

Communication

Engineering Intrinsic Flexibility in Polycrystalline Molecular Semiconductor Films by Grain Boundary Plasticization

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Engineering Intrinsic Flexibility in Polycrystalline Molecular Semiconductor Films by Grain Boundary Plasticization

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ABSTRACT: Mechanically flexible films of the highly crystalline core-cyanated perylenediimide (PDIF-CN₂) molecular semiconductor are achieved via a novel grain boundary plasticization strategy in which a specially designed polymeric binder (PB) is used to connect crystallites at the grain boundaries. The new PB has a naphthalenediimide-dithiophene π -conjugated backbone end-functionalized with PDI units. In contrast to conventional polymer-small molecule blends, where distinct phase separation occurs, this blend film with plasticized grain boundaries exhibits a morphology typical of homogeneous PDIF-CN₂ films which is preserved upon bending at radii as small as 2 mm. Thinfilm transistors fabricated with PB/PDIF-CN₂ blends exhibit substantial electron mobilities even after repeated bending. This design represents a new approach to realizing flexible and textured semiconducting π -electron films with good mechanical properties and charge transport properties.

Advances in flexible organic thin-film transistors (FOTFTs) have driven new applications in displays, human interactivity, and health care.¹⁻³ The properties of organic π -electron semiconductors, which function as key components in organic electronics, dominate both the intrinsic charge transport and the ultimate mechanical flexibility.⁴⁻⁵ Although semiconducting polymers are excellent candidates for FOTFTs,6-7 small molecules typically exhibit superior charge transport due to enhanced film texturing/crystallinity.8 However, a significant limitation of molecular semiconductors is that the thin-film crystallinity and the presence of grain boundaries can severely compromise charge transport under mechanical stress.⁹⁻¹⁰ Furthermore, effective strategies to enhance mechanical flexibility of such small molecule films while preserving effective charge transport remain elusive.11-

It is known that positioning structurally sensitive semiconducting layers in the neutral plane of multilayer device stacks can alleviate mechanical deformation upon bending. This strategy has been utilized to fabricate flexible pentacene and F_{16} CuPc devices.¹³⁻¹⁵ Additionally, flexible devices have been fabricated with polymeric semiconductors. Poly(3hexylthiophene)-polyethylene diblock co-polymers exhibit outstanding mechanical and transport properties by tuning block ratios.¹³ Bao reported that introducing non-covalent crosslinking significantly enhances conjugated polymer film flexibility.⁵ Such crosslinks provide energy dissipation via bond breaking under strain while retaining charge transport. Regarding n-type materials, the widely investigated naphthalenediimide (NDI)-dithiophene (T2) π -conjugated polymer N2200 structure is known to provide good FOTFT mechanical flexibility,⁶ retaining 75% of the original mobility on bending to a 1 mm radius.¹⁶ Furthermore, solar cells using N2200-containing blends retain >96% of the initial power-conversion efficiency after 50 stretching cycles under 20% strain.¹⁷

In principal, direct blending of small molecules with polymers could provide the good electronic performance of small molecules and the superior film-forming/mechanical attributes of polymers. In a pioneering study, the small molecule 2,8-difluoro-5,11-bis(triethylsilyl-ethynyl)anthra-dithiophene and a poly(triarylamine) were blended to achieve a TFT mobility of 2.4 cm²/Vs.¹⁸ In this and similar approaches the two semiconductors phase-separate vertically, with the polymer promoting of molecular crystal growth in the transistor channel, enhancing mobility, but without improving the elastic behavior.¹⁹



Figure 1. (a) Chemical structures of materials (b) FOTFT structure used. Crystallite (c) size and (d) electron mobility for PB/PDIF- CN_2 blends as a function of PB content.

Here a new approach to achieving highly crystalline small molecule FOTFTs with good flexibility is realized by introducing a polymeric binder (PB, Figure 1a) which functions as a grain boundary plasticizer of the highly crystalline small molecule (N,N'-1H,1H-perfluorobutyl PDIF-CN₂ semiconductor dicyanoperylene-carboxydiimide, Figure 1a). PB was designed using the N2200 polymer as the backbone and end-functionalizing it with two monocyanodperylene-carboxydiimide (PDIF-CN) groups. The NDI-T2 backbone provides mechanical flexibility, good electron transport, and a LUMO energy slightly above that of PDIF-CN₂, to suppress electron trapping, while the endcaps should promote anchoring to the PDIF-CN₂ crystallites. It will be seen that PB effectively suppresses polymer-PDIF-CN₂ phase separation while localizing primarily in the PDIF-CN2 grain boundaries and plasticizing them. Owing to the unique PB localization within the crystallites, mechanical stress is effectively released without damaging the contact between the crystal boundaries. Thus, FOTFTs with 5 wt % PB in the PB/PDIF-CN₂ blend exhibit substantially greater mechanical stress-tolerance and excellent nchannel mobility.

