

ADVANCED FUNCTIONAL MATERIALS

Supporting Information

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Controlled Dedoping and Redoping of N-Doped Poly(benzodifurandione) (n-PBDF)

*Zhifan Ke, Jagrity Chaudhary, Lucas Q. Flagg, Kyle N. Baustert, Augustine O. Yusuf, Guangchao Liu, Liyan You, Kenneth R. Graham, Dean M. DeLongchamp and Jianguo Mei**

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Zhifan Ke¹, Jagrity Chaudhary¹, Lucas Q. Flagg², Kyle N. Baustert³, Guangchao Liu¹, Liyan You¹, Kenneth R. Graham³, Dean M. DeLongchamp² and Jianguo Mei^{1*}

¹Department of Chemistry, Purdue University, West Lafayette, Indiana 47907, United States

²Materials Measurement Laboratory, National Institute of Standards and Technology Gaithersburg, Maryland, 20899, United States

³Department of Chemistry, University of Kentucky, Lexington, Kentucky 40506, United States

Correspondence to: jgmei@purdue.edu

Section 1: Dedope n-PBDF with Different Types of Oxidants

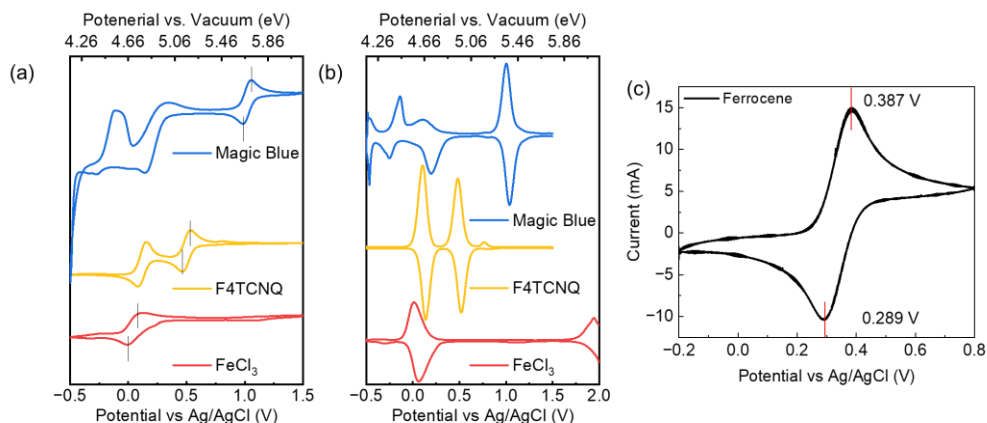


Figure S1. (a) CV and (b) DPV of Magic Blue, F4TCNQ and FeCl₃ in 0.2 M Li-TFSI measured in acetonitrile electrolyte. The CV scan rate was 10 mV/s and the DPV scan rate was 8 mV/s. (c) Calibration of Ag/AgCl electrode by measuring the CV of ferrocene in 0.2 M Li-TFSI.

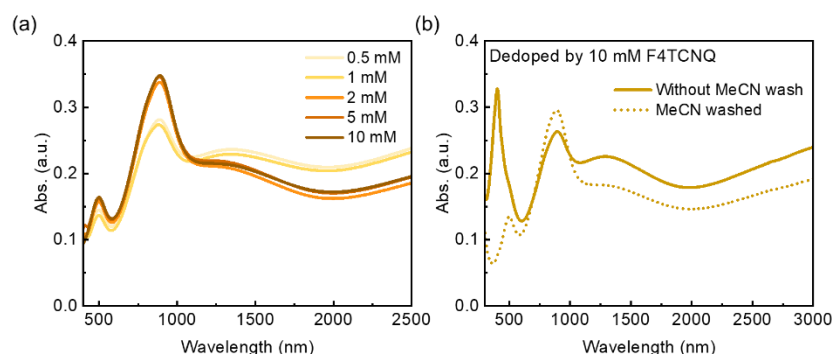


Figure S2. (a) UV-Vis-NIR absorption of n-PBDF thin films dedoped by F4TCNQ solution at different concentrations. (b) UV-Vis-NIR absorption of n-PBDF thin films dedoped by 10 mM F4TCNQ without and with acetonitrile (MeCN) wash. The strong peak at 400 nm in (b) presents the formation of F4TCNQ^{•-} radical anion during dedoping.

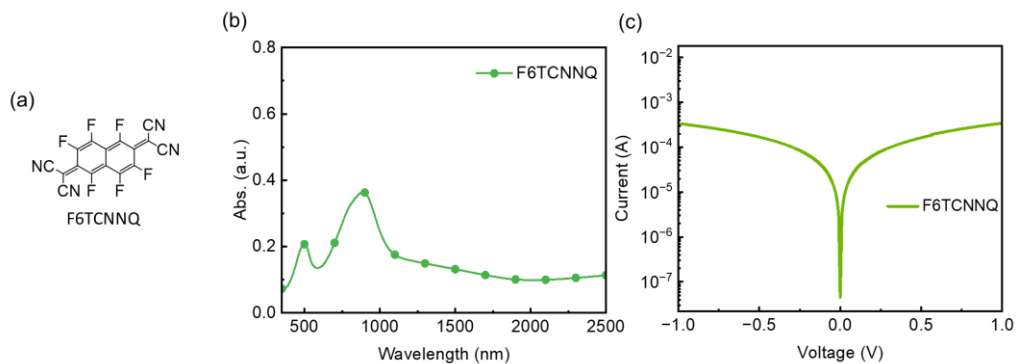


Figure S3. (a) Chemical structure of F6TCNNQ. (b) UV-Vis-NIR absorption and (c) logarithmic I-V characteristics of 10 mM F6TCNNQ-dedoped PBDF.

