# Supporting Information

## Water robustness in organic thin-film transistors based on pyrazino[2,3-g]quinoxaline-dione conjugated polymer

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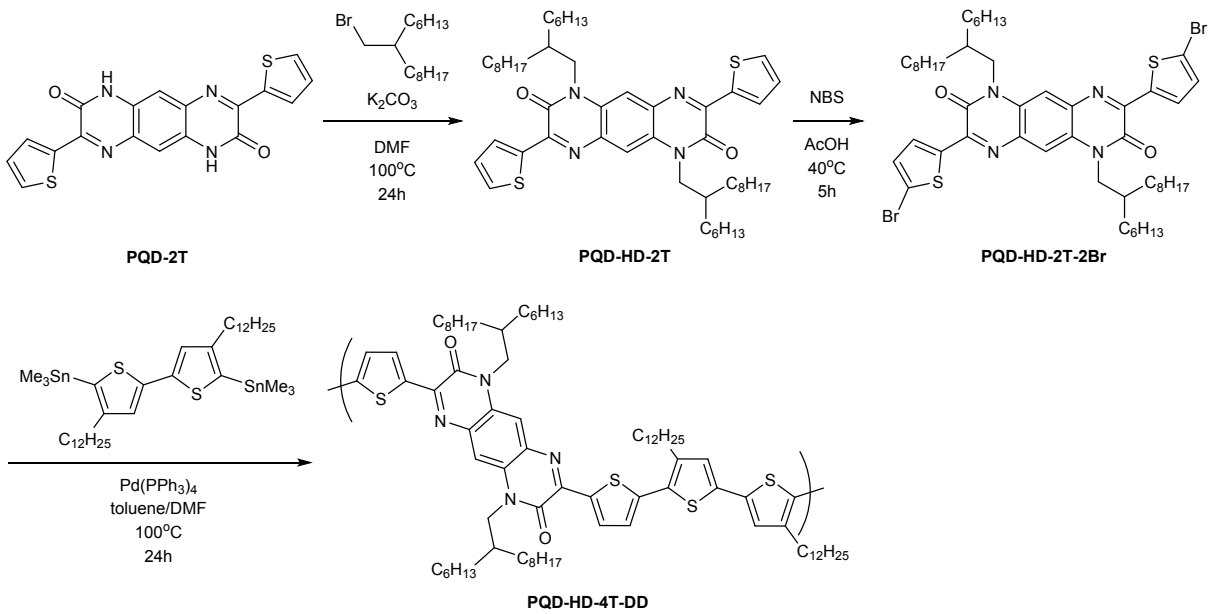
**Synthesis of polymers**

The synthesis of the π-conjugated donor acceptor (D-A) block copolymer, PQD-HD-4T-DD polymer, modified from reported procedures,[1] is shown below in Supporting Scheme 1. From the cyclic voltammetry (CV) and UV-vis absorption data, the highest occupied molecular orbital (HOMO) energy and optical band gap are determined to -5.24 eV and 1.78 eV respectively (Figure S1, ESI). The molecular weight ($M_w$) of the polymer was determined to be 34,457 g/mol with polydispersity index (PDI) of 2.15. The thermal stability of the polymer was also investigated by thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC). The polymer was thermally stable until 300 °C and did not show any noticeable endothermal or exothermal peaks other than the glass transition temperature at around 230 °C (Figure S2).




**Scheme S1.** Synthesis of polymer PQD-HD-4T-DD.

*Synthesis of 3,8-di(thiophen-2-yl)-1,6-dihydropyrazino[2,3-g]quinoxaline-2,7-dione (**PQD-2T**)*: 2 g of 1,2,4,5-benzenetetramine tetrahydrochloride (1 equiv., 7.04 mmol), 80 mL of AcOH and 2.08 mL of ethyl thiophene-2-glyoxylate (2 equiv., 14.08 mmol) was added into a two-necked round-bottom flask with a condenser attached. The reaction setup was purged with nitrogen and refluxed for 24 hours. At the end of the reaction, the reaction mixture was cooled to room temperature, precipitated in water and filtered. The solids were washed with

water and dried in the oven. An isomeric by-product, **PQD-2Ta** was formed together with **PQD-2T** and the crude mixture was used for the next step without further purification. Yield: 1.67 g (63 %). Brown solids. MALDI-TOF-MS *m/z*: 378.646 $[M]^+$; calcd. for $C_{18}H_{10}N_4O_2S_2$ $[M]^+$: 378.02 (Figure S10).

