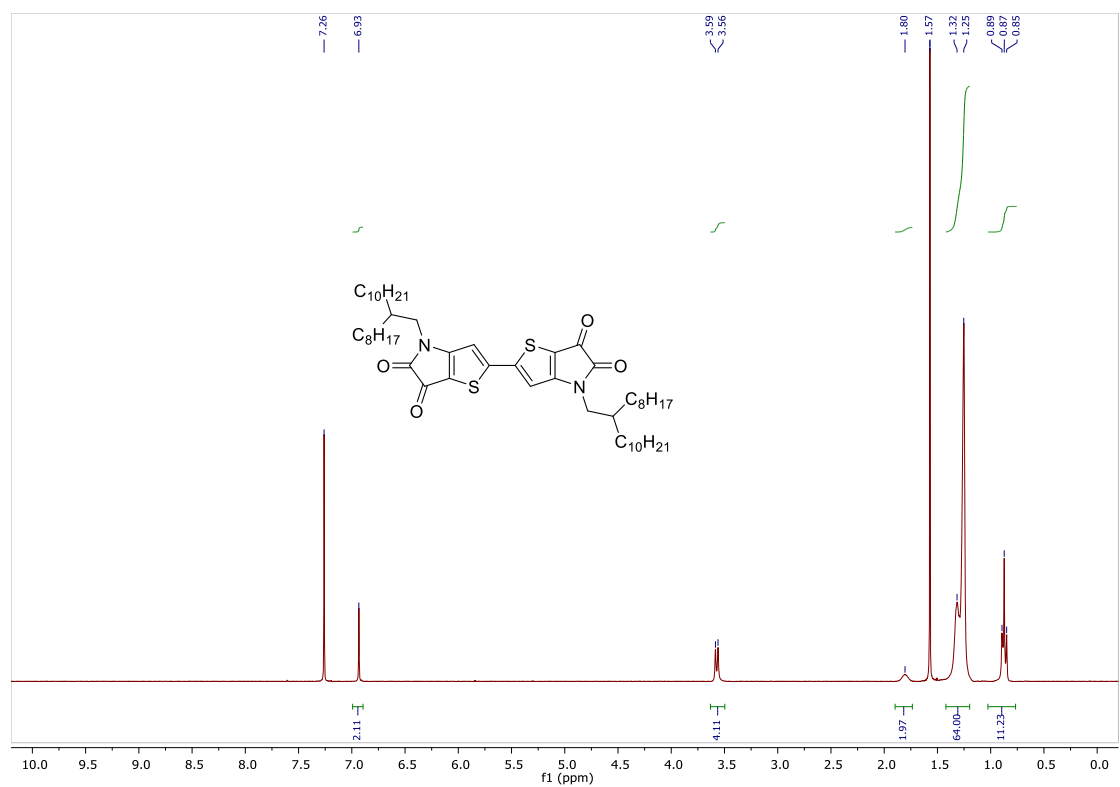
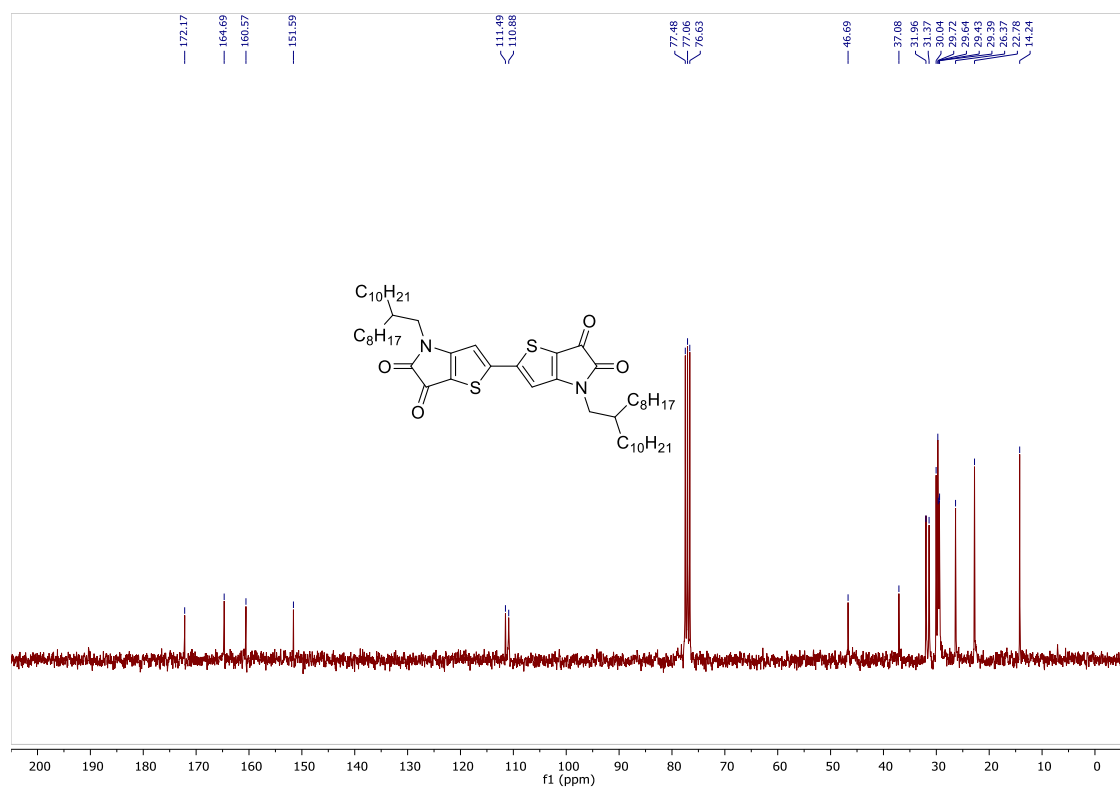
Table S3. Summary of Bis-IID OFET devices with BGTC architecture and Al contacts under vacuum.