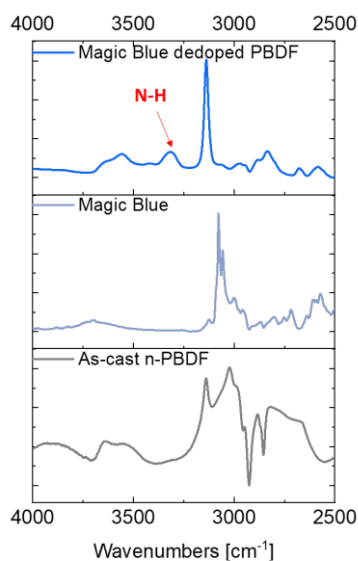


Figure S4. FTIR absorption of n-PBDF, Magic Blue and Magic Blue-dedoped PBDF in the N-H stretching region. To amplify the signal from Magic Blue, the dedoping reaction was performed by dipping the n-PBDF thin film into Magic Blue solution for 10 seconds and the sample was not washed by acetonitrile.

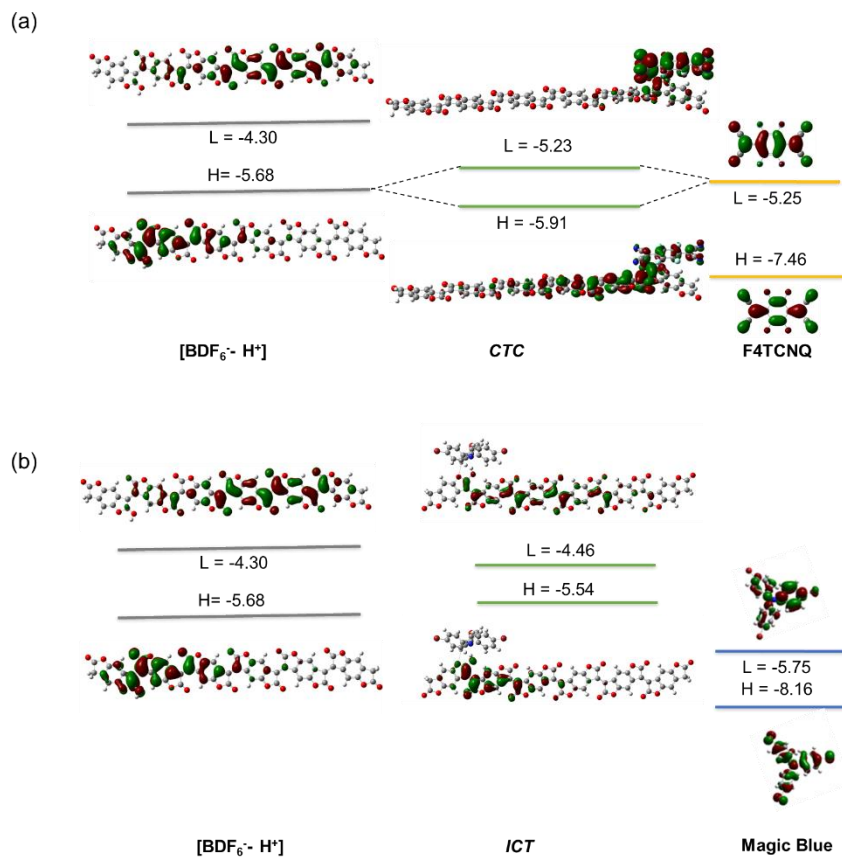


Figure S5. (a) Energetics for CTC formation between $\text{BDF}_6^- \cdot \text{H}^+$ and F4TCNQ; (b) Energetics for ICT process between $\text{BDF}_6^- \cdot \text{H}^+$ and Magic Blue

Section 2: Optoelectrical Performance and Energetics of n-PBDF at Different Doping Levels

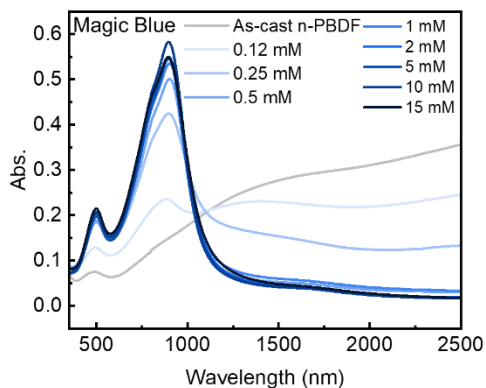


Figure S6. UV-Vis-NIR absorption of n-PBDF thin films dedoped by Magic Blue solution with the concentration varying from 0.12 mM to 15 mM.