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PB synthesis is shown in Scheme S1. Intermediate asymmetric PDIF-CN-Br required for PB end-capping, was prepared by reacting CuCN and PDIF-Br2. 20 To obtain PB, the N2200 backbone was synthesized using excess distannylated-dithiophene (T2-Sn2) in a Stille protocol, followed by adding excess PDIF-CN-Br. The product polymer was purified by Soxhlet extraction and characterized by high temperature ¹H and ¹⁹F NMR, GPC, elemental analysis, and optical absorption spectroscopy (see SI). Due to the significant PDIF-CN₂ hydrophobicity, producing highly textured films and blends required modifying the spin-coating procedure (see SI). For FOTFT fabrication (Figure 1b) and morphological analysis, the semiconductor films were spin-coated using PB/PDIF-CN₂ solutions 0-10 wt % in DCB, on 130 µm PEN substrates with pre-patterned Au source and drain electrodes (25 nm). FOTFTs were completed by spin-coating a CYTOP gate dielectric (capacitance = 3.2 nF/cm^2) and thermally evaporating the Au gate electrodes (40 nm).



Figure 2. AFM images before deformation (left, scale bar = 4 μ m) and top-view SEM images (right, scale bar = 2 μ m) of PB (x wt%)/PDIF-CN₂ before and after bending at the indicated radii.

Before FOTFT measurements, the PDIF-CN₂/PB blend film morphologies were characterized as a function of PB content using cross-polarized optical microscopy and tapping-mode AFM (Figures 2 and S6). The microscopic images reveal highly textured films with crystalline domain sizes decreasing first minimally from ~91 μ m to ~83 μ m to ~71 μ m when the PB content increased from 0% to 2.5% to 5%, followed by a steeper decline (~42 μ m and ~37

 μ m) for blends with 7.5% and 10% PB, respectively (Figure 1c). Note that smaller crystals have a larger grain boundary density, which may compromise mobility as in vapor-deposited PDIF-CN₂ films/TFTs.⁹ Interestingly, the AFM images show that all the present films have comparable ~7-9 nm rms roughness (Figure 2).

FOTFT measurements were next conducted in ambient and performance parameters, including field-effect mobility (μ), were extracted using standard MOSFET equations.²¹ Although all blend films exhibit similar surface roughness, the transistor performance is affected by crystallite size as shown in Figures 1d and S7. Thus, pristine PDIF-CN₂ devices (0 wt% PB) exhibit a μ of 0.40±0.05 cm²/Vs with negligible I-V hysteresis. As the PB content increases from 2.5 wt% to 10 wt%, both the I_{on} and I_{off} currents first fall minimally (2.5-5%) and then substantially. Thus, the electron mobility decreases from 0.38 ± 0.01 (2.5 wt%) $\rightarrow 0.35\pm0.05$ (5 wt%) $\rightarrow 0.16 \pm 0.03$ (7.5 wt%), and finally to 0.13 ± 0.02 cm²/Vs (10 wt%). This mobility decline likely reflects reduction of crystallite size, hence increased grain boundary densities, rather than PB presence since a similar trend was seen for TFTs based on vapordeposited PDIF-CN₂ films fabricated at progressively lower temperatures, which reduces crystal domain size.⁹



Figure 3. Electron mobility variations of PB (x wt%)/PDIF- CN_2 FOTFTs (x = 0-10) upon deformation at (a) different bending radii and (b) for different bending cycles. Electron mobility of PB (5 wt%):PDIF- CN_2 FOTFTs upon bending deformation at different radii (c) along the L channel direction and (d) perpendicular to the L direction. (e) Optical images of bended FOTFTs before testing.