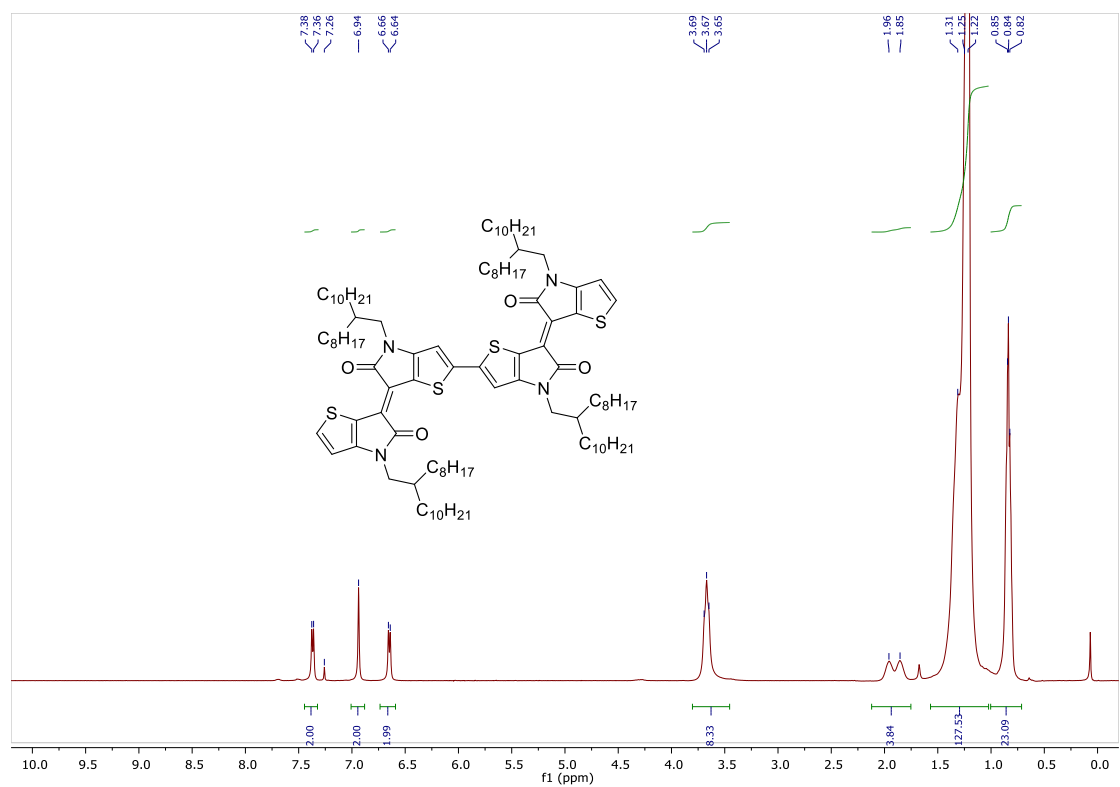
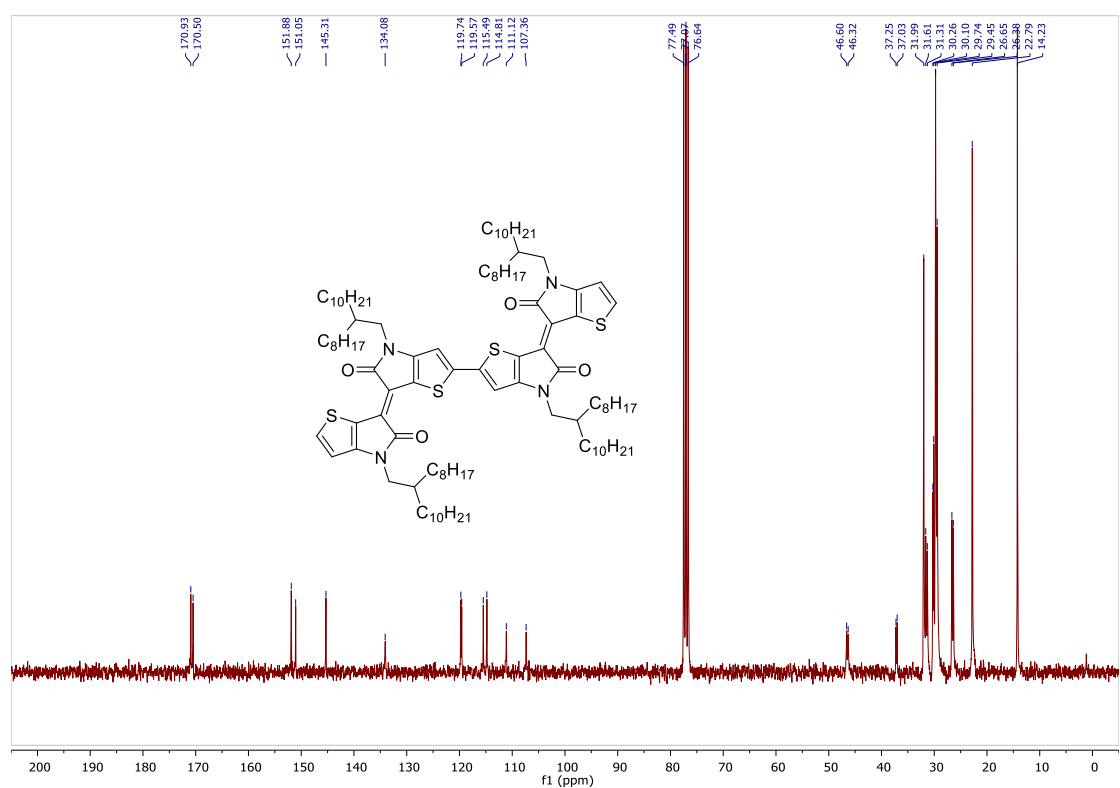
Polymers	$\mu_{\text{e, average}}$ ($\text{cm}^2\text{V}^{-1}\text{s}^{-1}$)	$\mu_{\text{e, max}}$ ($\text{cm}^2\text{V}^{-1}\text{s}^{-1}$)	$I_{\text{on/off}}$	$\mu_{\text{h, average}}$ ($\text{cm}^2\text{V}^{-1}\text{s}^{-1}$)	$\mu_{\text{h, max}}$ ($\text{cm}^2\text{V}^{-1}\text{s}^{-1}$)	$I_{\text{on/off}}$
P1	3.82×10^{-4}	4.63×10^{-4}	~50	0.018	0.023	~50
P1F	1.73×10^{-4}	2.15×10^{-4}	~10	0.0011	0.0013	~10
P2	1.67×10^{-3}	2.16×10^{-3}	~15	0.003	0.005	10
P2F	1.27×10^{-3}	1.71×10^{-3}	~6	2.25×10^{-4}	2.8×10^{-4}	~5