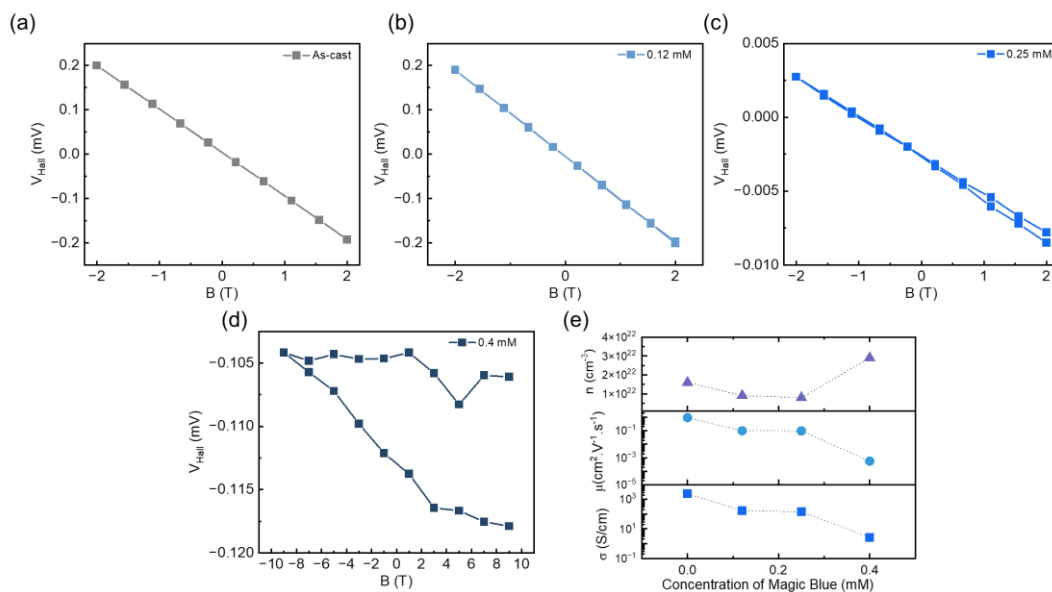


Figure S7. DC-Hall effect measurement of n-PBDF with different doping levels. (a)-(d) Hall potential (V_{Hall}) as a function of magnetic field B , (e) conductivity (σ), calculated charge carrier concentration (n) and charge carrier mobility (μ) of as-cast n-PBDF and n-PBDF dedoped by Magic Blue solution at different concentrations.

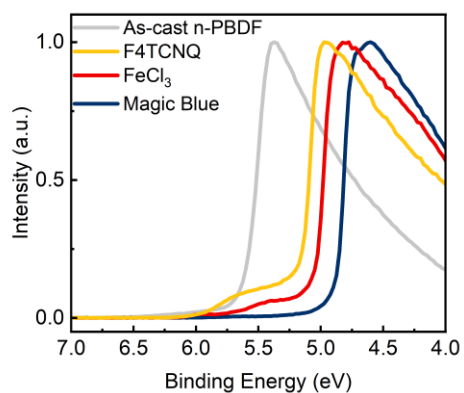


Figure S8. Secondary on-set for work function in UPS measurement spectrum of as-cast n-PBDF, and n-PBDF dedoped 10 mM by F4TCNQ, FeCl_3 and Magic Blue.

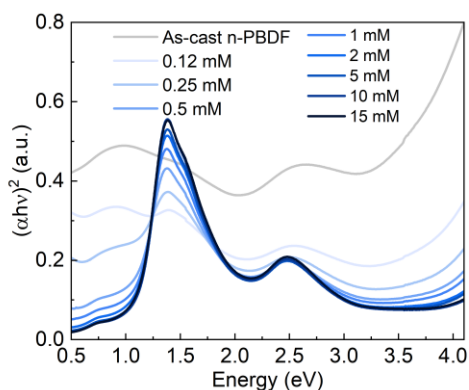


Figure S9. Tauc plot of n-PBDF dedoped by Magic Blue solution with different concentration. The optical band gap can be estimated by using equation $(h\nu - E_g) = (\alpha h\nu)^{1/\gamma}$ where γ is 0.5 for direct bandgap materials.

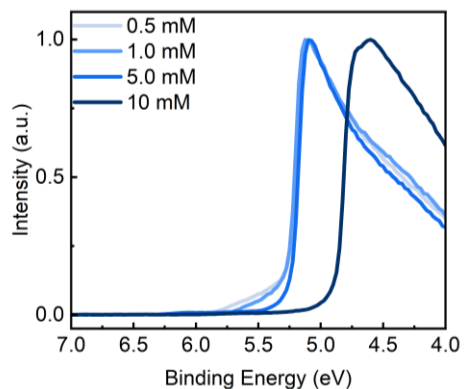


Figure S10. Secondary on-set for work function in UPS measurement spectrum of n-PBDF dedoped by Magic Blue solution at different concentrations.

