

Supporting Information

Synthesis, Morphology, and Electrical Memory Application of Oligosaccharide-based Block Copolymers with π -Conjugated Pyrene Moiety and Their Supramolecules

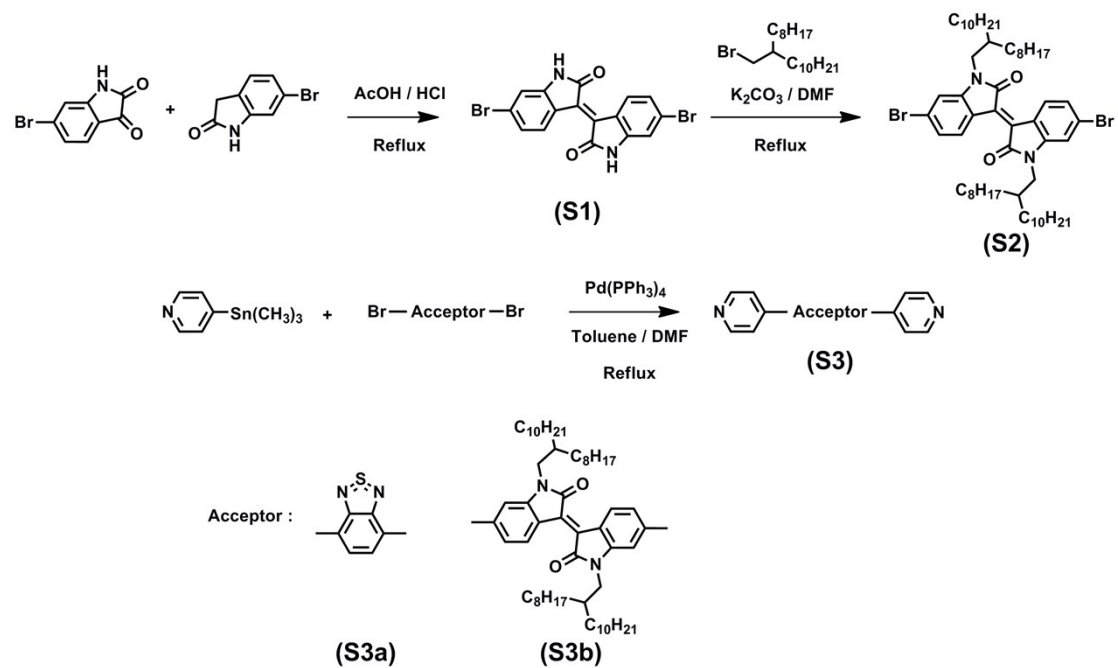
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Scheme S1. The synthetic route for 4Py-Acceptor-4Py.

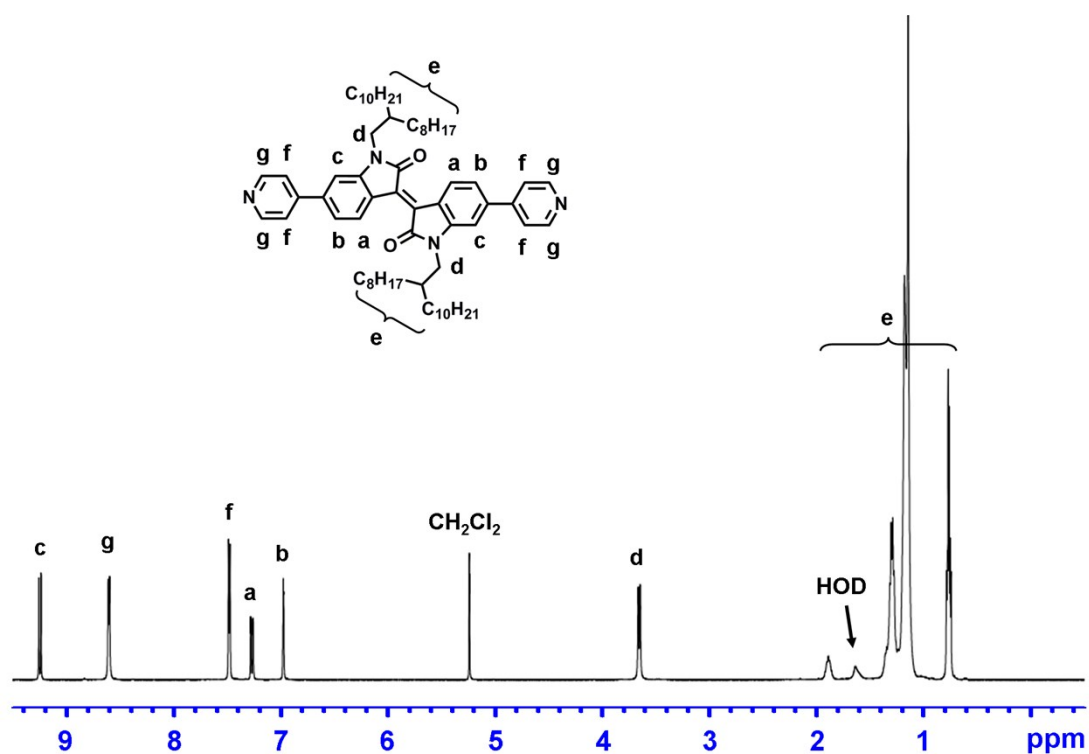


Fig. S1 ¹H NMR spectrum of 6,6'-di(4-pyridyl)-*N,N'*-bis(2-octyldodecyl)-isoindigo in CD₂Cl₂.

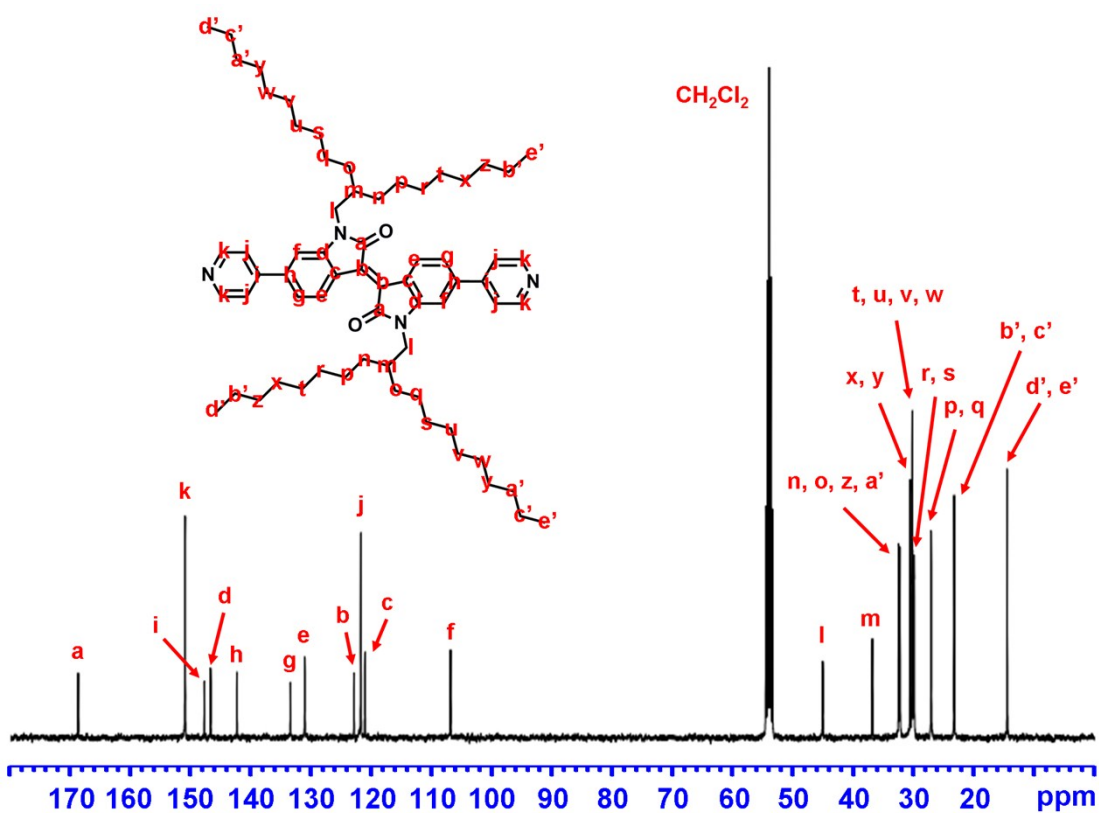


Fig. S2 ¹³C NMR spectrum of 6,6'-di(4-pyridyl)-*N,N'*-bis(2-octyldodecyl)-isoindigo in CD₂Cl₂.

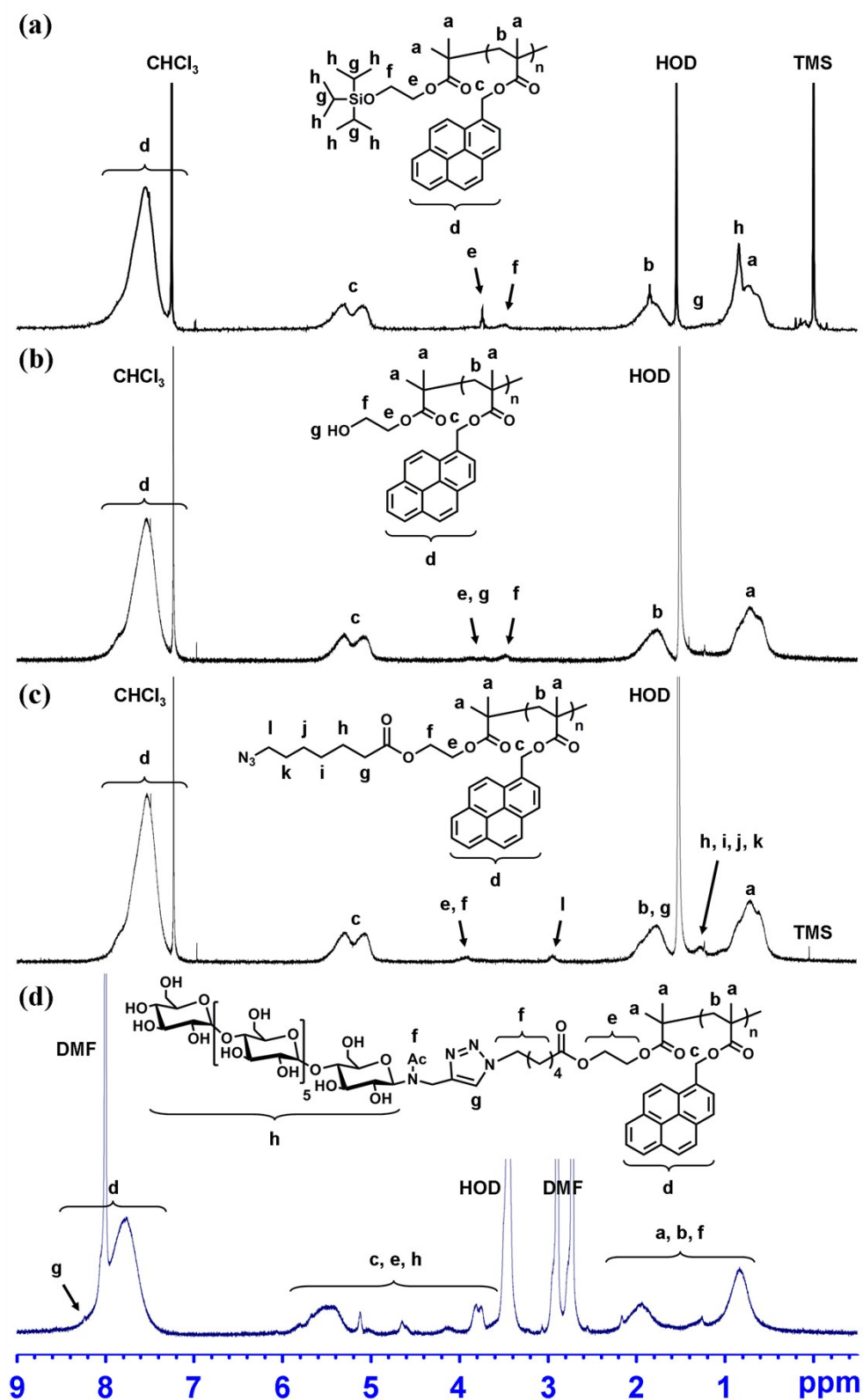


Fig. S3 ^1H NMR spectra of (a) PPyMA₂₀-OSi/Pr₃ in CDCl_3 , (b) PPyMA₂₀-OH in CDCl_3 , (c) PPyMA₂₀-N₃ in CDCl_3 , and (d) MH-*b*-PPyMA₂₀ diblock copolymer in DMF-d_7 .