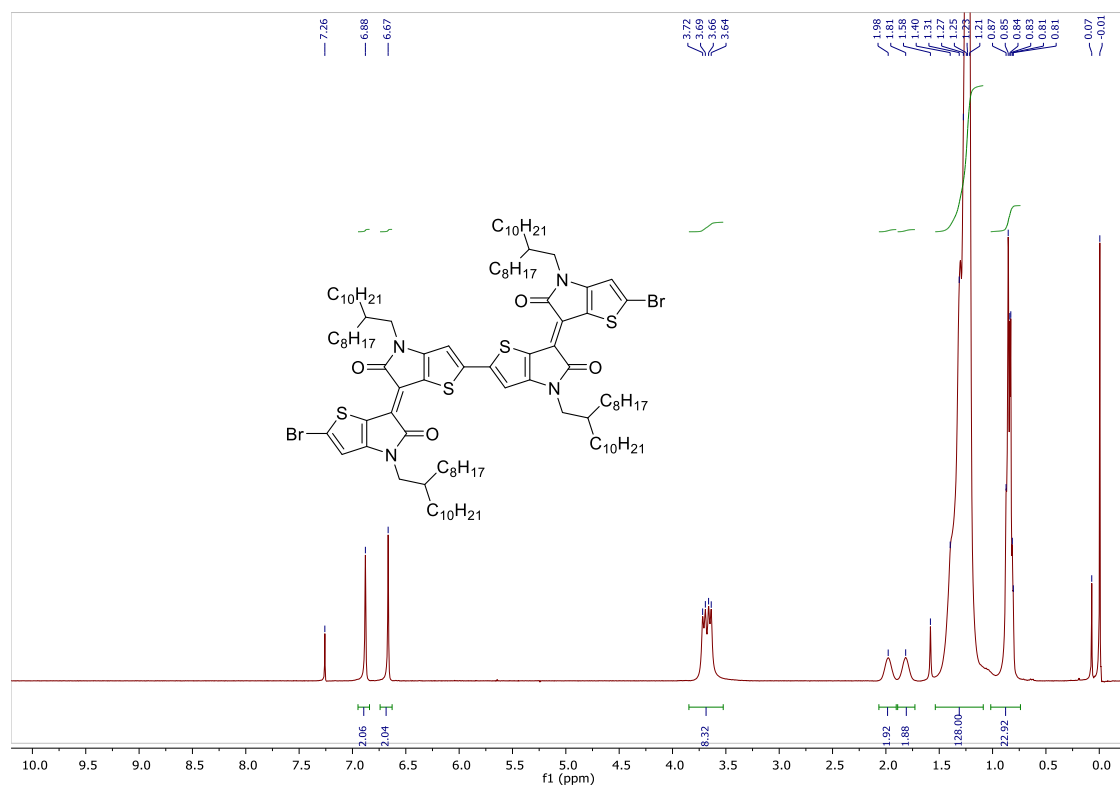
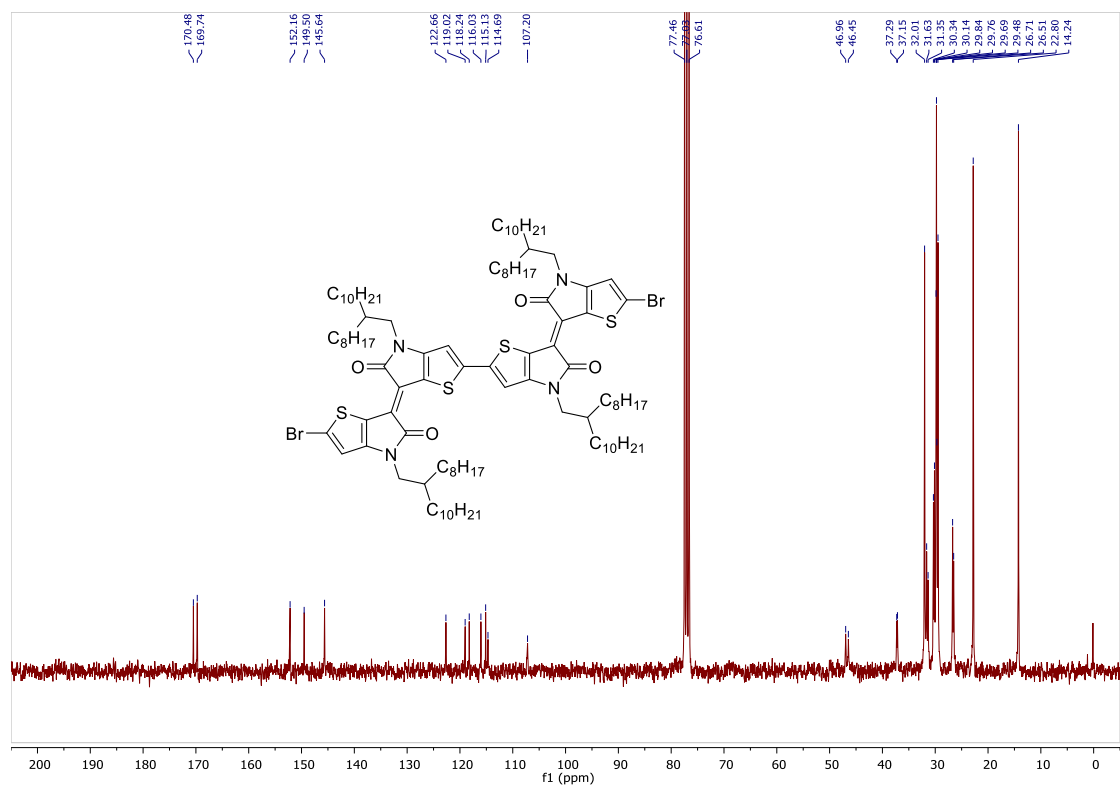
V. ^1H - , ^{13}C -NMR, and mass spectra