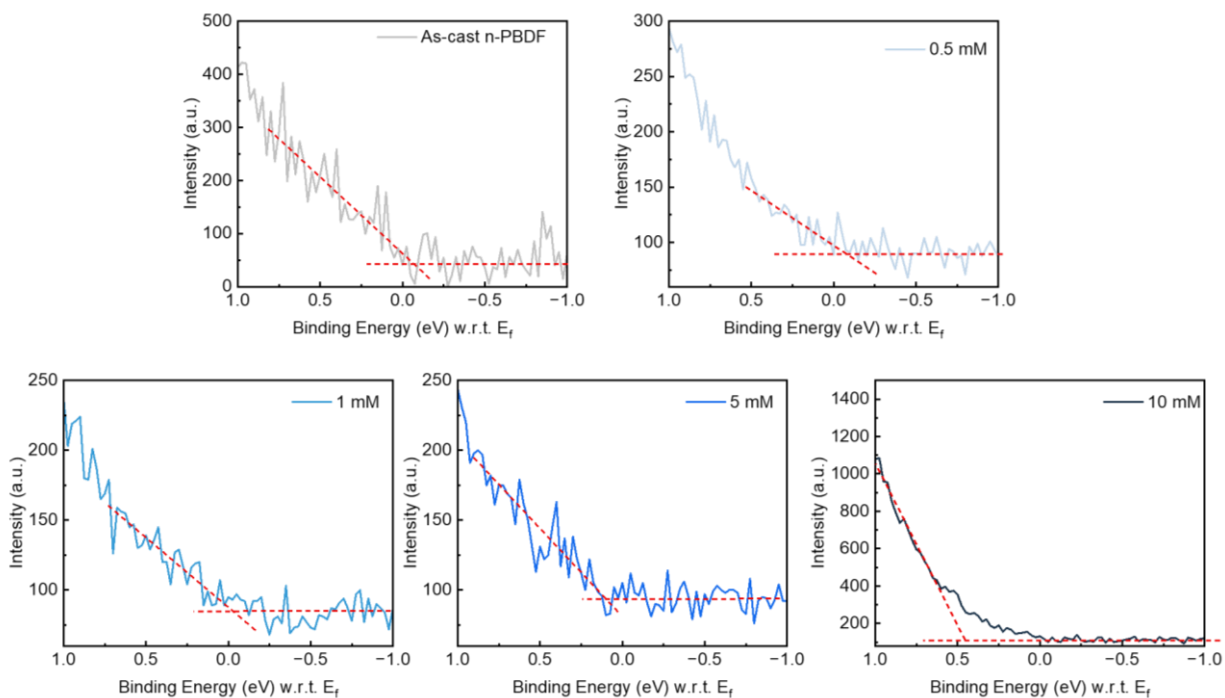


Figure S11. UPS spectra of as-cast n-PBDF and n-PBDF thin films dedoped with Magic Blue at different concentrations.

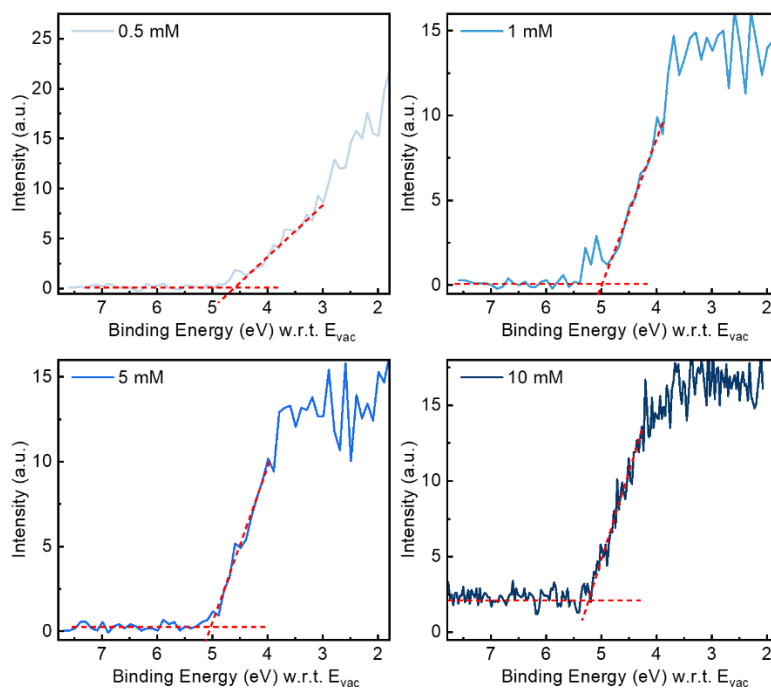


Figure S12. IPES spectra of n-PBDF thin films dedoped with Magic Blue at different concentrations.

Table S1. Summary of work function (WF), HOMO onset, IE and EA of as-cast n-PBDF and Magic Blue-dedoped PBDF.

	UPS			IPES
	WF (eV)	HOMO onset (eV)	IE (eV)	EA (eV)
As-cast	4.58	-0.08	4.50	
0.5 mM	4.95	-0.10	4.85	4.60
1.0 mM	4.94	-0.05	4.89	5.00
5.0 mM	4.97	0.10	5.07	5.00
10 mM	5.32	0.42	5.74	5.20

Section 3: Morphology study of n-PBDF with Different Doping Levels

Table S2. Summary of (*h*00) and (*h*00)* peak position, stacking distance and coherence length (CL) of as-cast n-PBDF thin film. The coherence length (CL) is calculated via the Scherrer equation: $CL = 2\pi K / FWHM$, where K is a shape factor (here uses 0.9).