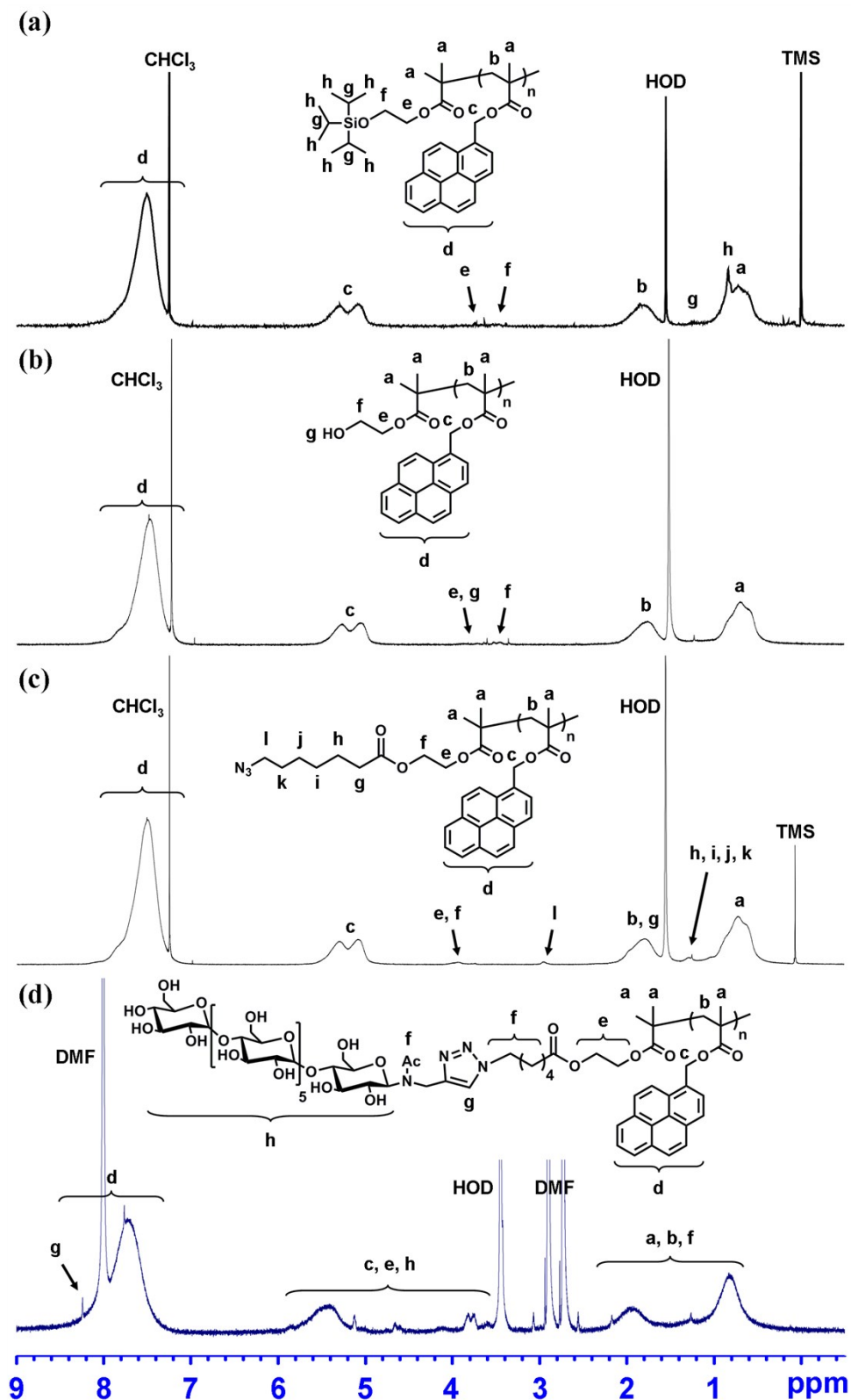


Fig. S4 ^1H NMR spectra of (a) PPyMA₄₀-OSi/Pr₃ in CDCl_3 , (b) PPyMA₄₀-OH in CDCl_3 , (c) PPyMA₄₀-N₃ in CDCl_3 , and (d) MH-b-PPyMA₄₀ diblock copolymer in DMF-d_7 .

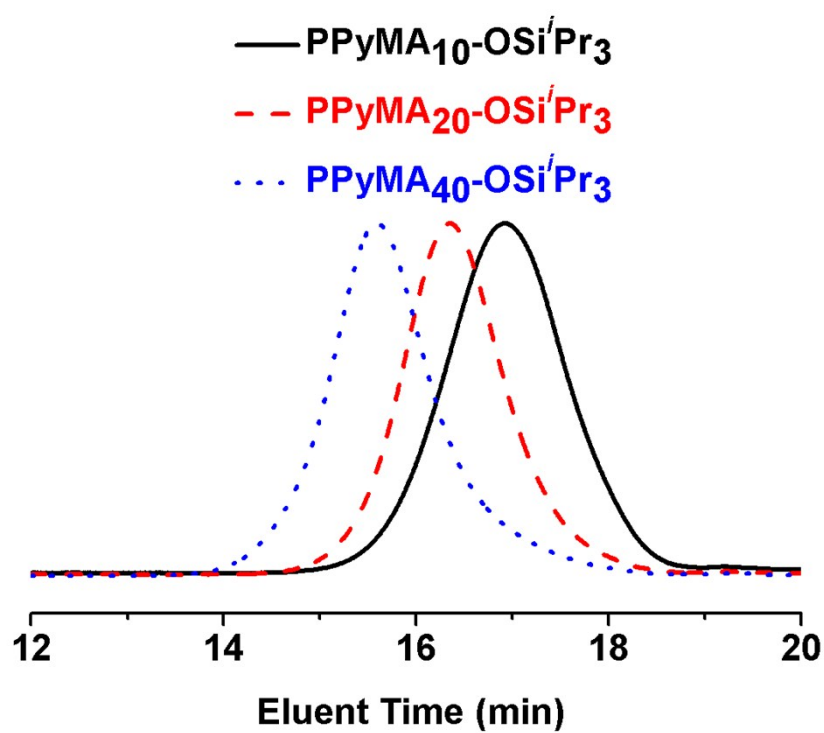
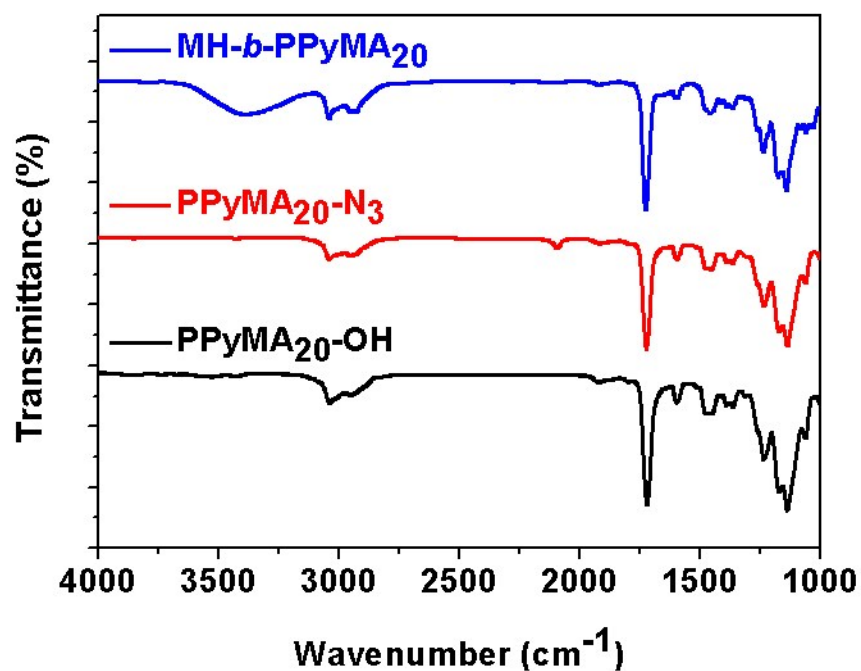


Fig. S5 GPC traces of the triisopropylsilyloxy-terminated PPyMA_n (PPyMA_n-OSiⁱPr₃, n = 10, 20 and 40) homopolymers.

(a)



(b)

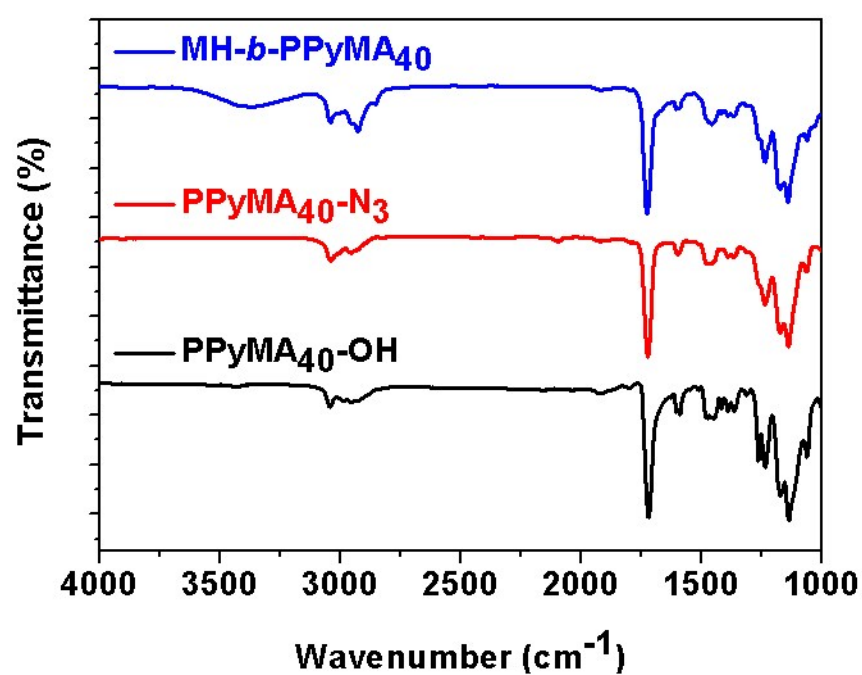


Fig. S6 FTIR spectra of (a) the hydroxyl- and azido-terminated PPyMA₂₀ homopolymers and MH-*b*-PPyMA₂₀ diblock copolymer, and (b) the hydroxyl- and azido-terminated PPyMA₄₀ homopolymers and MH-*b*-PPyMA₄₀ diblock copolymer.