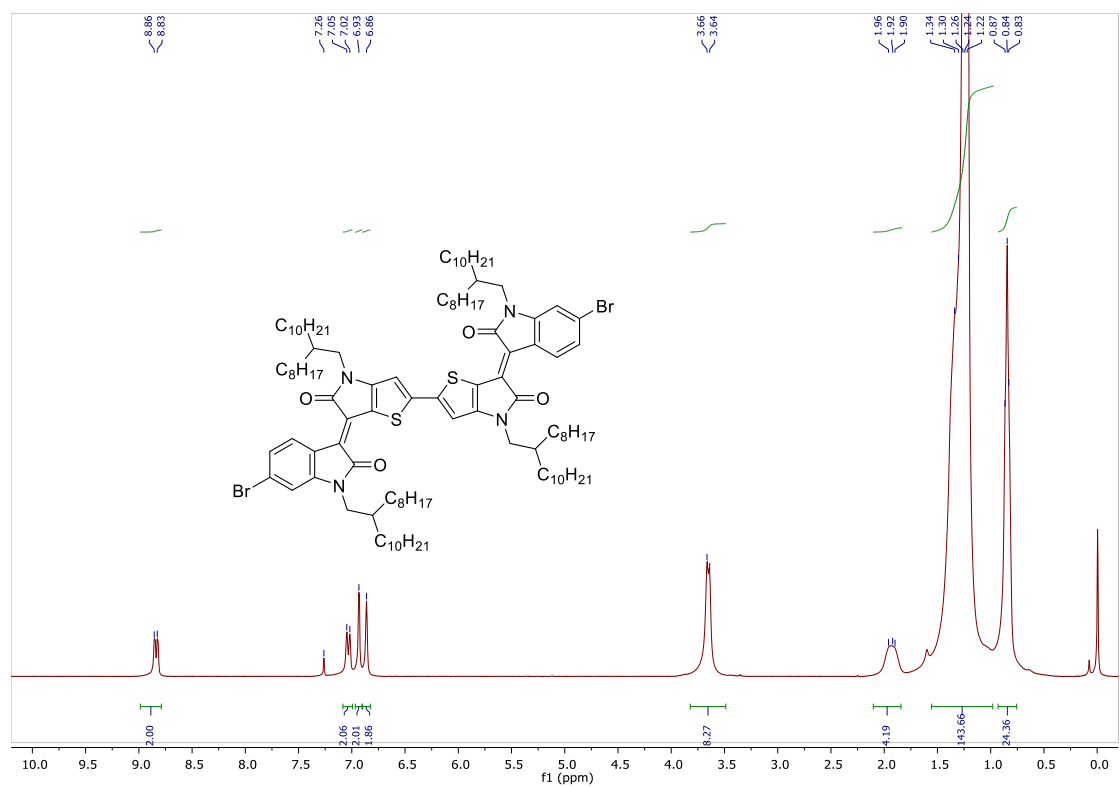
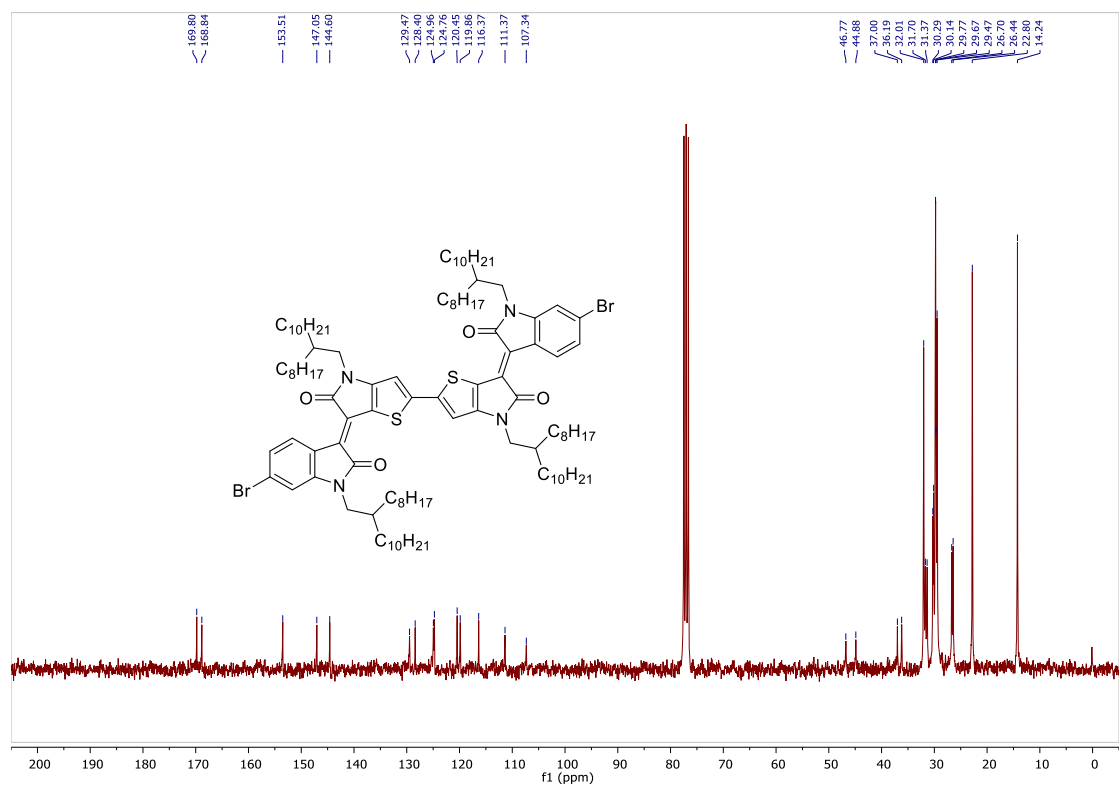
NMR spectra