As-cast	(<i>h</i> 00) peak			(<i>h</i> 00)* peak		
	$\text{\AA}^{-1}$	$\text{\AA}$	CL (nm)	$\text{\AA}^{-1}$	$\text{\AA}$	CL (nm)
h=1	0.56	11.21	5.4	0.46	13.51	5.0
h=2	1.09	5.75	3.5	0.88	7.13	4.3
h=3	1.68	3.73	1.7	1.35	4.65	2.5
h=4	2.30	2.73	2.6			

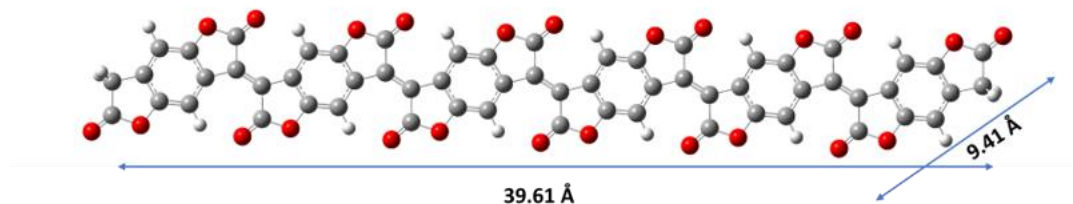


Figure S13. The length of the neutral a 6-BDF oligomer built in DFT calculation. The length is calculated from both ends of CH₂ carbons.

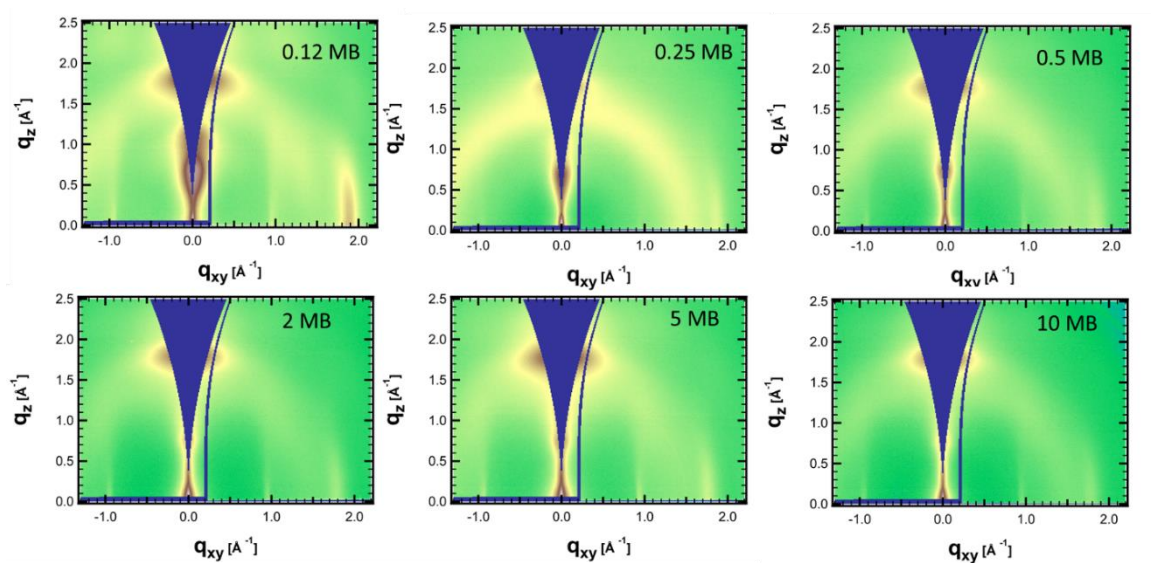


Figure S14. 2-D GIWAXS pattern of Magic Blue dedoped PBDF, with the dedopant concentrations from 0.12 mM to 10 mM.

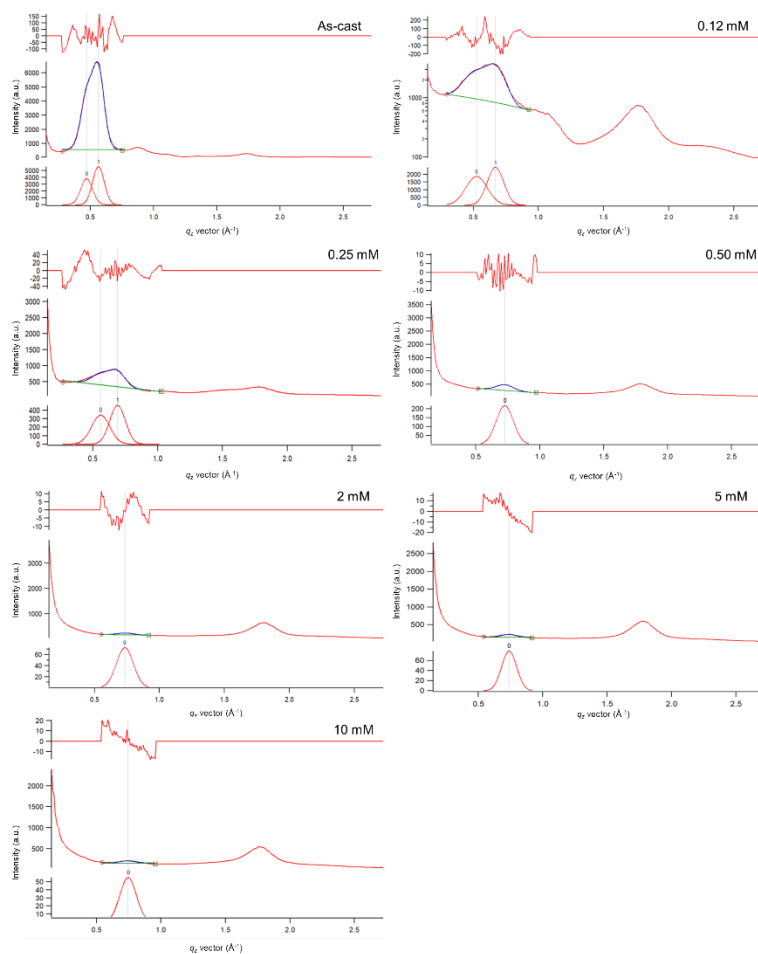


Figure S15. (100) and (100)* peaks fitting results of Magic Blue dedoped PBDF at the dedopant concentrations from 0 mM to 10 mM. Peak fitting is performed by Origin Pro using Gauss peaks fitting.