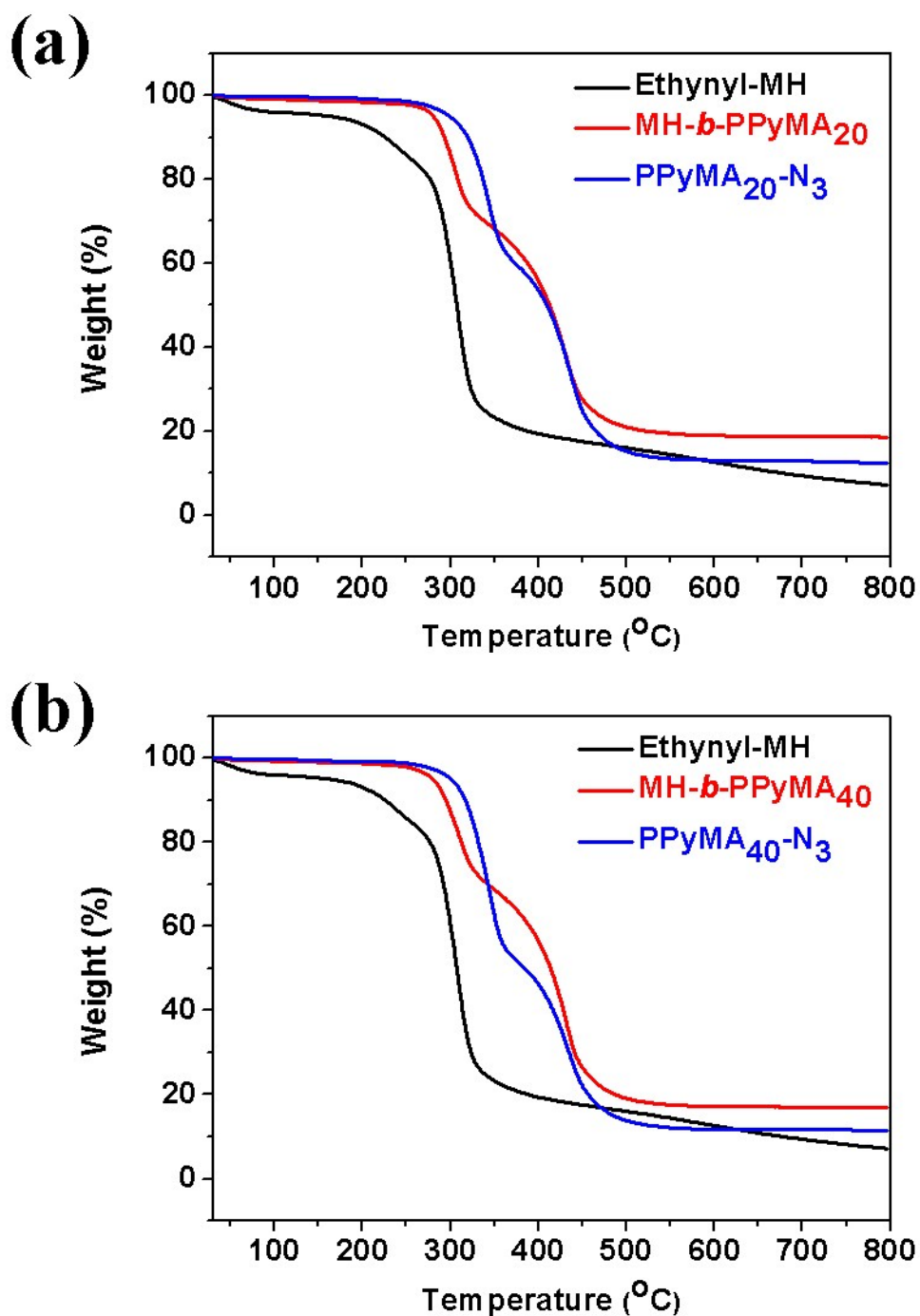


Fig. S7 TGA diagrams of (a) the ethynyl end-functionalized MH, azido-terminated PPyMA₂₀ homopolymer, and MH-*b*-PPyMA₂₀ block copolymer, and (b) the ethynyl end-functionalized MH, azido-terminated PPyMA₄₀ homopolymer, and MH-*b*-PPyMA₄₀ block copolymer.

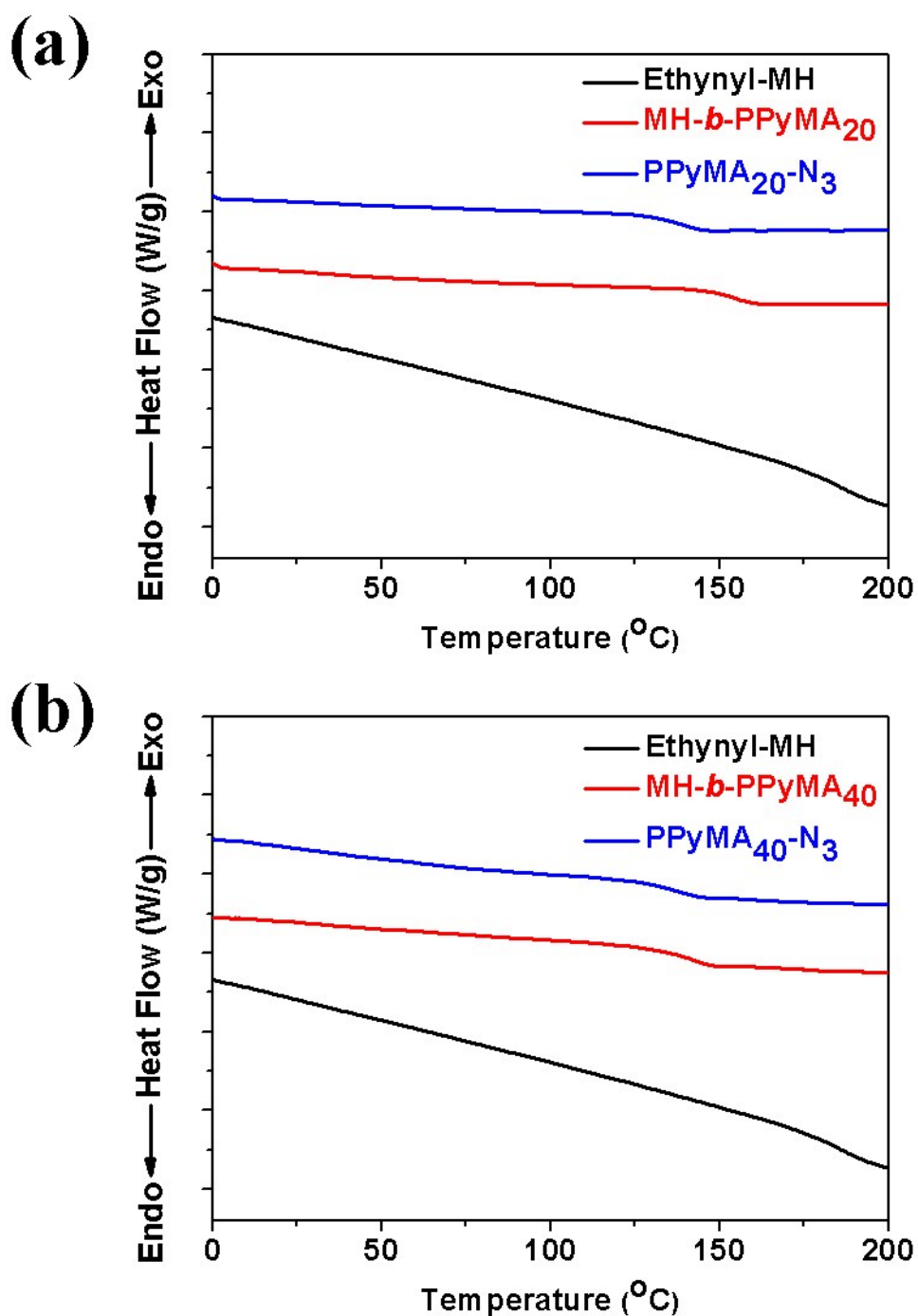


Fig. S8 DSC curves of (a) ethynyl end-functionalized MH, azido-terminated PPyMA₂₀ homopolymer, and MH-*b*-PPyMA₂₀ block copolymer, and (b) the ethynyl end-functionalized MH, azido-terminated PPyMA₄₀ homopolymer, and MH-*b*-PPyMA₄₀ block copolymer.

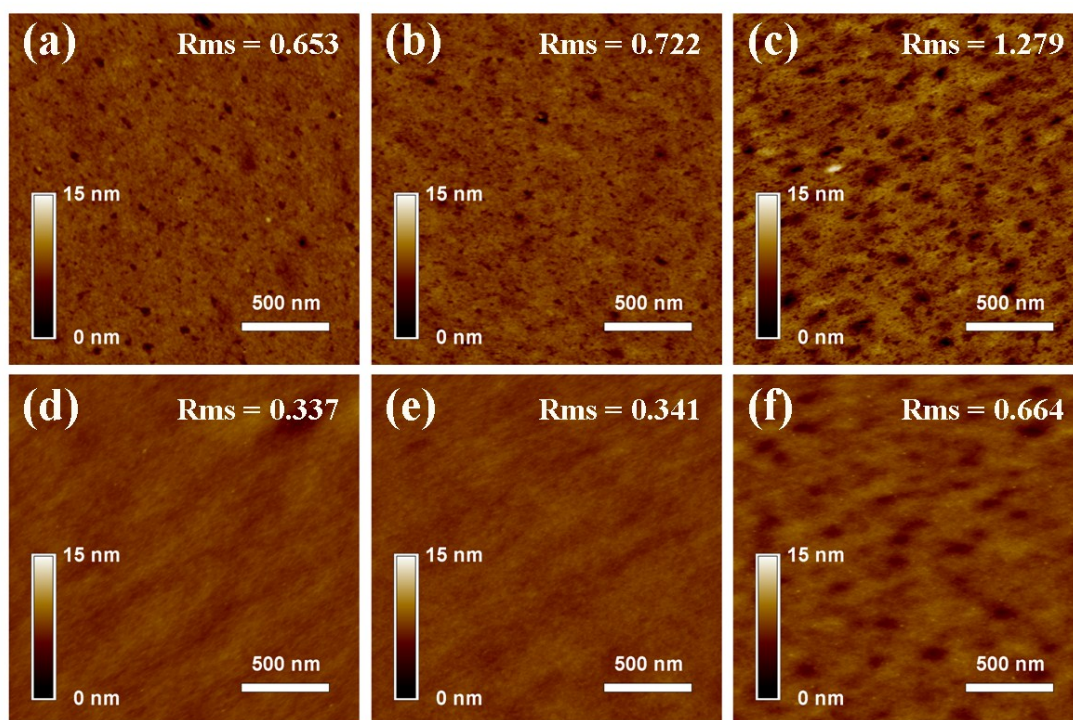


Fig. S9 AFM images of the surfaces of the MH-*b*-PPyMA_n thin films: (a) as-cast MH-*b*-PPyMA₁₀ thin film, (b) as-cast MH-*b*-PPyMA₂₀ thin film, (c) as-cast MH-*b*-PPyMA₄₀ thin film, (d) thermo-annealed MH-*b*-PPyMA₁₀ thin film, (e) MH-*b*-PPyMA₂₀ thin film, and (f) MH-*b*-PPyMA₄₀ thin film.

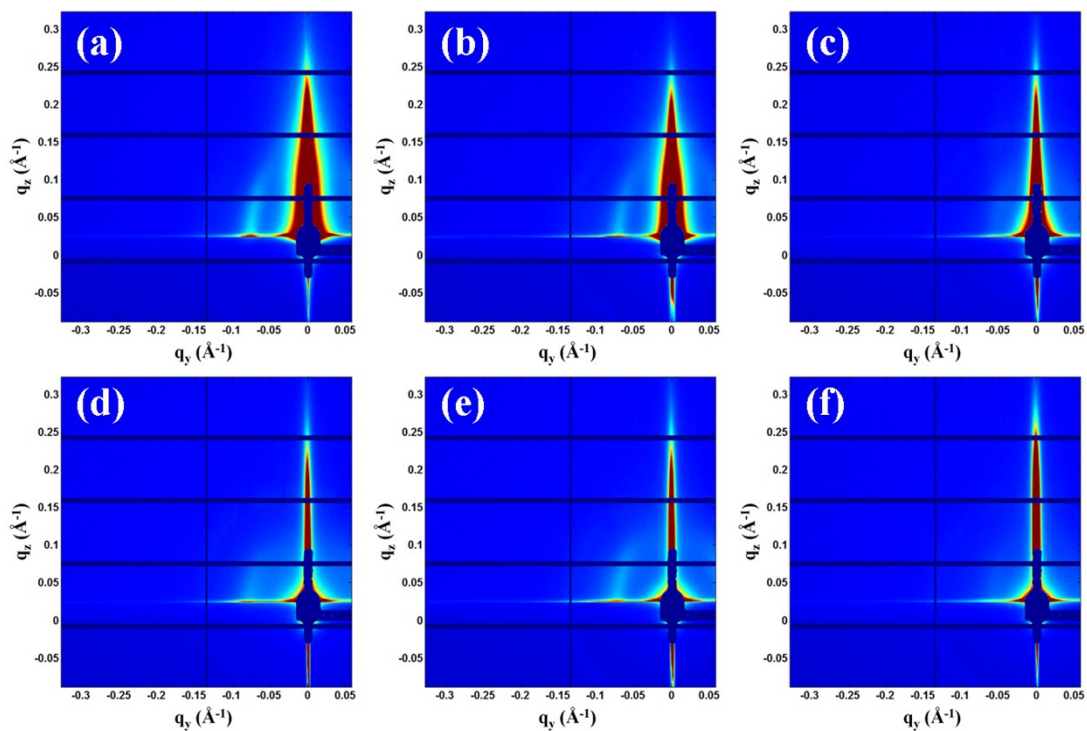


Fig. S10 2-D GISAXS patterns of the MH-*b*-PPyMA_n thin films: (a) as-cast MH-*b*-PPyMA₁₀ thin film, (b) as-cast MH-*b*-PPyMA₂₀ thin film, (c) as-cast MH-*b*-PPyMA₄₀ thin film, (d) thermo-annealed MH-*b*-PPyMA₁₀ thin film, (e) MH-*b*-PPyMA₂₀ thin film, and (f) MH-*b*-PPyMA₄₀ thin film.