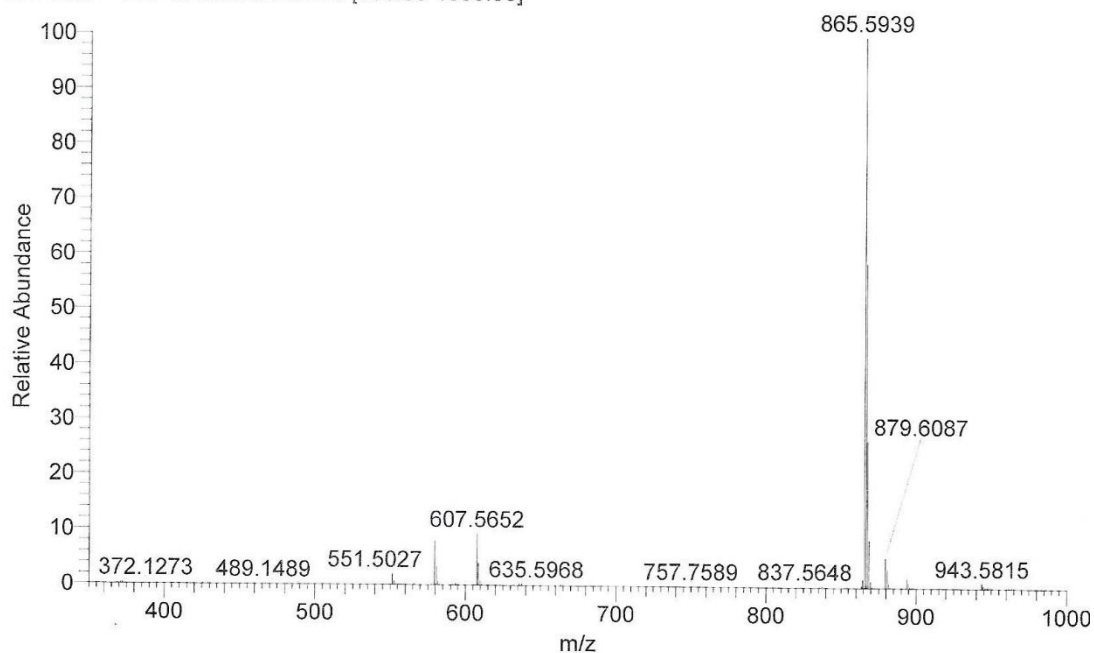




Mass spectra

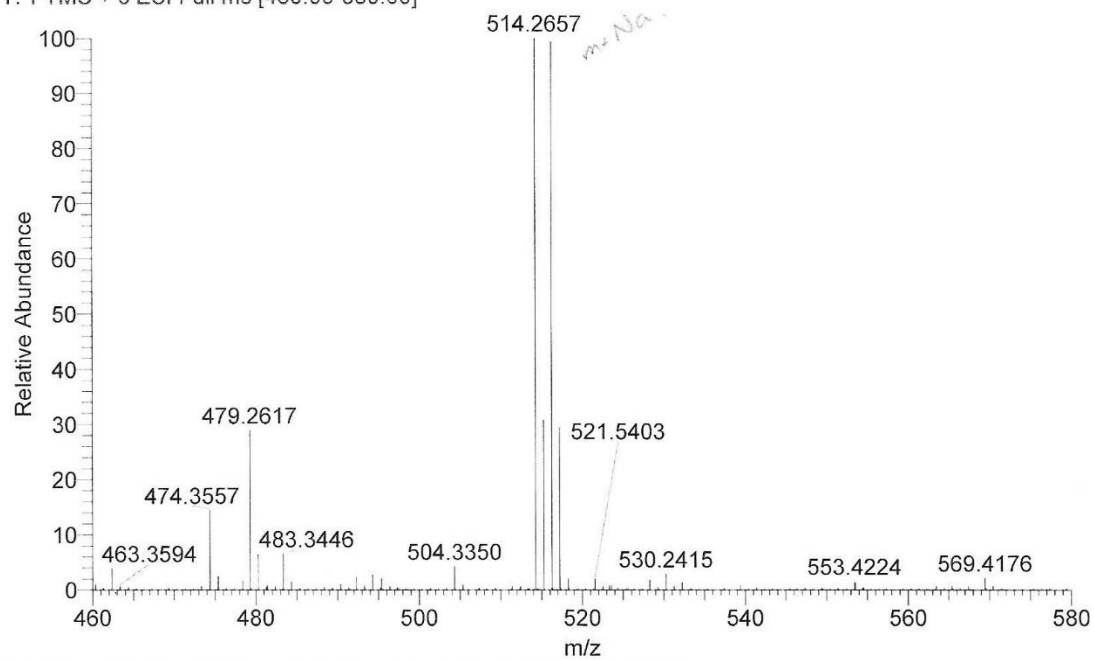