For as-cast n-PBDF, 0.12 mM and 0.25 mM dedoped PBDF, we can fit (100) and (100)* peaks, represented by peak 0 and peak 1 respectively. At higher Magic Blue concentrations, we can only fit the (100) peak, represented by peak 0.

Table S3. Summary of (100) and (010) peak position, stacking distance and coherence length (CL) and fitted peak area of as-cast n-PBDF, and n-PBDF dedoped by Magic Blue solution with different concentration. The coherence length (CL) is calculated via the Scherrer equation: $CL = 2\pi K / FWHM$, where K is a shape factor (here uses 0.9).

	(100) peak				(010) peak		
	$\text{\AA}^{-1}$	$\text{\AA}$	CL (nm)	Area	$\text{\AA}^{-1}$	$\text{\AA}$	CL (nm)
As-cast	0.56	11.21	5.4	732.15	1.83	3.32	4.8
0.12 mM	0.67	9.39	4.1	390.27	1.90	3.31	3.5
0.25 mM	0.69	9.05	4.1	69.45	1.87	3.36	3.3
0.5 mM	0.73	8.66	3.6	36.91	1.83	3.43	3.1
2 mM	0.73	8.58	3.3	11.88	1.81	3.47	3.2
5 mM	0.74	8.54	3.8	11.52	1.78	3.53	3.2
10 mM	0.75	8.41	3.8	8.83	1.77	3.55	3.3

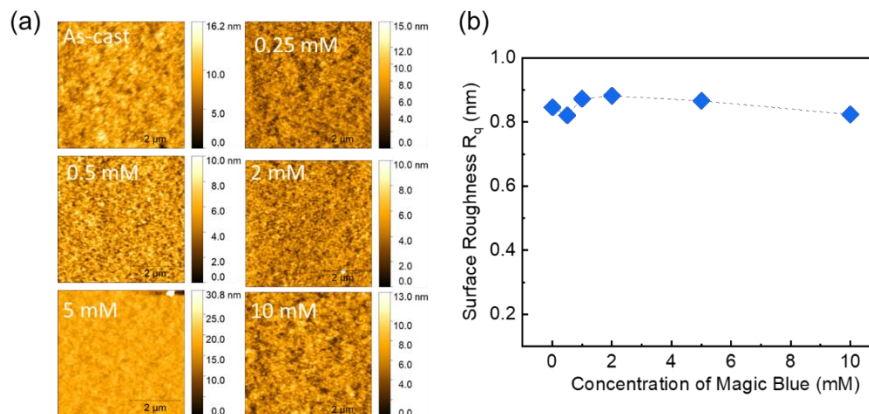


Figure S16. (a) AFM images and (b) root-mean-square roughness (R_q) value of as-cast and Magic Blue dedoped PBDF, with the dedopant solution concentration ranging from 0.25 mM to 10 mM.

Section 4: Reversibly Redope Chemically-dedoped PBDF

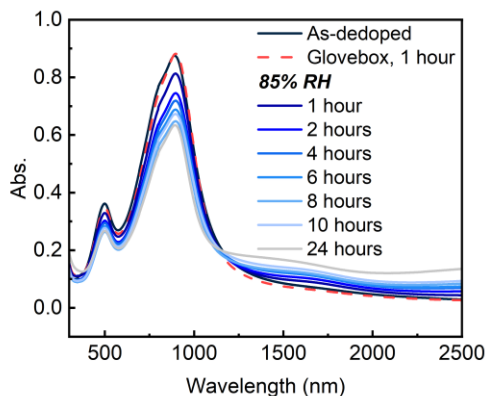


Figure S17. The UV-Vis-NIR absorption of as-dedoped PBDF thin film and PBDF thin films stored in wreathing chamber with 85% RH from 1 hour to 24 hours. The dedoped-PBDF thin film stored in glovebox for one hour was also measured as a comparison sample.

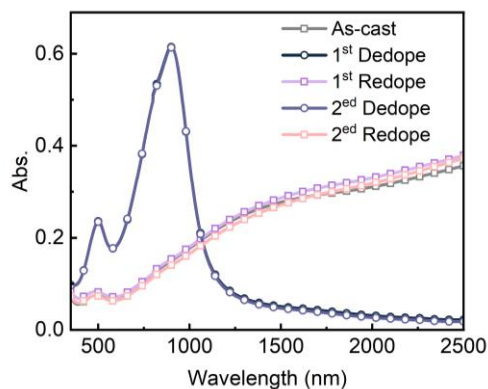


Figure S18. Reversible dedoping and doping of n-PBDF thin film. The UV-Vis-NIR absorption of n-PBDF thin film dedoped by 10 mM Magic Blue solution and redoped by 5 mM TMHQ solution. The dedoping and redoping treatment time was 1 minute.