*Synthesis of 1,6-bis(2-hexyldecyl)-3,8-di(thiophen-2-yl)-1,6-dihydropyrazino[2,3-g]quinoxaline-2,7-dione (**PQD-HD-2T**)*: 1.5 g of crude **PQD-2T** (1 equiv., 3.96 mmol), 20 mL of DMF, 1.32 g of $K_2CO_3$ (2.4 equiv., 9.50 mmol) and 2.67 mL of 2-hexyldecylbromide (2.2 equiv., 8.71 mmol) was added into a two-necked round-bottom flask with a condenser attached. The reaction setup was purged with nitrogen and heated at 100°C for 24 hours. At the end of the reaction, the reaction mixture was cooled to room temperature, precipitated in water and extracted with 3 x 20 mL ether. The solvent was removed under vacuum and the crude residue was purified by column chromatography (hexane, then hexane/dichloromethane 7:3). Yield: 389 mg (12 %). Yellow solids. $^1$H NMR (500 MHz, $CDCl_3$) δ 8.43 – 8.37 (m, 2H), 8.33 – 8.29 (m, 2H), 7.58 (m, 2H), 7.21 (m, 2H), 4.62 (d, J = 5.5 Hz, 4H), 2.07 – 1.94 (m, 2H), 1.67 – 1.22 (m, 48H), 0.88 (m, 12H) (Figure S11). $^{13}$C{$^1$H} NMR (125 MHz, $CDCl_3$) δ 154.27, 142.52, 140.72, 138.81, 137.83, 131.57, 131.03, 128.30, 124.19, 70.26, 37.76, 32.06, 32.01, 31.89, 31.87, 30.15, 29.82, 29.75, 29.49, 27.05, 27.03, 22.83, 22.82, 14.26 (Figure S12). MALDI-TOF-MS *m/z*: 827.361 $[M]^+$; calcd. for $C_{50}H_{74}N_4O_2S_2$ $[M]^+$: 827.29. Anal. calcd for $C_{50}H_{74}N_4O_2S_2$: C 72.59, H 9.02, N 6.77; found: C 72.11, H 9.12, N 6.76 (Figure S13).

*Synthesis of 3,8-bis(5-bromothiophen-2-yl)-1,6-bis(2-decyltetradecyl)-1,6-dihydropyrazino[2,3-g]quinoxaline-2,7-dione (**PQD-HD-2T-2Br**)*: 350 mg of **PQD-HD-2T** (1 equiv., 0.42 mmol), 12 mL of THF and 158 mg of N-bromosuccinimide (NBS) (2.1 equiv., 0.88 mmol) was added into a two-necked round-bottom flask. The reaction setup was purged with nitrogen and heated at 40°C for 5 hours in the absence of light. At the end of the reaction, the reaction mixture was cooled to room temperature, washed with sodium sulfite solution

and extracted with 3 x 30 mL dichloromethane. The solvent was removed under vacuum and the crude residue was purified by column chromatography (hexane/dichloromethane 10:1, then hexane/dichloromethane 5:1). Yield: 270 mg (65 %). Yellow orange solids. $^{1}$H NMR (500 MHz, $CDCl_3$) δ 8.25 (s, 2H), 7.98 (d, J = 4.1 Hz, 2H), 7.11 (d, J = 4.1 Hz, 2H), 4.59 (d, J = 5.6 Hz, 4H), 2.06 – 1.93 (m, 2H), 1.32 (m, 48H), 0.88 (m, 12H) (Figure S14). $^{13}$C{$^{1}$H} NMR (125 MHz, $CDCl_3$) δ 153.93, 142.19, 141.38, 138.61, 137.72, 131.72, 131.32, 124.16, 119.34, 70.42, 37.72, 32.08, 32.03, 31.88, 31.85, 30.17, 29.84, 29.77, 29.51, 27.05, 27.03, 22.85, 22.84, 14.28 (Figure S15). MALDI-TOF-MS *m*/*z*: 985.189 $[M]^+$; calcd. for $C_{50}H_{72}Br_2N_4O_2S_2$ $[M]^+$: 985.08. Anal. calcd for $C_{50}H_{72}Br_2N_4O_2S_2$: C 60.96, H 7.37, N 5.69; found: C 61.41, H 7.61, N 5.49 (Figure S16).