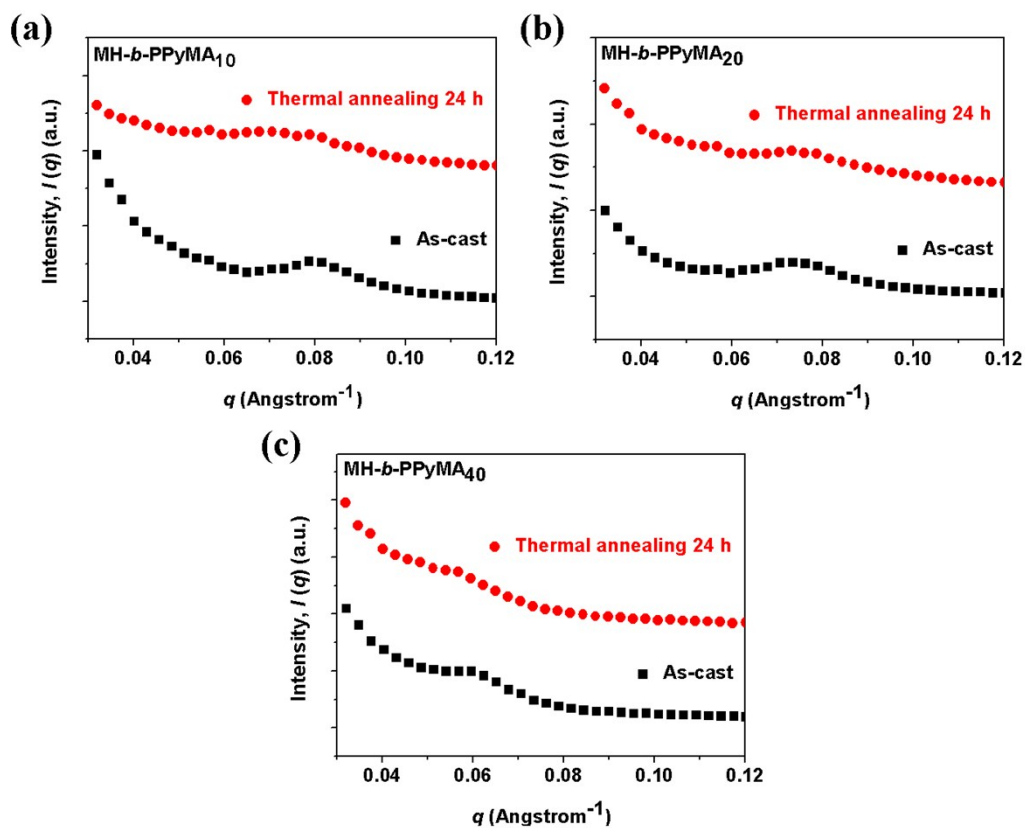


Fig. S11 1-D GISAXS q_y scanning plots of as-cast and thermo-annealed MH-*b*-PPyMA_n thin films: (a) MH-*b*-PPyMA₁₀, (b) MH-*b*-PPyMA₂₀ and (c) MH-*b*-PPyMA₄₀.

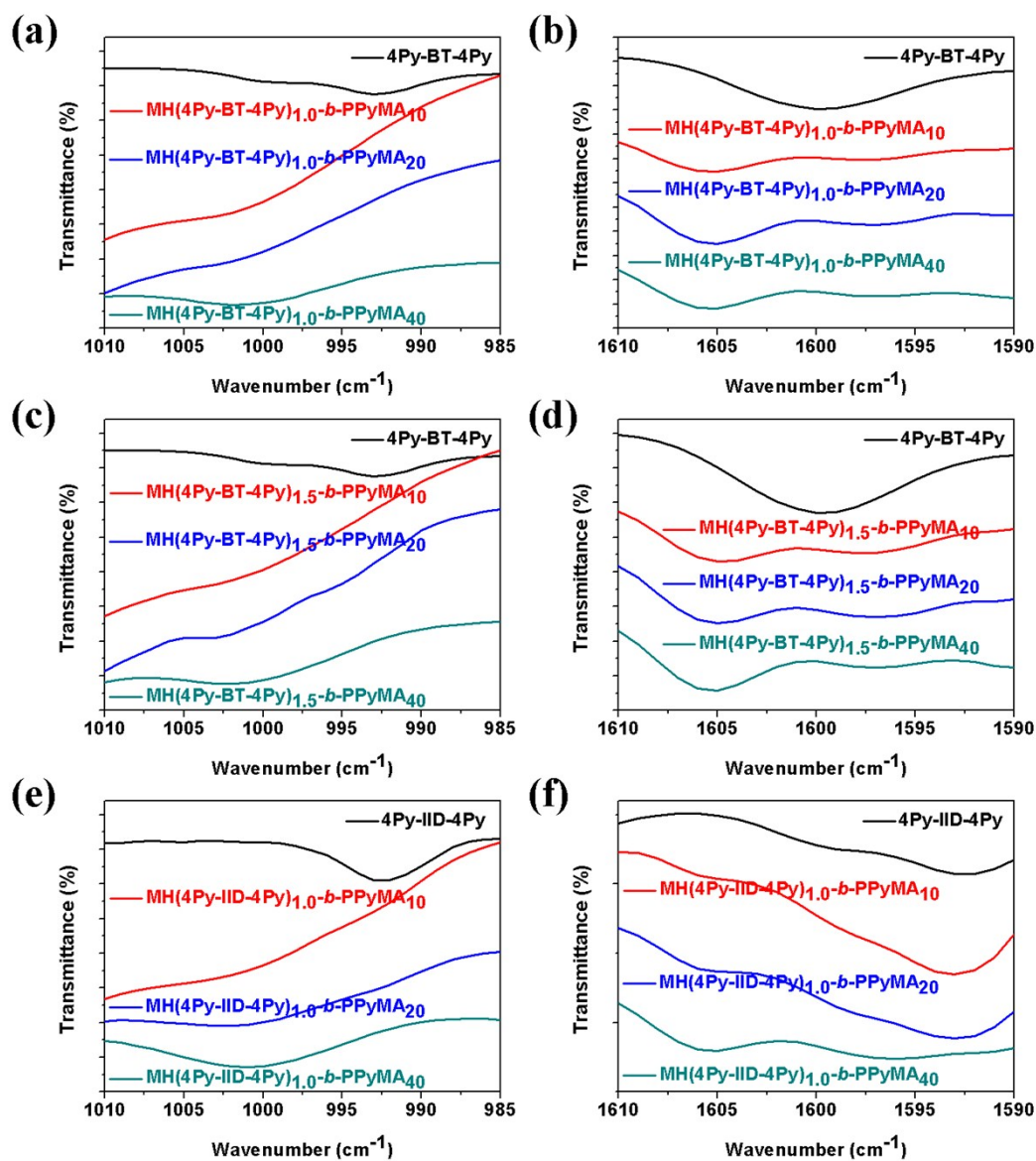


Fig. S12 FTIR spectra of $\text{MH}(4\text{Py-Acceptor-4Py})_x\text{-}b\text{-PPyMA}_n$ supramolecular thin films: (a) and (b), $\text{MH}(4\text{Py-BT-4Py})_{1.0}\text{-}b\text{-PPyMA}_n$; (c) and (d), $\text{MH}(4\text{Py-BT-4Py})_{1.5}\text{-}b\text{-PPyMA}_n$; (e) and (f), $\text{MH}(4\text{Py-IID-4Py})_{1.0}\text{-}b\text{-PPyMA}_n$.

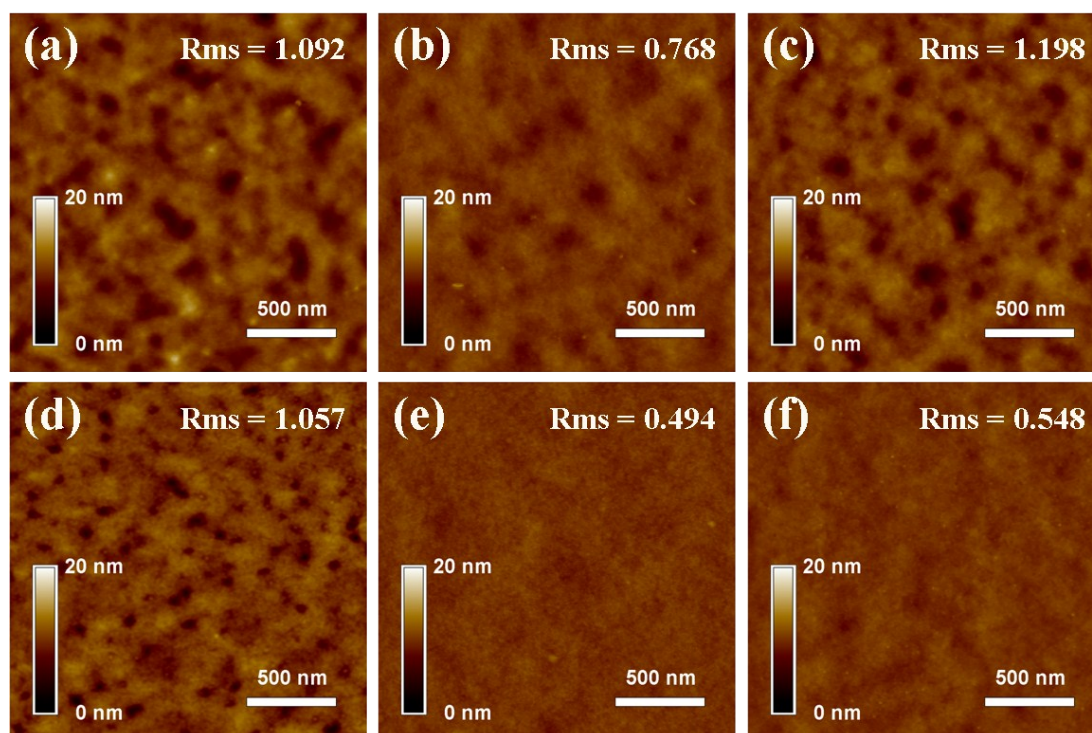


Fig. S13 AFM images of the surfaces of the thermo-annealed MH(4Py-Acceptor-4Py)_x-*b*-PPyMA_n thin films (electret layers): (a) MH(4Py-BT-4Py)_{1.5}-*b*-PPyMA₁₀, (b) MH(4Py-BT-4Py)_{1.5}-*b*-PPyMA₂₀, (c) MH(4Py-BT-4Py)_{1.5}-*b*-PPyMA₄₀, (d) MH(4Py-IID-4Py)_{1.0}-*b*-PPyMA₁₀, (e) MH(4Py-IID-4Py)_{1.0}-*b*-PPyMA₂₀, and (f) MH(4Py-IID-4Py)_{1.0}-*b*-PPyMA₄₀.