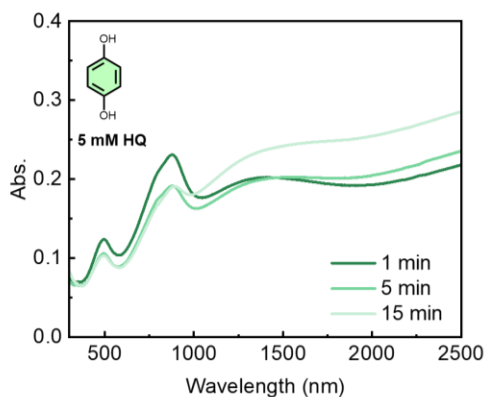


Figure S19. The UV-Vis-NIR absorption of chemically dedoped PBDF thin film treated by 5 mM HQ solution for 1, 5 and 15 minutes.

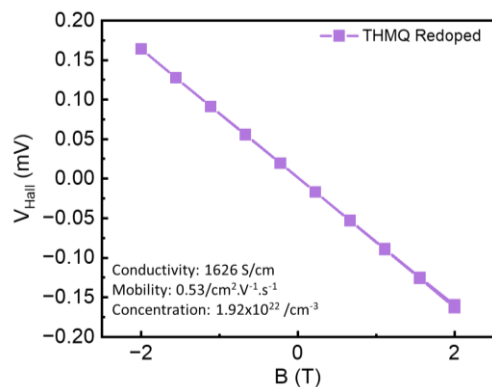


Figure S20. DC-Hall effect measurement of TMHQ-redoped PBDF. Charge carrier concentration (n) and charge carrier mobility (m) are calculated from V_{Hall} vs. B plot.

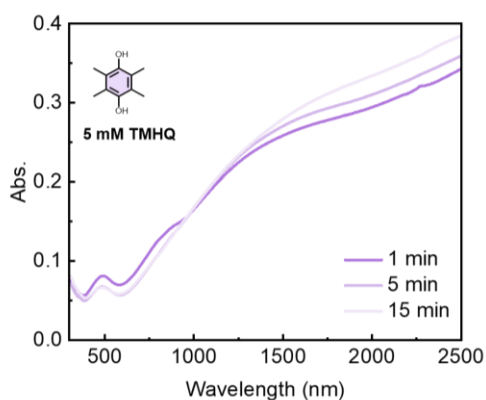


Figure S21. The UV-Vis-NIR absorption of chemically dedoped PBDF thin film redoped by 5 mM TMHQ solution for 1, 5 and 15 minutes.

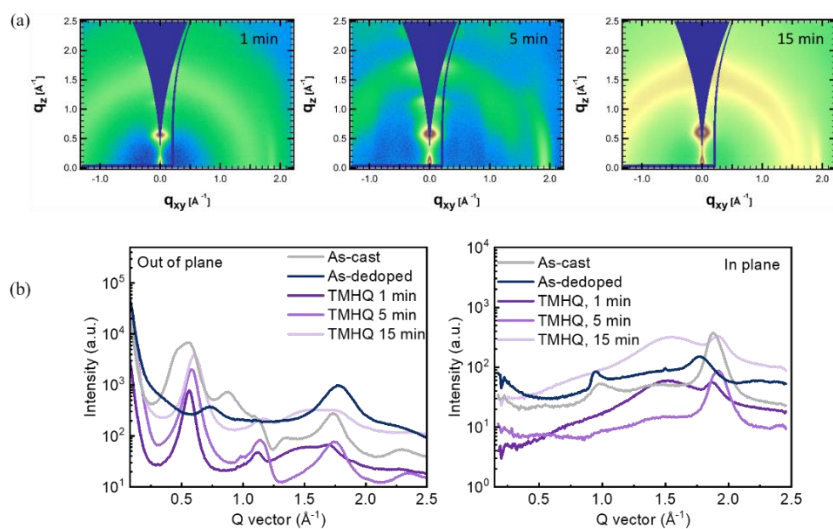


Figure S22. (a) 2-D GIWAXS patterns of TMHQ-redoped PBDF. (b) out-of-plane and in-plane line plots comparison between as-cast n-PBDF, Magic Blue-dedoped PBDF and TMHQ-redoped PBDF. The redoping treatment time ranges from 1 minute, 5 minutes to 15 minutes.