*Polymerization for **PQD-HD-4T-DD**:* 147.8 mg of **PQD-HD-2T-2Br** (1 equiv., 0.15 mmol), 124.3 mg of (4,4′-Didodecyl-2,2′-bithiophene-5,5′-diyl)bis(trimethylstannane) (1 equiv., 0.15 mmol) and 7 mg of $Pd(PPh_3)_4$ (4 mol%) was added into an oven dried Schlenk flask. The Schlenk flask was evacuated and backfilled with nitrogen at least three times and 15 mL of dry toluene and 5.5 mL of dry dimethylformamide (DMF) were injected into the flask. The reaction mixture was stirred at 100°C for one day, allowed to cool to room temperature and poured into 200 mL of methanol. The mixture was stirred and filtered and the resultant crude polymer was purified by Soxhlet extraction with acetone, followed by hexane and lastly by chloroform. The resultant co-polymer was obtained as a bronze coloured solid. Yield: 130 mg (65 %). Anal. Calcd. for $(C_{81}H_{124}N_4O_2S_3)_n$: C 75.88, H 9.75, N 4.37; Found: C 74.27, H 9.66, N 4.37. GPC in trichlorobenzene, 150°C: Mw: 34,457, PDI: 2.15

**Reference**

[1] J. Quinn, C. Guo, L. Ko, B. Sun, Y. He, Y. Li, RSC Advances 2016, 6, 22043.

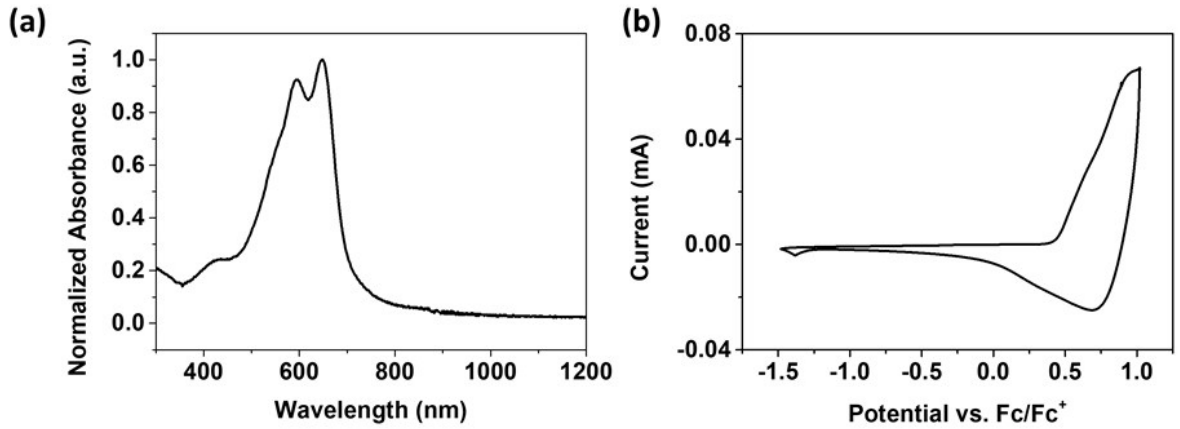



**Figure S1.** (a) Absorption spectra of PQD-HD-4T-DD thin films. (b) Cyclic voltammogram of PQD-HD-4T-DD thin film in 0.1M tetrabutylammonium hexafluorophosphate in acetonitrile.