Next, we evaluated charge transport behavior after the FOTFTs were deformed by bending at a radius from ∞ (no extensional stress) to 2 mm (stress \sim 3%) parallel to the charge transport direction (along the channel length, L). From Figure 3, the μ variation upon bending strongly depends on the semiconductor composition. Thus, while the mobility of both pristine and 2.5 wt% devices degrades substantially from 0.40±0.05 and 0.38±0.01 cm^2/Vs to 0.15±0.02 and 0.10±0.01 cm^2/Vs , respectively, that of the 7.5 and 10 wt% blend-based FOTFTs deteriorates only moderately, from 0.16±0.03 to 0.12±0.01 cm²/Vs and from 0.13 ± 0.02 to 0.07 ± 0.02 cm²/Vs, respectively. TFTs with the 5 wt% blend exhibit the best compromise between initial performance (μ $= 0.35 \pm 0.05$ cm²/Vs) and mobility degradation after 2 mm bending ($\mu = 0.22 \pm 0.03$ cm²/Vs). The 5 wt% blend exhibits negligible variations of other TFT parameters such as threshold voltage and current on-off ratio (Figure S8c), as well as no substantial changes in transport when measured in the 2 mm bended state versus after bending at 2 mm (Figure S8d).

Repeated bending tests were performed on all devices at 4 mm for 500 cycles (Figures 3b and S8). Clearly, the greatest mobility decline occurs after 1 bending cycle for the pristine material (0.44 \rightarrow 0.14 cm²/Vs) and 2.5 wt% (0.40 \rightarrow 0.24 cm²/Vs), and generally before 50 bending cycles for all devices. After ~100 cycles the

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mobility tends to stabilize. Again, these data confirm that the 5wt% TFT blend affords the best compromise between initial and final performance. $(0.37 \rightarrow 0.18 \text{ cm}^2/\text{Vs})$. Multiple bending cycles for the 5 wt% device at various bending radii and directions were also investigated (Figures 3c-d). The magnitude of device performance degradation increases as the bending radius decreases. After a 500-cycle bending tests at 15, 7, 4, and 3 mm radii, μ falls by ~0%, 15%, 45%, and 65%, respectively, on bending parallel to the L direction, and only ~0%, 5%, 8%, and 12%, respectively, on bending perpendicular to the L direction. This result agrees with the direction of the crack propagation on bending observed by SEM, *vide infra*) as well as demonstrating that performance degradation is mainly due to semiconductor fracture. Additionally, the 5 wt% blend TFTs retain ~90% of the initial mobility after ~7 months storage in ambient (Figure S9b).

To understand charge transport trends upon bending, top-view SEM images of the blend films were recorded (Figure 2). Before bending, all films appear smooth with randomly distributed, interconnected crystallites. However, upon bending the PDIF-CN₂ films at radii of 4 and 2 mm, several cracks are observed demonstrating poor mechanical stress resistance. Although most of cracks propagate along the same orientation, perpendicular to the bending direction, some also develop in other directions (Figure S12). Similar behavior, yet greatly mitigated, is observed for the 2.5 wt% blend film indicating that limited amounts of polymer are insufficient for film softening. However, on addition of 5%, 7.5%, and 10wt % PB, the crystalline films become highly flexible, maintaining smooth, continuous morphologies for bending radii as small as 2 mm. Importantly, control experiments using 5 wt% pure N2200 as the additive underscore the PB molecular design effectiveness. Thus, SEM images (Figure 4a-inset and S14) show that N2200 + PDIF-CN₂ films exhibit substantial cracking upon bending, while AFM images (Figure S15) reveal N2200-PDIF-CN₂ phase separation, in marked contrast to the PB + PDIF-CN₂ blends. More importantly, the mobility of the N2200 + PDIF-CN₂ FOTFTs bent at a 4 mm radius for 500 cycles decreases by ~90% (from 0.55 to 0.06 cm²/Vs, Figure 4a). Together these results demonstrate that N2200 alone cannot increase PDIF-CN2 film flexibility.



Figure 4. (a) Electron mobility variation of N2200(5 wt%)/PDIF-CN₂ FOTFTs upon varied bending cycles (R = 4 mm). Inset SEM image after the first bending at R = 4 mm (scale bar = 2 μ m). (b) STEM image and (c) magnification and EDS elemental maps [Fluorine (red) and Sulfur (green)] for the indicated area in (b) for the PB(5 wt%)/PDIF-CN₂ blend.