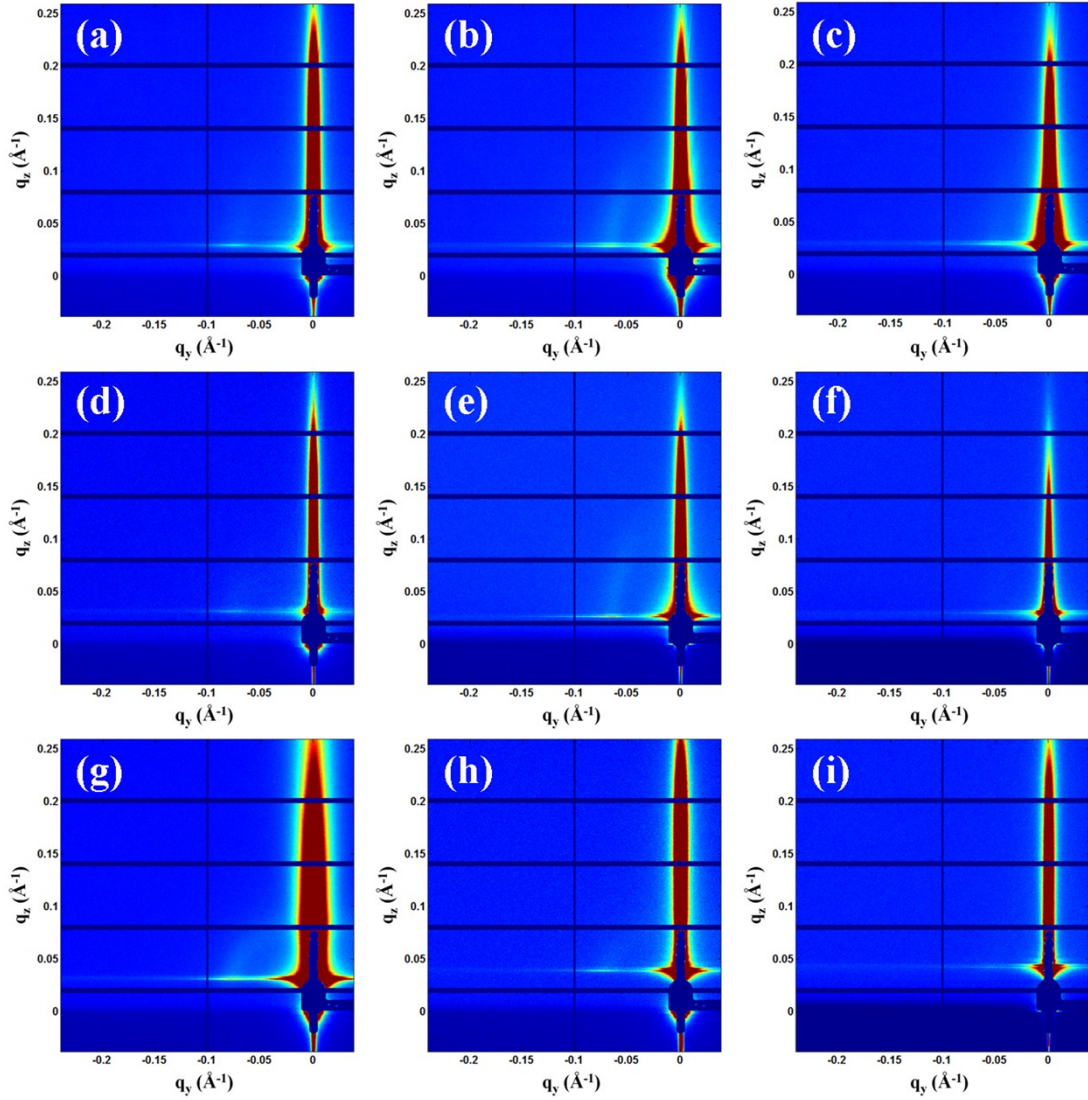


Fig. S14 2-D GISAXS patterns of the thermo-annealed $\text{MH}(4\text{Py-Acceptor-4Py})_x\text{-}b\text{-PPyMA}_n$ thin films: (a) $\text{MH}(4\text{Py-BT-4Py})_{1.0}\text{-}b\text{-PPyMA}_{10}$, (b) $\text{MH}(4\text{Py-BT-4Py})_{1.0}\text{-}b\text{-PPyMA}_{20}$, (c) $\text{MH}(4\text{Py-BT-4Py})_{1.0}\text{-}b\text{-PPyMA}_{40}$, (d) $\text{MH}(4\text{Py-BT-4Py})_{1.5}\text{-}b\text{-PPyMA}_{10}$, (e) $\text{MH}(4\text{Py-BT-4Py})_{1.5}\text{-}b\text{-PPyMA}_{20}$, (f) $\text{MH}(4\text{Py-BT-4Py})_{1.5}\text{-}b\text{-PPyMA}_{40}$, (g) $\text{MH}(4\text{Py-IID-4Py})_{1.0}\text{-}b\text{-PPyMA}_{10}$, (h) $\text{MH}(4\text{Py-IID-4Py})_{1.0}\text{-}b\text{-PPyMA}_{20}$, and (i) $\text{MH}(4\text{Py-IID-4Py})_{1.0}\text{-}b\text{-PPyMA}_{40}$.

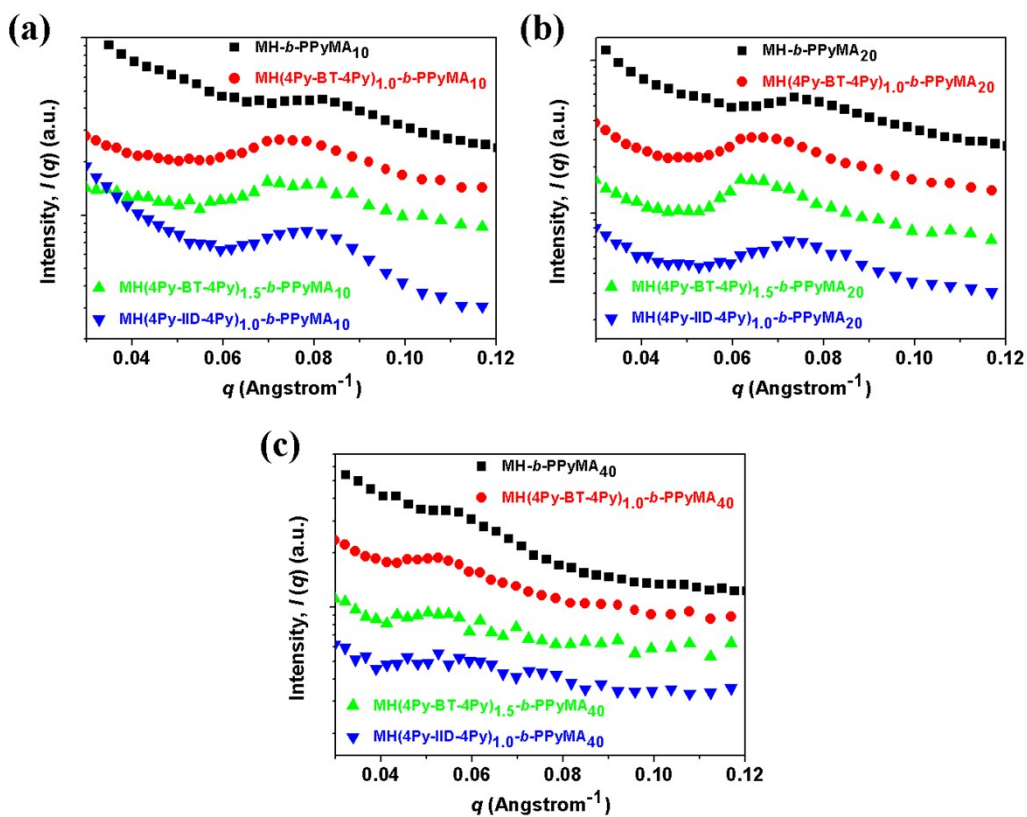


Fig. S15 1-D GISAXS q_y scanning plots of $\text{MH}(4\text{Py-Acceptor-4Py})_x\text{-}b\text{-PPyMA}_n$ thin films: (a) $\text{MH}(4\text{Py-Acceptor-4Py})_x\text{-}b\text{-PPyMA}_{10}$, (b) $\text{MH}(4\text{Py-Acceptor-4Py})_x\text{-}b\text{-PPyMA}_{20}$, and (c) $\text{MH}(4\text{Py-Acceptor-4Py})_x\text{-}b\text{-PPyMA}_{40}$.

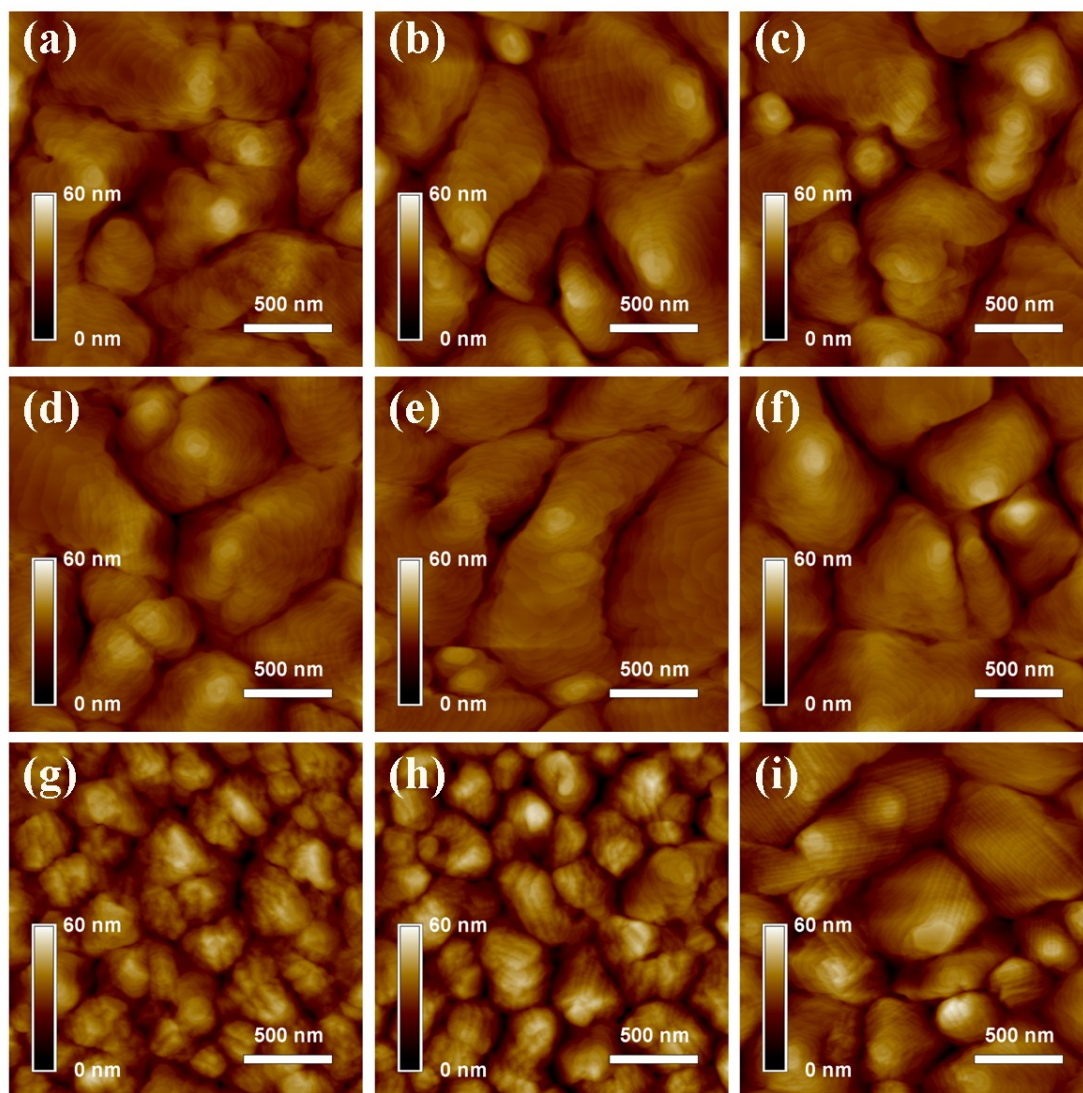


Fig. S16 AFM images of the surfaces of the pentacene layers grown from thermo-annealed $\text{MH}(4\text{Py-Acceptor-4Py})_x\text{-}b\text{-PPyMA}_n$ thin films (electret layers): (a) $\text{MH}(4\text{Py-BT-4Py})_{1.0}\text{-}b\text{-PPyMA}_{10}$, (b) $\text{MH}(4\text{Py-BT-4Py})_{1.0}\text{-}b\text{-PPyMA}_{20}$, (c) $\text{MH}(4\text{Py-BT-4Py})_{1.0}\text{-}b\text{-PPyMA}_{40}$, (d) $\text{MH}(4\text{Py-BT-4Py})_{1.5}\text{-}b\text{-PPyMA}_{10}$, (e) $\text{MH}(4\text{Py-BT-4Py})_{1.5}\text{-}b\text{-PPyMA}_{20}$, (f) $\text{MH}(4\text{Py-BT-4Py})_{1.5}\text{-}b\text{-PPyMA}_{40}$, (g) $\text{MH}(4\text{Py-IID-4Py})_{1.0}\text{-}b\text{-PPyMA}_{10}$, (h) $\text{MH}(4\text{Py-IID-4Py})_{1.0}\text{-}b\text{-PPyMA}_{20}$, and (i) $\text{MH}(4\text{Py-IID-4Py})_{1.0}\text{-}b\text{-PPyMA}_{40}$.