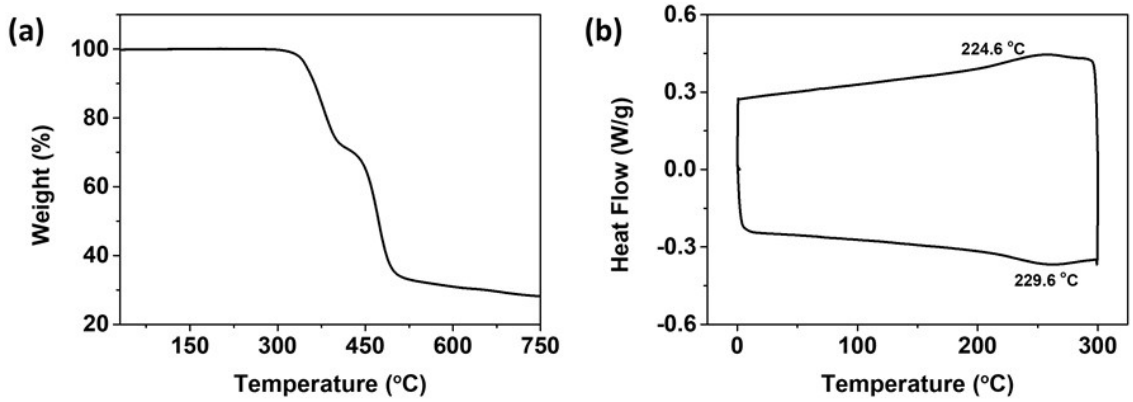



**Figure S2.** (a) Thermogravimetric analysis (TGA) and (b) differential scanning calorimetry (DSC) of PQD-HD-4T-DD. DSC measurements show the glass transition temperature of the polymer at around 230 °C.

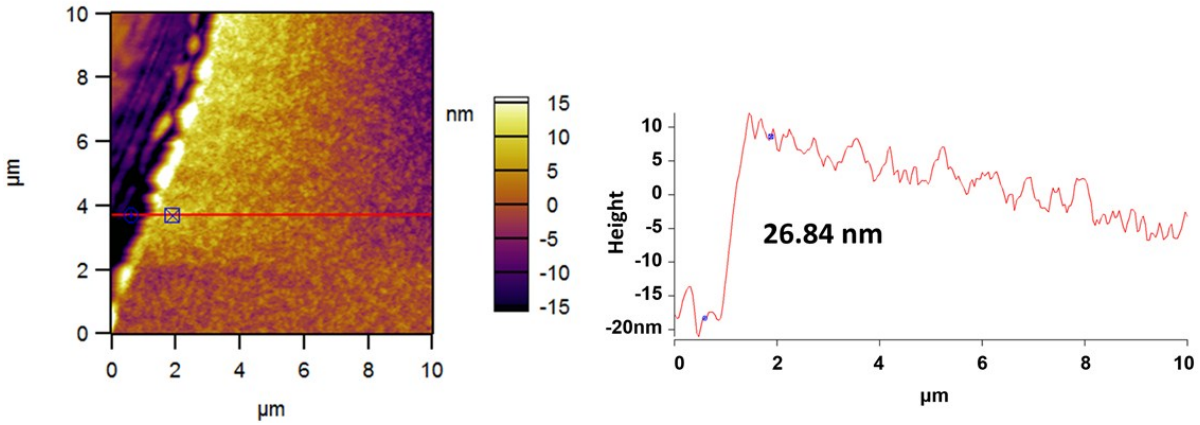



**Figure S3.** Atomic force microscopy (AFM) characterization for thickness measurement. The step height of the PQD-HD-4T-DD film was measured by removing part of the film with chlorobenzene.