Since PB addition to PDIF-CN₂ clearly enhances film mechanical properties, the question of how PB creates a more elastic morphology and whether this reflects a specific PB special distribution within the crystalline domains, arises. SEM images show that increasing the blend PB content, particularly beyond 5 wt%, creates brighter features along the film grain boundaries,

suggesting preferential PB localization at the crystallite edges. To better understand this, STEM-EDS mapping of the 5 wt% blend was carried out (Figures 4b,c). By mapping the F (PDIF-CN₂ and PB end groups) and S (PB only) distributions, PB mainly accumulates at the PDIF-CN₂ grain boundaries. This result underscores the importance of the PB PDIF-CN₂-like end groups in anchoring at PDIF-CN₂ grain boundaries during film formation. Therefore, PB acts as a grain boundary plasticizer, releasing stress between adjacent grains and suppressing crack formation during film bending. This approach differs from conventional polymersmall molecule semiconductor blends where the polymer enhances small molecule crystallinity by phase separation.¹⁹



Figure 5. GIWAXS of the indicated PB(x wt%)/PDIF-CN2 blends.

Finally, grazing incidence wide-angle X-ray scattering (GIWAXS) was performed to assess crystallinity (Figures 5, S16 and S17). The pristine PDIF-CN₂ films exhibit three major (00n)reflections along the out-of-plane direction at $q = 0.34 \text{ Å}^{-1}$, 0.97 \AA^{-1} and 1.28 Å⁻¹. From the (001) reflection, a periodicity of 18.47 Å is found, indicating that the PDIF-CN₂ molecules are aligned with the long molecular axes perpendicular to the substrate surface.²² This edge-on orientation favors higher carrier mobility.²³ The pristine PB films exhibit a (100) reflection at q = 0.26 Å⁻¹ and a (010) reflection at $q = 1.62 \text{ Å}^{-1}$ (Figure S17),²⁴ indicating that the polymer chains are oriented in a preferential face-on arrangement, as seen for N2200.²⁵ Interestingly, for the blend film, the PDIF-CN₂ reflection positions are identical, indicating that PB incorporation does not alter the crystal domain phase, but rather the small rings indicate multiple crystallite orientations. Furthermore, the GIWAX data are consistent with the reported PDIF-CN₂ single crystal structure, excluding solid solution formation.²²

In conclusion, a new approach to enhance the flexibility of crystalline small molecular semiconductors and the corresponding FOTFTs by grain boundary plasticization is reported. Because of the similarity between the PB end-capping units and PDIF-CN₂, the polymeric chains preferentially localize in the grain boundaries during crystallization/film formation rather than vertically phase-separating. Thus, this work offers new guidelines to design semiconducting binders and films with enhanced elastic properties complimenting other approaches.^{5-7, 11-17, 26}

ASSOCIATED CONTENT

Supporting Information. Experimental procedures, small molecule and polymer synthesis, characterization, and optical microscopy images; AFM, SEM, and GIWAXS images, and FOTFT transfer curves; Scheme S1 and Figures S1-S17. This material is available free of charge via the Internet at http://pubs.acs.org.

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Author Contributions

#D. Z. and J. C. contributed equally.

Notes

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The authors declare no competing financial interest.

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REFERENCES

1. Wang, B.; Facchetti, A., Mechanically flexible conductors for stretchable and wearable e-skin and e-textile devices. *Adv. Mater.* **2019**, 1901408.

2. Yao, Y.; Dong, H.; Hu, W., Charge transport in organic and polymeric semiconductors for flexible and stretchable devices. *Adv. Mater.* **2016**, *28*, 4513.

3. Zhu, H.; Shin, E. S.; Liu, A.; Ji, D.; Xu, Y.; Noh, Y. Y., Printable
semiconductors for backplane TFTs of flexible OLED displays. *Adv. Funct. Mater.* 2019, 1904588.

Adv. Funct. Mater. 2019, 1904588.
4. Choi, D.; Kim, H.; Persson, N.; Chu, P.-H.; Chang, M.; Kang, J.-H.; Graham, S.; Reichmanis, E., Elastomer–polymer semiconductor blends for high-performance stretchable charge transport networks. *Chem. Mater.* 2016, 28, 1196.

5. Oh, J. Y.; Rondeau-Gagne, S.; Chiu, Y. C.; Chortos, A.; Lissel,
F.; Wang, G. N.; Schroeder, B. C.; Kurosawa, T.; Lopez, J.;
Katsumata, T.; Xu, J.; Zhu, C.; Gu, X.; Bae, W. G.; Kim, Y.; Jin,
L.; Chung, J. W.; Tok, J. B.; Bao, Z., Intrinsically stretchable and
healable semiconducting polymer for organic transistors. *Nature*2016, *539*, 411.