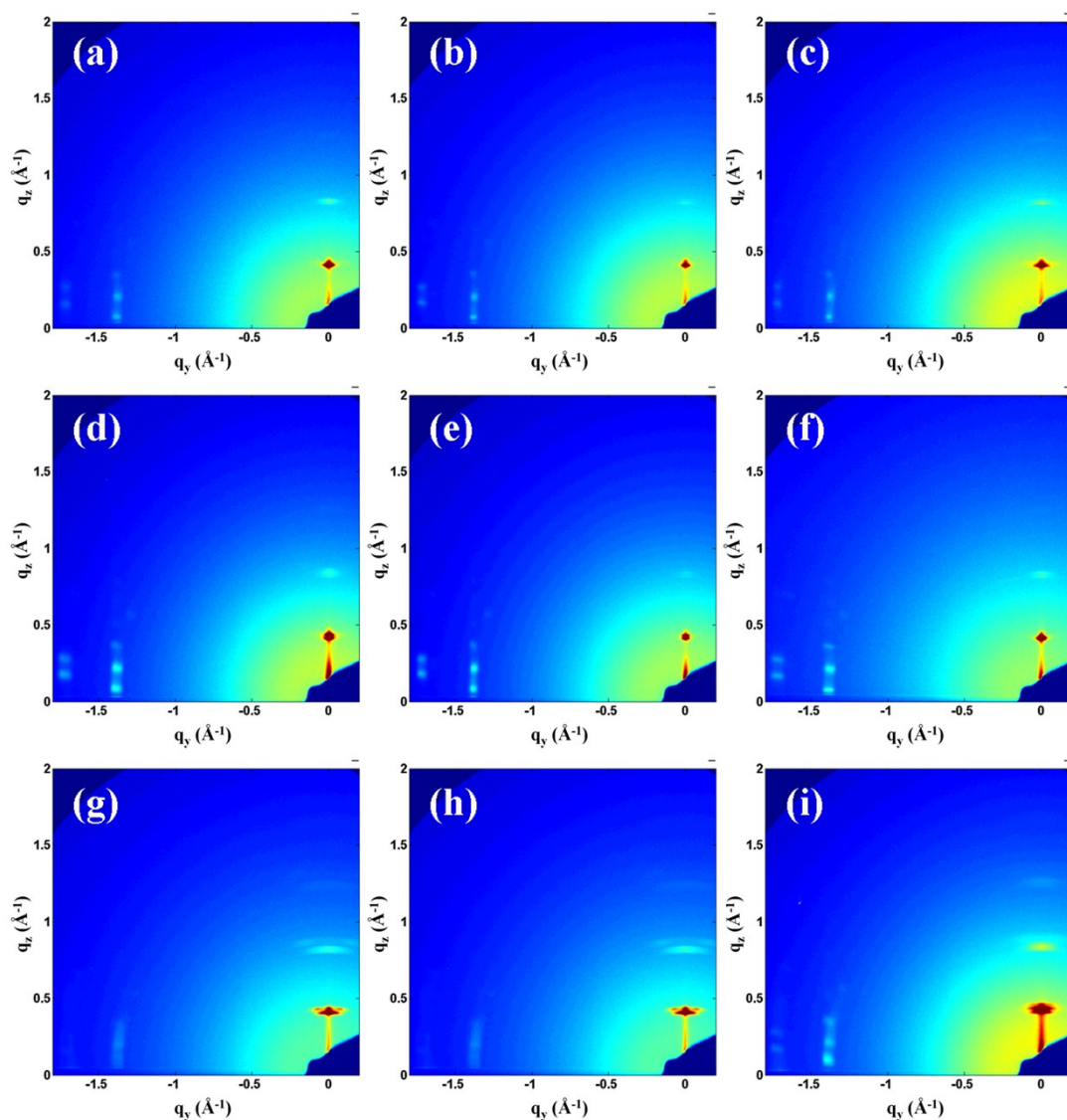


Fig. S17 2-D GIWAXS patterns of the pentacene layers grown from thermo-annealed MH(4Py-Acceptor-4Py)_x-*b*-PPyMA_n thin films (electret layers) : (a) MH(4Py-BT-4Py)_{1.0}-*b*-PPyMA₁₀, (b) MH(4Py-BT-4Py)_{1.0}-*b*-PPyMA₂₀, (c) MH(4Py-BT-4Py)_{1.0}-*b*-PPyMA₄₀, (d) MH(4Py-BT-4Py)_{1.5}-*b*-PPyMA₁₀, (e) MH(4Py-BT-4Py)_{1.5}-*b*-PPyMA₂₀, (f) MH(4Py-BT-4Py)_{1.5}-*b*-PPyMA₄₀, (g) MH(4Py-IID-4Py)_{1.0}-*b*-PPyMA₁₀, (h) MH(4Py-IID-4Py)_{1.0}-*b*-PPyMA₂₀, and (i) MH(4Py-IID-4Py)_{1.0}-*b*-PPyMA₄₀.

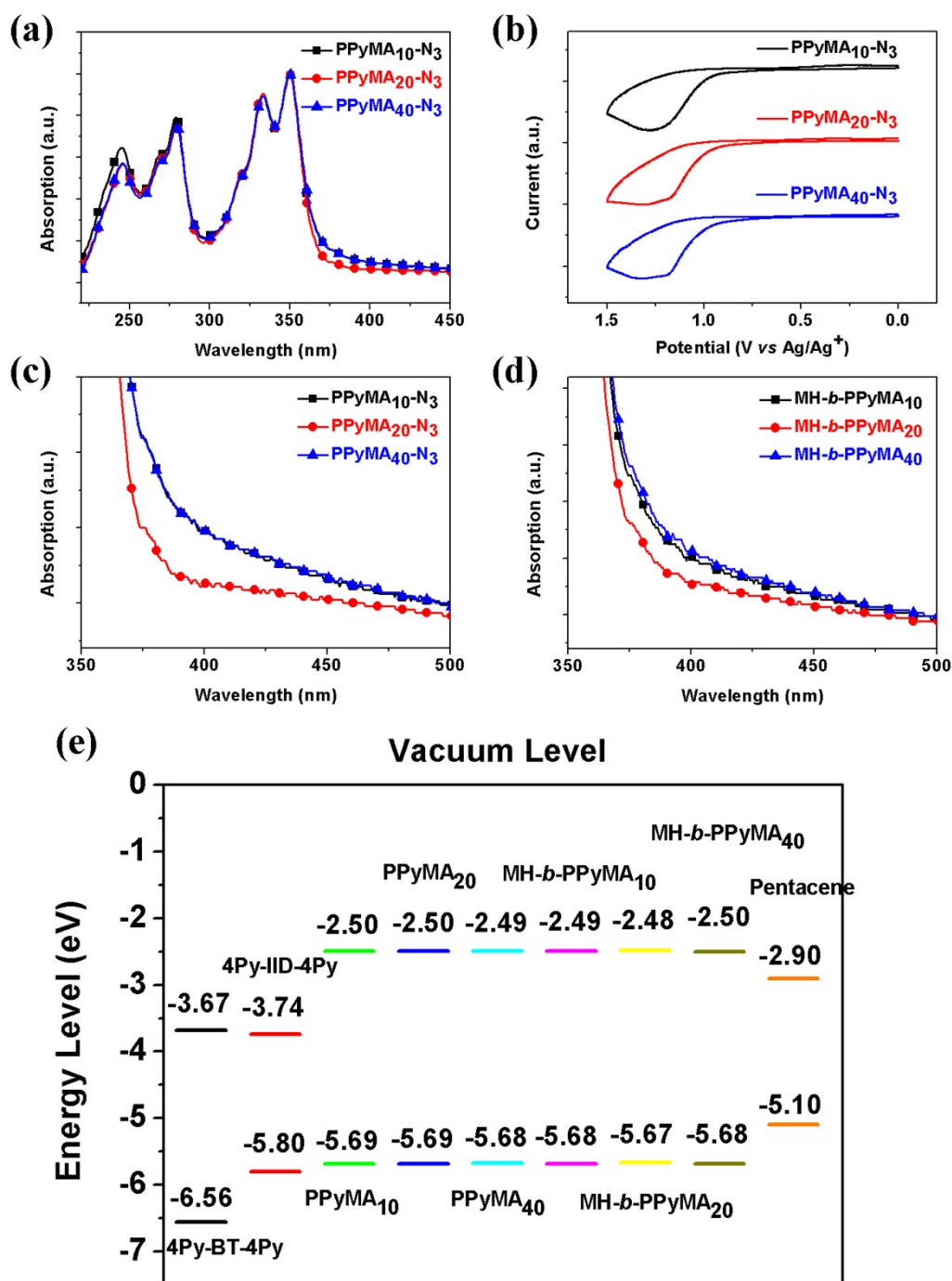


Fig. S18 (a) UV-Vis spectra of PPyMA_n-N₃ homopolymers in the region of 220 ~ 450 nm, (b) cyclic voltammograms of PPyMA_n-N₃ homopolymers, (c) UV-Vis spectra of PPyMA_n-N₃ homopolymers in the region of 350 ~ 500 nm, (d) UV-Vis spectra of MH-*b*-PPyMA_n block copolymers in the region of 350 ~ 500 nm, and (e) energy levels of 4Py-Acceptor-4Py, PPyMA_n-N₃ homopolymers, MH-*b*-PPyMA_n block copolymers, and pentacene.