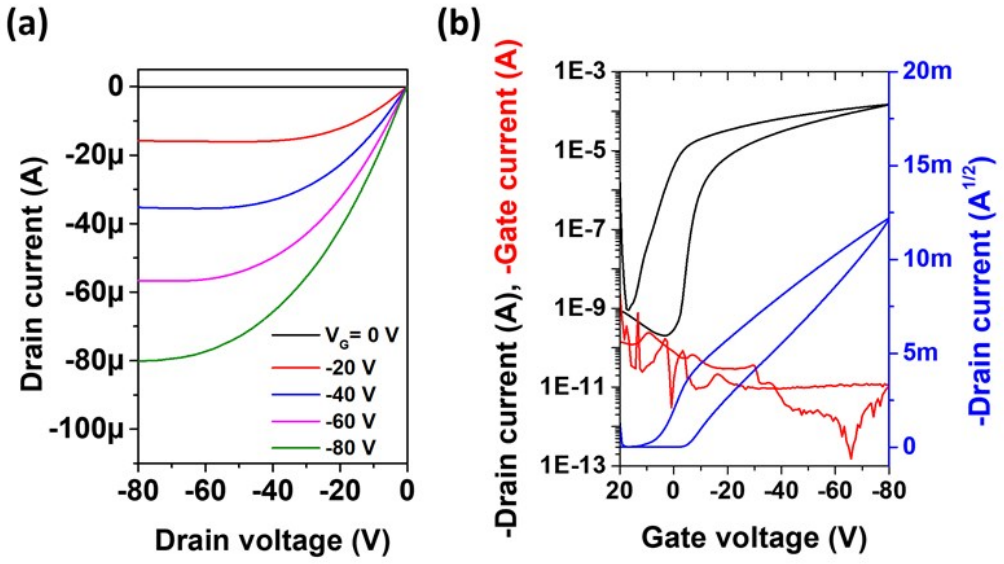



**Figure S4.** (a) Output and (b) transfer curves of PQD-HD-4T-DD OTFT wit OTS layer. ($V_D$=-80v, $V_G$=+20~-80 V).

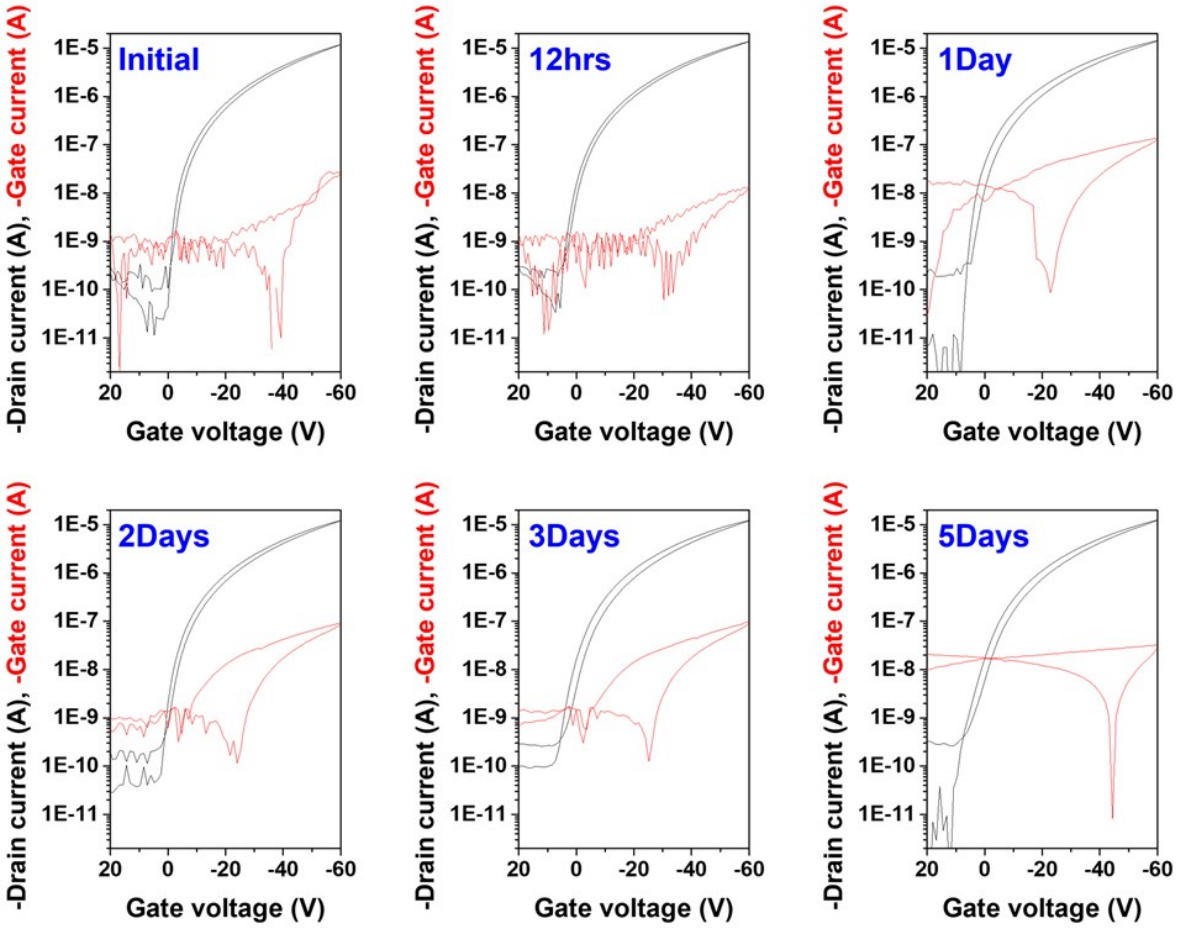



**Figure S5.** Hysteresis of PQD-HD-4T-DD OTFTs ($V_D$=-60 V, $V_G$=+20 ~ -40 V).

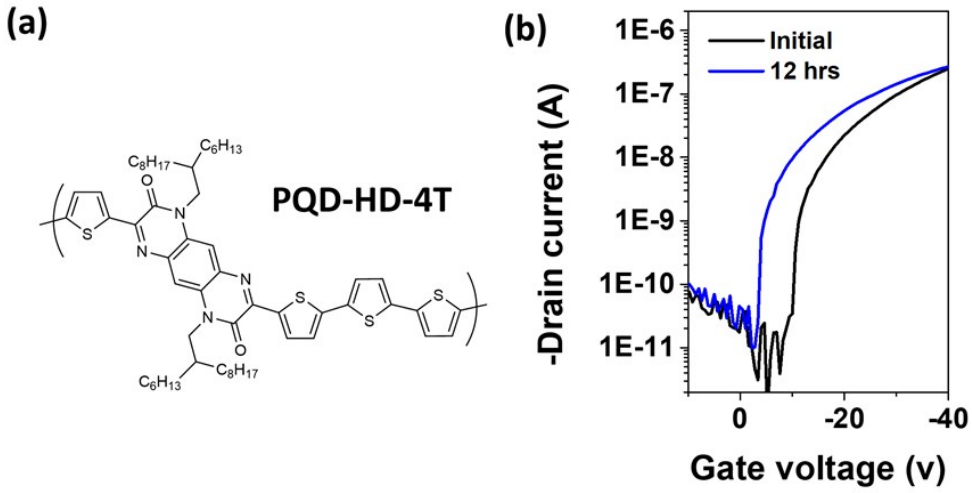