32 6. Yan, H.; Chen, Z.; Zheng, Y.; Newman, C.; Quinn, J. R.; Dotz,
33 F.; Kastler, M.; Facchetti, A., A high-mobility electron34 transporting polymer for printed transistors. *Nature* 2009, 457, 679.
35 7. Zhang, G.; Lee, S.; Gutiérrez-Meza, E.; Buckley, C.; McBride,
36 M.; Valverde-Chávez, D. A.; Kwon, Y. H.; Savikhin, V.; Xiong,
37 H.; Dunn, T. J.; Toney, M. F.; Yuan, Z.; Silva, C.; Reichmanis, E.,
38 Robust and stretchable polymer semiconducting networks: from

film microstructure to macroscopic device performance. *Chem. Mater.* 2019, 31, 6530. *Human D. K.: Francisco Human International Conference on the Conference on t*

8. Hwang, D. K.; Fuentes-Hernandez, C.; Berrigan, J. D.; Fang, Y.;
Kim, J.; Potscavage, W. J.; Cheun, H.; Sandhage, K. H.; Kippelen,

Kim, J.; Potscavage, W. J.; Cheun, H.; Sandhage, K. H.; Kippelen,
B., Solvent and polymer matrix effects on TIPS-pentacene/polymer
blend organic field-effect transistors. J. Mater. Chem. 2012, 22, 5531.

9. Jones, B. A.; Facchetti, A.; Wasielewski, M. R.; Marks, T. J.,
Effects of arylene diimide thin film growth conditions on n-channel
OFET performance. *Adv. Funct. Mater.* 2008, *18*, 1329.

10. Müller, C.; Goffri, S.; Breiby, D. W.; Andreasen, J. W.;
Chanzy, H. D.; Janssen, R. A. J.; Nielsen, M. M.; Radano, C. P.;
Sirringhaus, H.; Smith, P.; Stingelin-Stutzmann, N., Tough,
semiconducting polyethylene-poly(3-hexylthiophene) diblock
copolymers. Adv. Funct. Mater. 2007, 17, 2674.

51 11. Rodriquez, D.; Savagatrup, S.; Valle, E.; Proctor, C. M.;
52 McDowell, C.; Bazan, G. C.; Nguyen, T. Q.; Lipomi, D. J.,
53 Mechanical properties of solution-processed small-molecule
54 semiconductor films. *ACS Appl. Mater. Interfaces* 2016, *8*, 11649.
55 12. Kayser, L. V.; Lipomi, D. J., Stretchable conductive polymers

55 12. Kayser, L. V.; Lipomi, D. J., Stretchable conductive polymers and composites Based on PEDOT and PEDOT:PSS. *Adv. Mater.* 2019, *31*, 1806133.

13. Sekitani, T.; Zschieschang, U.; Klauk, H.; Someya, T., Flexible organic transistors and circuits with extreme bending stability. *Nat. Mater.* **2010**, *9*, 1015.

14. Wang, X.; Yang, H.; Cao, S.; Zhong, J.; Fang, Y.; Liu, Y.; Lin, Z.; Chen, H.; Guo, T., A universal strategy to improve the mechanical stability of flexible organic thin film transistors. *J. Mater. Chem. C* **2019**, *7*, 6323.

15. Reyes-Martinez, M. A.; Crosby, A. J.; Briseno, A. L., Rubrene crystal field-effect mobility modulation via conducting channel wrinkling. *Nat. Commun.* **2015**, *6*, 6948.

16. Hu, Y.; Warwick, C.; Sou, A.; Jiang, L.; Sirringhaus, H., Fabrication of ultra-flexible, ultra-thin organic field-effect transistors and circuits by a peeling-off method. *J. Mater. Chem. C* **2014**, *2*, 1260.

17. Yu, Y.-Y.; Chen, C.-H.; Chueh, C.-C.; Chiang, C.-Y.; Hsieh, J.-H.; Chen, C.-P.; Chen, W.-C., Intrinsically stretchable nanostructured silver electrodes for realizing efficient strain sensors and stretchable organic photovoltaics. *ACS Appl. Mater. Interfaces* **2017**, *9*, 27853.

18. Hamilton, R.; Smith, J.; Ogier, S.; Heeney, M.; Anthony, J. E.; McCulloch, I.; Veres, J.; Bradley, D. D. C.; Anthopoulos, T. D., High-performance polymer-small molecule blend organic transistors. *Adv. Mater.* **2009**, *21*, 1166.