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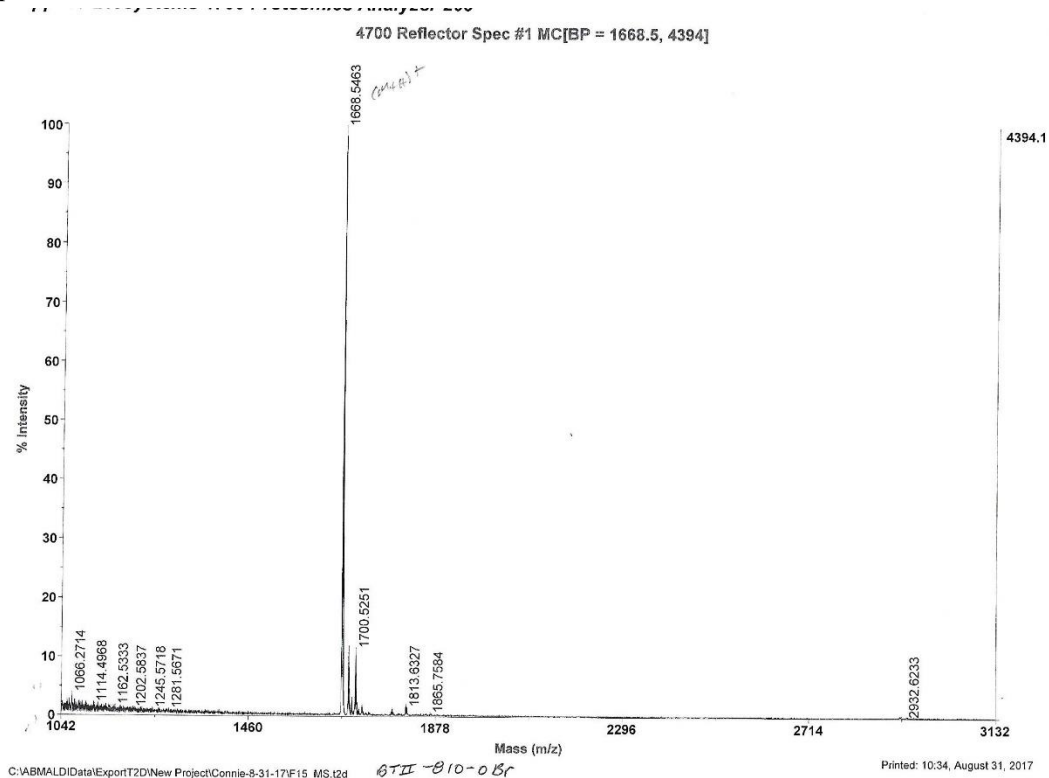


Compound 4:

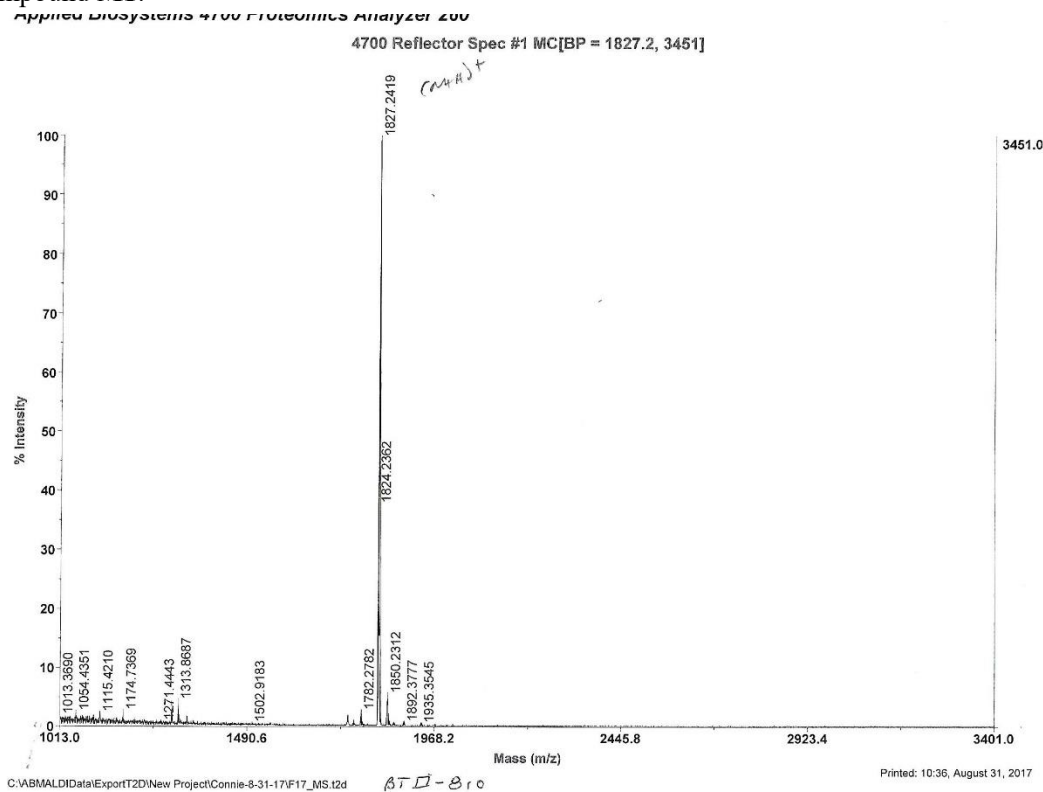
XL11 9 14 17 ESI_170724143442 #1 RT: 0.00 AV: 1 NL: 1.26E7
T: FTMS + c ESI Full ms [460.00-580.00]



Compound M1a:



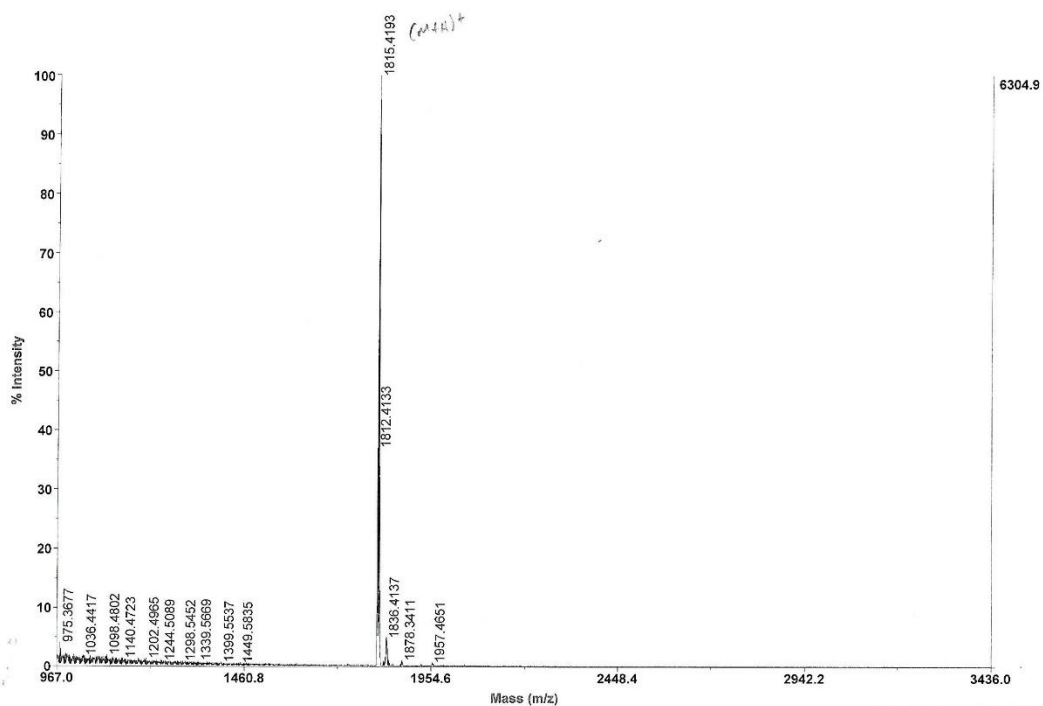
Compound M1:



Compound M2:

Applied Biosystems 4000 Proteomics Analyzer 200

4700 Reflector Spec #1 MC[BP = 1815.4, 6305]



C:\ABMALDI\Data\ExportT2D\New Project\Connie-8-31-17\F16_MS12d

B3TII-B10

Printed: 10:35, August 31, 2017

Reference:

- (1) Chen, M. S.; Niskala, J. R.; Unruh, D. A.; Chu, C. K.; Lee, O. P.; Fréchet, J. M. J. *Chem. Mater.* **2013**, 25 (20), 4088–4096.