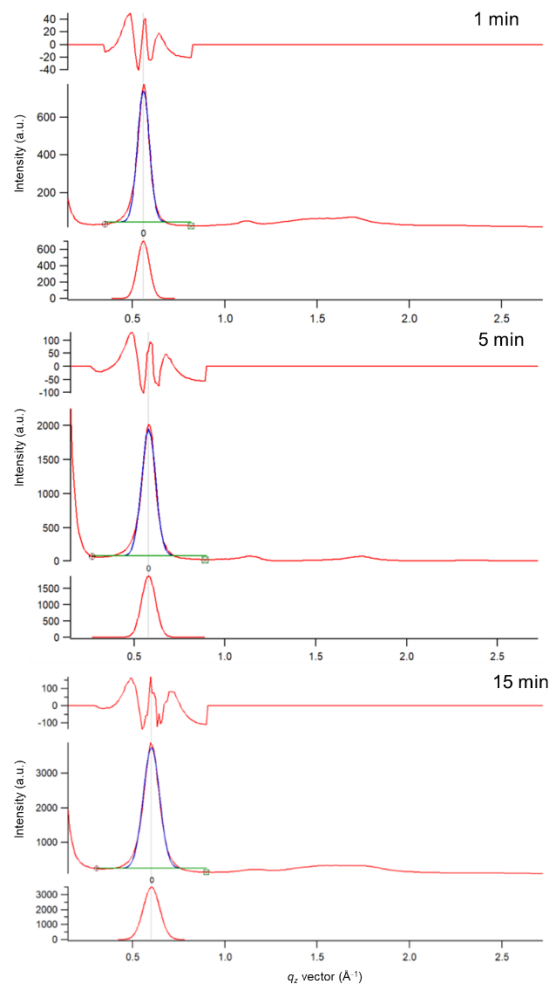


Figure S23. (100) peak fitting results of TMHQ-redoped PBDF at different treatment time. Peak fitting is performed by Origin Pro using Gauss peaks fitting.

Table S4. Summary of (100) and (010) peak position and stacking distance TMHQ-redoped PBDF.

	(100) peak			(010) peak	
	$\text{\AA}^{-1}$	$\text{\AA}$	Area	$\text{\AA}^{-1}$	$\text{\AA}$
1 min	0.56	11.21	57.19	1.86	3.38
5 min	0.58	10.82	180.29	1.92	3.27
15 min	0.60	10.47	388.59	1.92	3.27

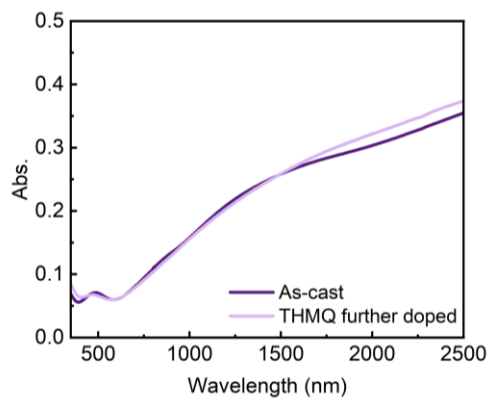


Figure S24. The UV-Vis-NIR absorption comparison between as-cast n-PBDF and n-PBDF further sequentially doped by 5 mM TMHQ solution. The treatment time is 1 min.

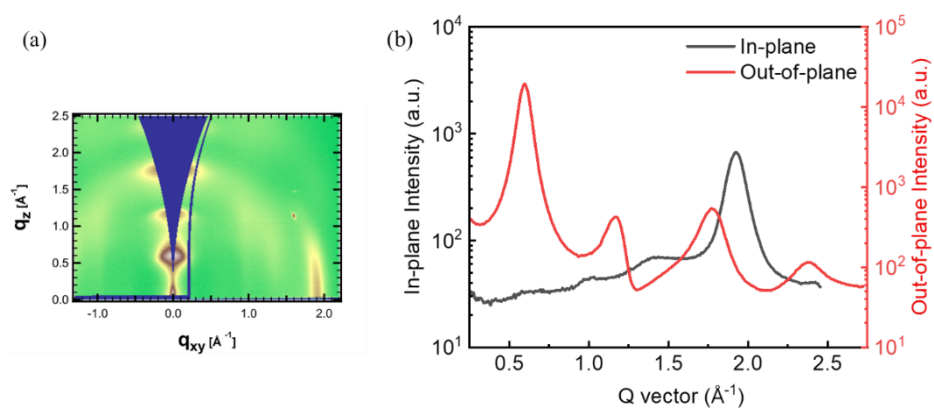


Figure S25. (a) 2-D GIWAXS patterns and (b) out-of-plane and in-plane lines of TMHQ further doped n-PBDF. The treatment time is 1 min.

Section 5: Applications

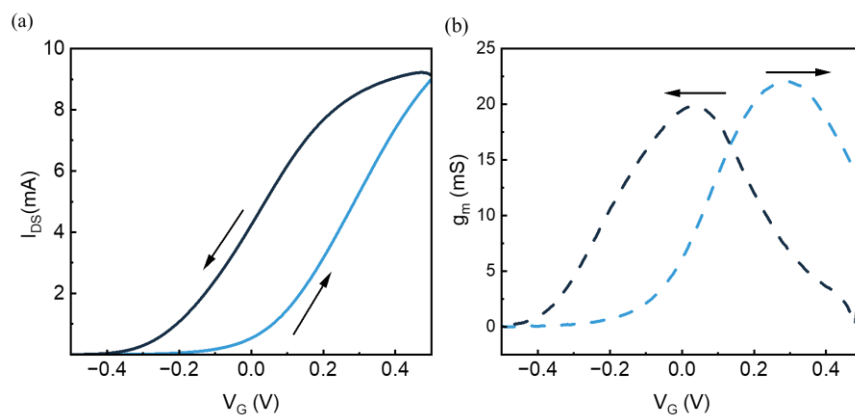


Figure S26. (a) Transfer curve characteristic and (b) transconductance for Magic Blue-dedoped PBDF measured from -0.5 V to 0.5 V (light blue) and from 0.5 V to -0.5 V (dark blue).