19. Smith, J.; Zhang, W.; Sougrat, R.; Zhao, K.; Li, R.; Cha, D.; Amassian, A.; Heeney, M.; McCulloch, I.; Anthopoulos, T. D., Solution-processed small molecule-polymer blend organic thin-film transistors with hole mobility greater than 5 cm²/Vs. *Adv. Mater.* **2012**, *24*, 2441.

20. Jones, B. A.; Ahrens, M. J.; Yoon, M.-H.; Facchetti, A.; Marks, T. J.; Wasielewski, M. R., High-Mobility air-stable n-type semiconductors with processing versatility: dicyanoperylene-3,4:9,10-bis(dicarboximides). *Angew. Chem.* **2004**, *116*, 6523.

21. Huang, W.; Guo, P.; Zeng, L.; Li, R.; Wang, B.; Wang, G.; Zhang, X.; Chang, R. P. H.; Yu, J.; Bedzyk, M. J.; Marks, T. J.; Facchetti, A., Metal composition and polyethylenimine doping capacity effects on semiconducting metal oxide-polymer blend charge transport. *J. Am. Chem. Soc.* **2018**, *140*, 5457.

22. Soeda, J.; Uemura, T.; Mizuno, Y.; Nakao, A.; Nakazawa, Y.; Facchetti, A.; Takeya, J., High electron mobility in air for N,N'-1H,1H-perfluorobutyldicyanoperylene carboxydi-imide solutioncrystallized thin-film transistors on hydrophobic surfaces. *Adv. Mater.* **2011**, *23*, 3681.

23. Rivnay, J.; Toney, M. F.; Zheng, Y.; Kauvar, I. V.; Chen, Z.; Wagner, V.; Facchetti, A.; Salleo, A., Unconventional face-on texture and exceptional in-plane order of a high mobility n-type polymer. *Adv. Mater.* **2010**, *22*, 4359.

24. Gao, L.; Zhang, Z. G.; Xue, L.; Min, J.; Zhang, J.; Wei, Z.; Li, Y., All-polymer solar cells based on absorption-complementary polymer donor and acceptor with high power conversion efficiency of 8.27%. *Adv. Mater.* **2016**, *28*, 1884.

25. Wang, G.; Huang, W.; Eastham, N. D.; Fabiano, S.; Manley, E. F.; Zeng, L.; Wang, B.; Zhang, X.; Chen, Z.; Li, R.; Chang, R. P. H.; Chen, L. X.; Bedzyk, M. J.; Melkonyan, F. S.; Facchetti, A.; Marks, T. J., Aggregation control in natural brush-printed conjugated polymer films and implications for enhancing charge transport. *Proc. Natl. Acad. Sci. U. S. A.* **2017**, *114*, E10066.

26. Andersson Ersman, P.; Lassnig, R.; Strandberg, J.; Tu, D.; Keshmiri, V.; Forchheimer, R.; Fabiano, S.; Gustafsson, G.; Berggren, M., All-printed large-scale integrated circuits based on organic electrochemical transistors. *Nat. Commun.* **2019**, *10*, 5053.

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Figure 2. AFM images before deformation (left, scale bar = 4 μ m) and top-view SEM images (right, scale bar = 2 μ m) of PB (x wt%)/PDIF-CN₂ before and after bending at the indicated radii.

85x79mm (300 x 300 DPI)



Figure 3. Electron mobility variations of PB (x wt%)/PDIF-CN₂ FOTFTs (x = 0-10) upon deformation at (a) different bending radii and (b) for different bending cycles. Electron mobility of PB (5 wt%):PDIF-CN₂ FOTFTs upon bending deformation at different radii (c) along the L channel direction and (d) perpendicular to the L direction. (e) Optical images of bended FOTFTs before testing.

85x57mm (300 x 300 DPI)



Figure 4. (a) Electron mobility variation of N2200(5 wt%)/PDIF-CN₂ FOTFTs upon varied bending cycles (R = 4 mm). Inset SEM image after the first bending at R = 4 mm (scale bar = 2 μ m). (b) STEM image and (c) magnification and EDS elemental maps [Fluorine (red) and Sulfur (green)] for the indicated area in (b) for the PB(5 wt%)/PDIF-CN₂ blend.

85x59mm (300 x 300 DPI)



Figure 5. GIWAXS of the indicated PB(x wt%)/PDIF-CN₂ blends.

85x41mm (300 x 300 DPI)