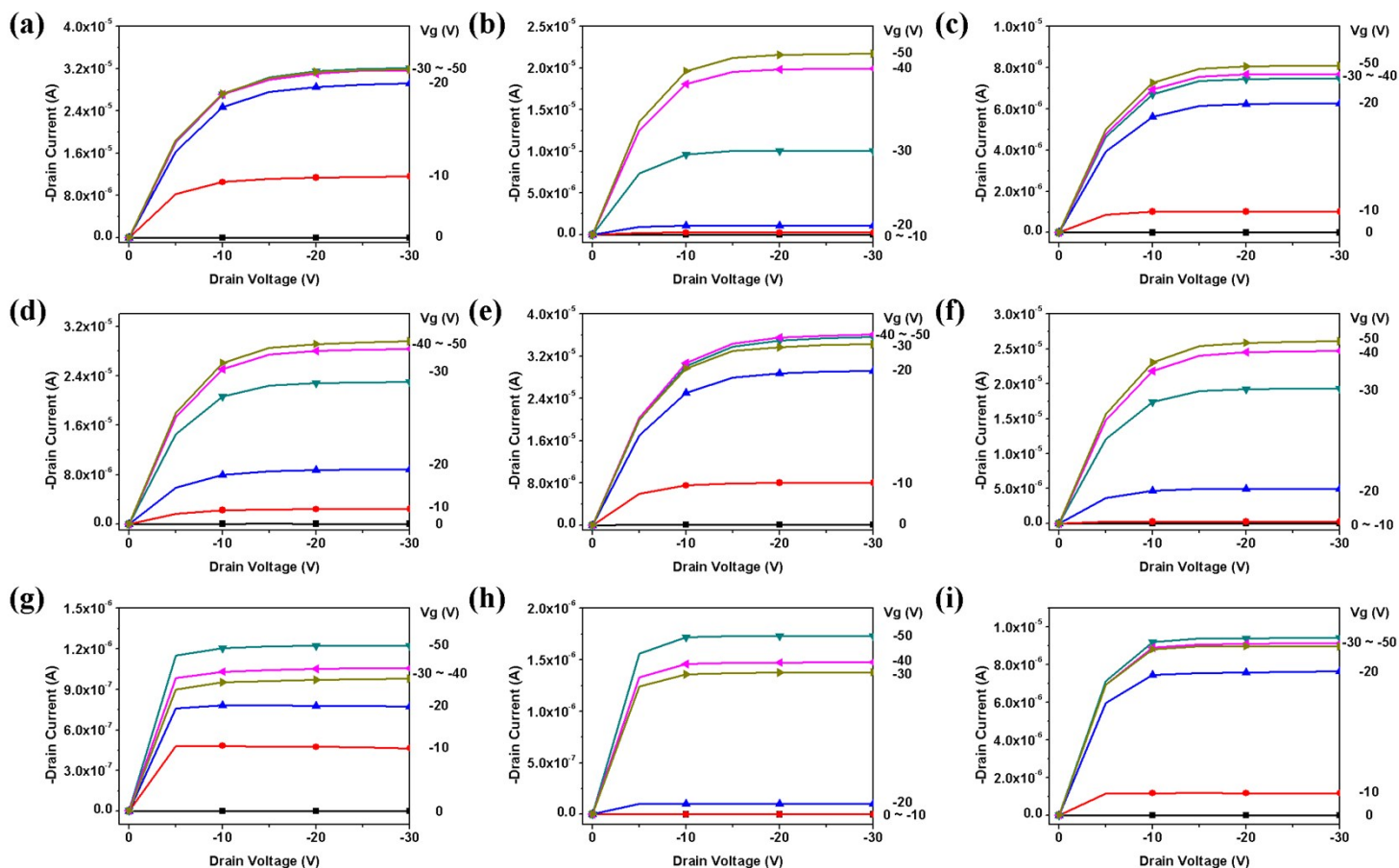


Fig. S19 The electric output curves of the devices using thermo-annealed MH(4Py-Acceptor-4Py)_x-*b*-PPyMA_n thin films as electret layers: (a) MH(4Py-BT-4Py)_{1.0}-*b*-PPyMA₁₀, (b) MH(4Py-BT-4Py)_{1.0}-*b*-PPyMA₂₀, (c) MH(4Py-BT-4Py)_{1.0}-*b*-PPyMA₄₀, (d) MH(4Py-BT-4Py)_{1.5}-*b*-PPyMA₁₀, (e) MH(4Py-BT-4Py)_{1.5}-*b*-PPyMA₂₀, (f) MH(4Py-BT-4Py)_{1.5}-*b*-PPyMA₄₀, (g) MH(4Py-IID-4Py)_{1.0}-*b*-PPyMA₁₀, (h) MH(4Py-IID-4Py)_{1.0}-*b*-PPyMA₂₀, and (i) MH(4Py-IID-4Py)_{1.0}-*b*-PPyMA₄₀.

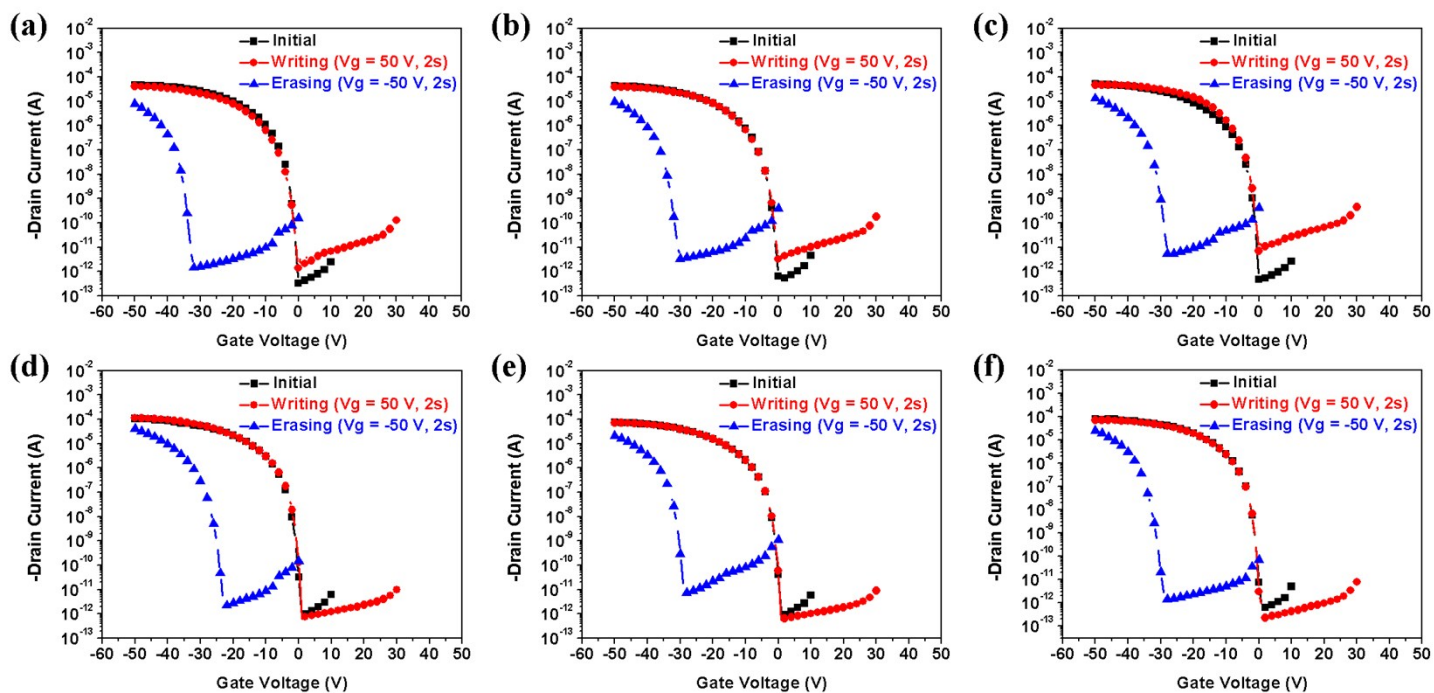


Fig. S20 The transfer curves of the devices using thermo-annealed PPyMA_n-N₃ and MH-*b*-PPyMA_n thin films as electret layers: (a) PPyMA₁₀-N₃, (b) PPyMA₂₀-N₃, (c) PPyMA₄₀-N₃, (d) MH-*b*-PPyMA₁₀, (e) MH-*b*-PPyMA₂₀, and (f) MH-*b*-PPyMA₄₀.

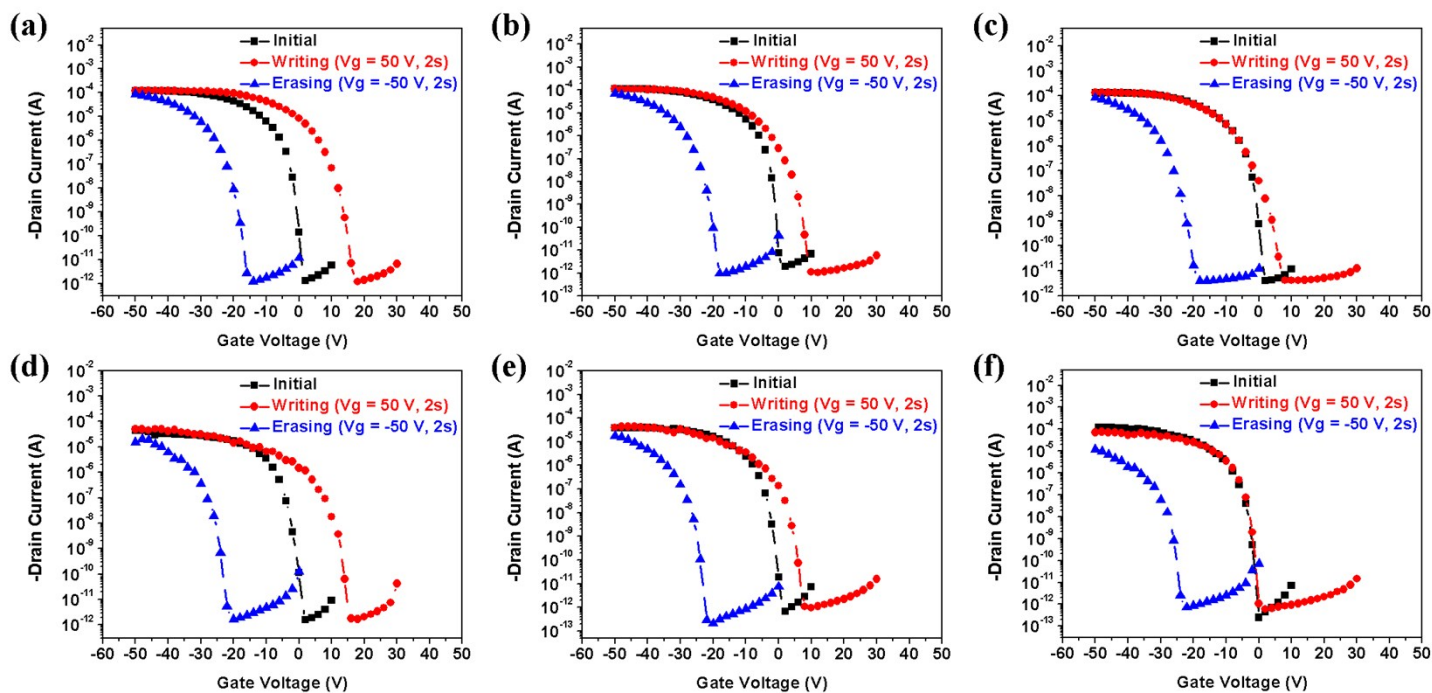


Fig. S21 The transfer curves of the devices using thermo-annealed MH(4Py-Acceptor-4Py)_x-*b*-PPyMA_n thin films as electret layers: (a) MH(4Py-BT-4Py)_{1.0}-*b*-PPyMA₁₀, (b) MH(4Py-BT-4Py)_{1.0}-*b*-PPyMA₂₀, (c) MH(4Py-BT-4Py)_{1.0}-*b*-PPyMA₄₀, (d) MH(4Py-IID-4Py)_{1.0}-*b*-PPyMA₁₀, (e) MH(4Py-IID-4Py)_{1.0}-*b*-PPyMA₂₀, and (f) MH(4Py-IID-4Py)_{1.0}-*b*-PPyMA₄₀.

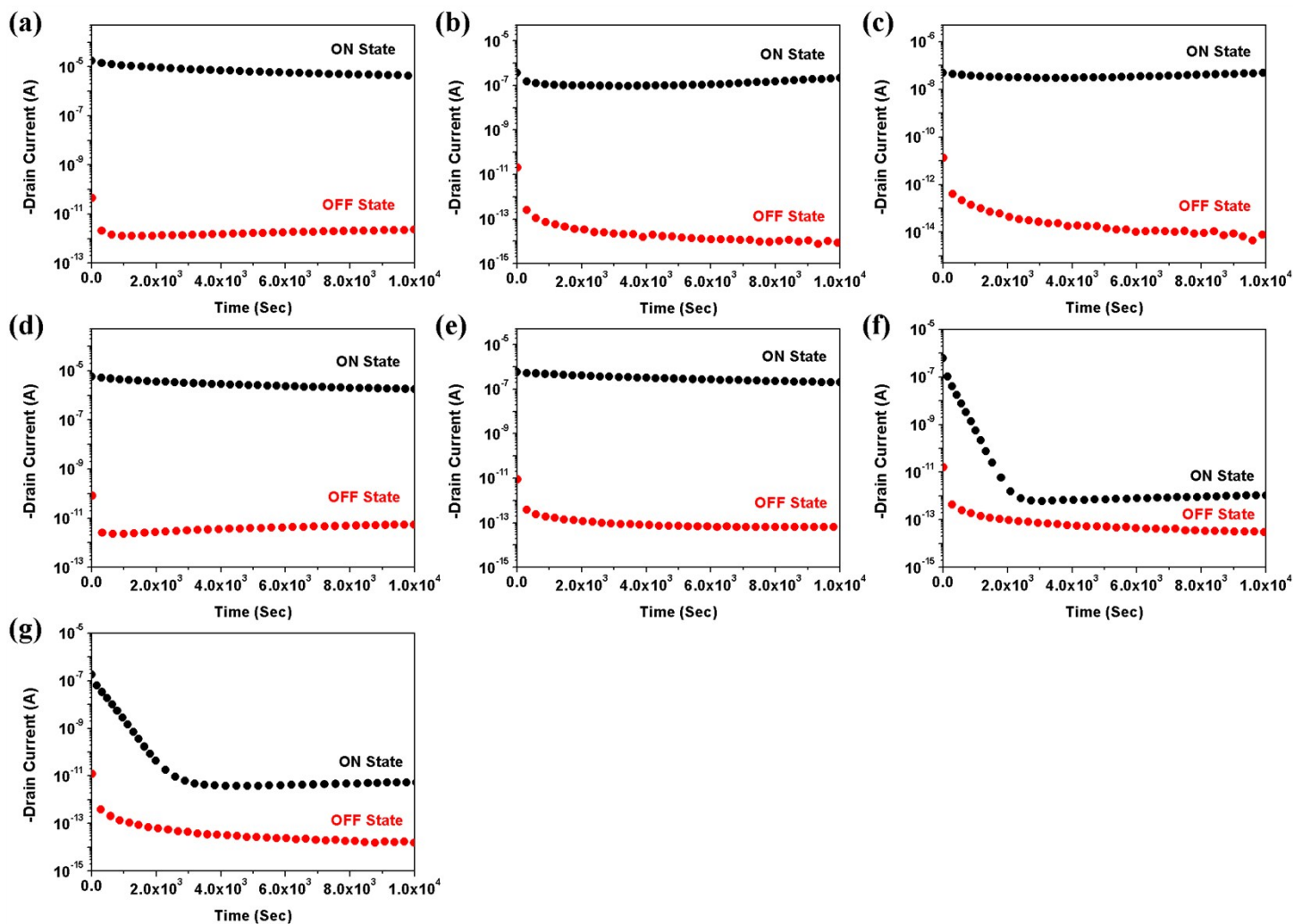


Fig. S22 The retention time curves of the devices using thermo-annealed MH(4Py-Acceptor-4Py)_x-*b*-PPyMA_n thin films as electret layers: (a) MH(4Py-BT-4Py)_{1.0}-*b*-PPyMA₁₀, (b) MH(4Py-BT-4Py)_{1.0}-*b*-PPyMA₂₀, (c) MH(4Py-BT-4Py)_{1.0}-*b*-PPyMA₄₀, (d) MH(4Py-IID-4Py)_{1.0}-*b*-PPyMA₁₀, (e) MH(4Py-IID-4Py)_{1.0}-*b*-PPyMA₂₀, and (f) MH(4Py-IID-4Py)_{1.0}-*b*-PPyMA₄₀.

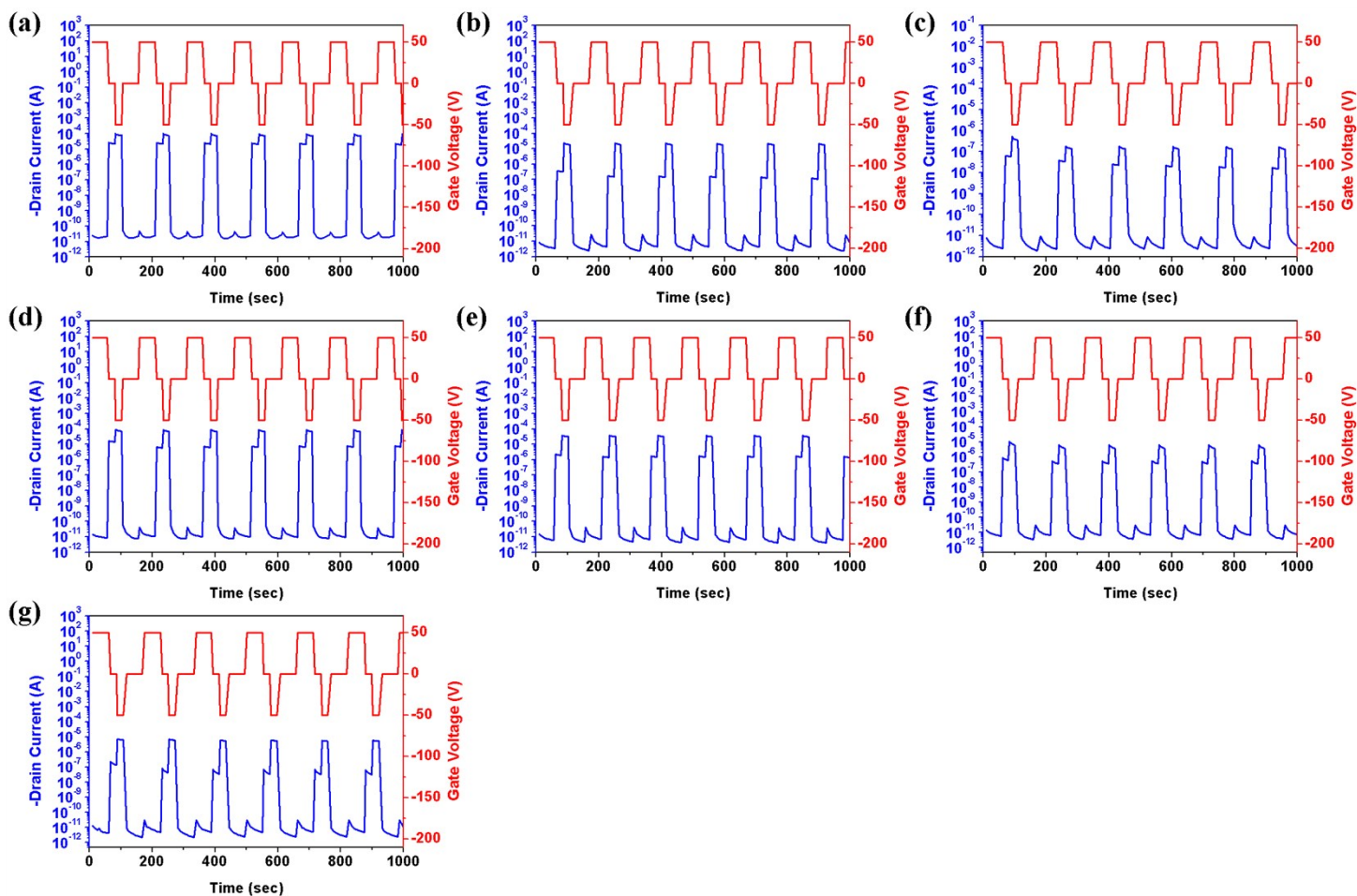


Fig. S23 The WRER (write-read-erase-read) cycles of the devices using thermo-annealed MH(4Py-Acceptor-4Py)_x-*b*-PPyMA_n thin films as electret layers: (a) MH(4Py-BT-4Py)_{1.0}-*b*-PPyMA₁₀, (b) MH(4Py-BT-4Py)_{1.0}-*b*-PPyMA₂₀, (c) MH(4Py-BT-4Py)_{1.0}-*b*-PPyMA₄₀, (d) MH(4Py-IID-4Py)_{1.0}-*b*-PPyMA₁₀, (e) MH(4Py-IID-4Py)_{1.0}-*b*-PPyMA₂₀, and (f) MH(4Py-IID-4Py)_{1.0}-*b*-PPyMA₄₀.

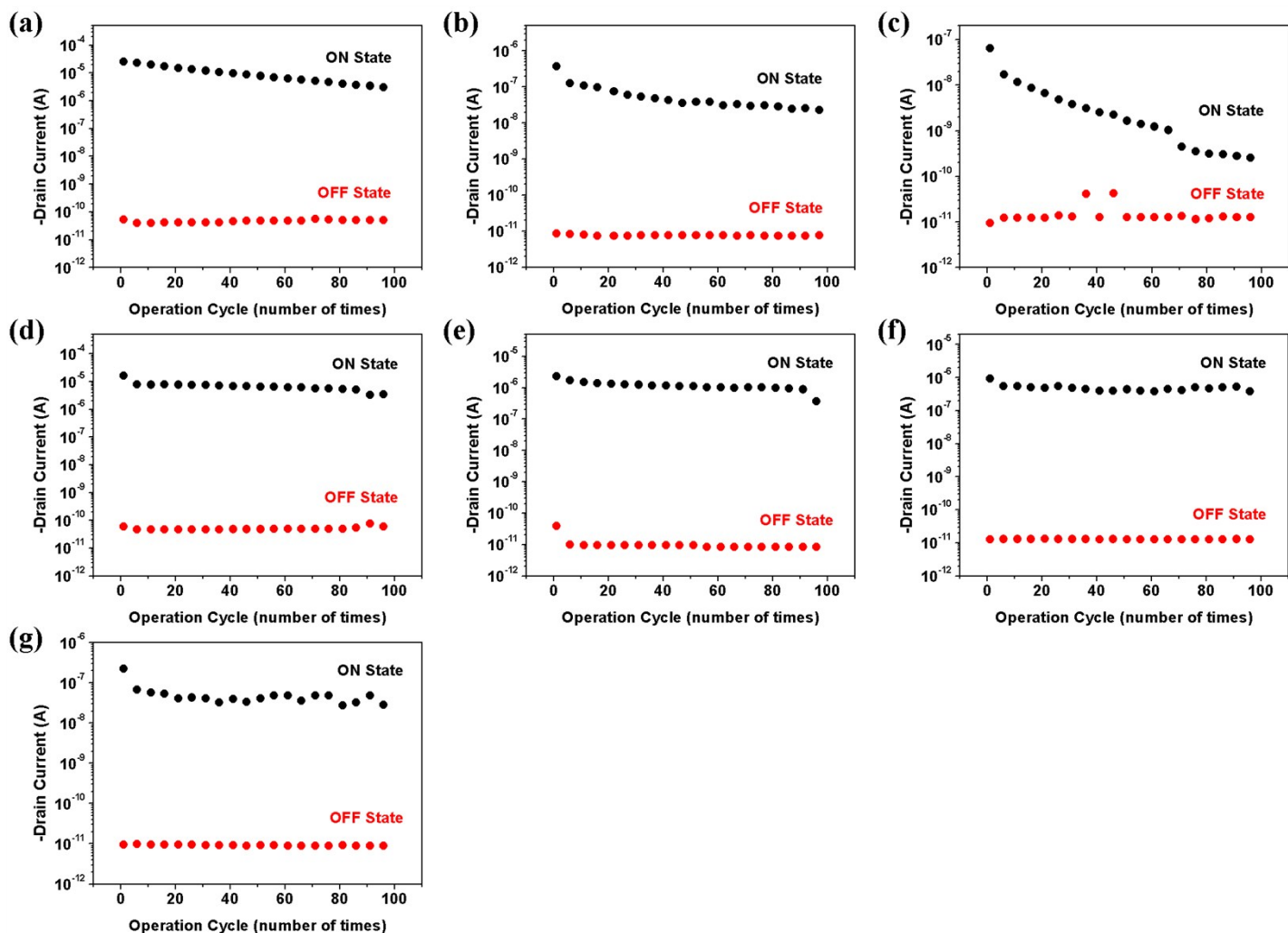


Fig. S24 The operation cycles (endurance) of the devices using thermo-annealed MH(4Py-Acceptor-4Py)_x-b-PPyMA_n thin films as electret layers: (a) MH(4Py-BT-4Py)_{1.0}-b-PPyMA₁₀, (b) MH(4Py-BT-4Py)_{1.0}-b-PPyMA₂₀, (c) MH(4Py-BT-4Py)_{1.0}-b-PPyMA₄₀, (d) MH(4Py-IID-4Py)_{1.0}-b-PPyMA₁₀, (e) MH(4Py-IID-4Py)_{1.0}-b-PPyMA₂₀, and (f) MH(4Py-IID-4Py)_{1.0}-b-PPyMA₄₀.