**Figure S6.** (a) Chemical structure of PQD-HD-4T. (b) Transfer characteristics of before and after 12hrs immersion in DI water.

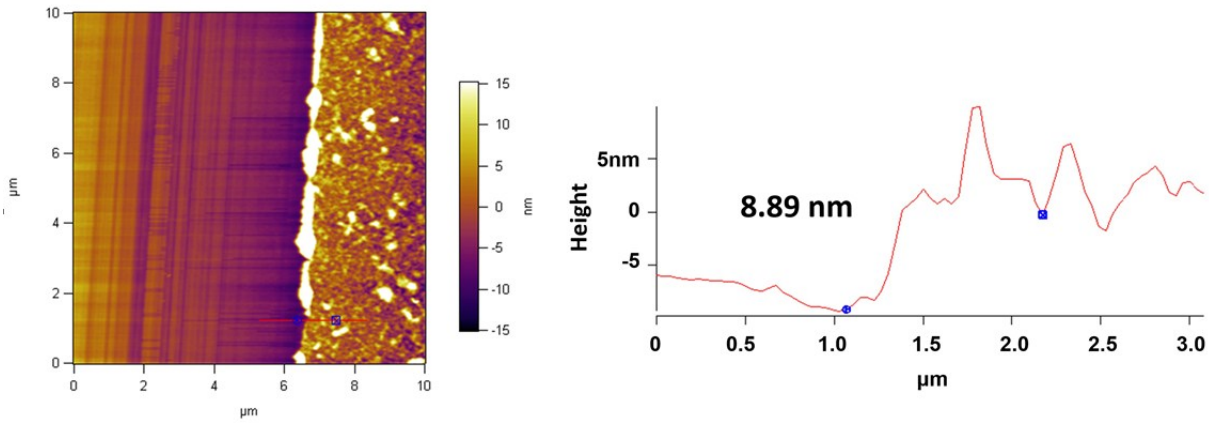



**Figure S7.** Atomic force microscopy (AFM) characterization for thickness measurement. The step height of the PQD-HD-4T film was measured by removing part of the film with dichlorobenzene.

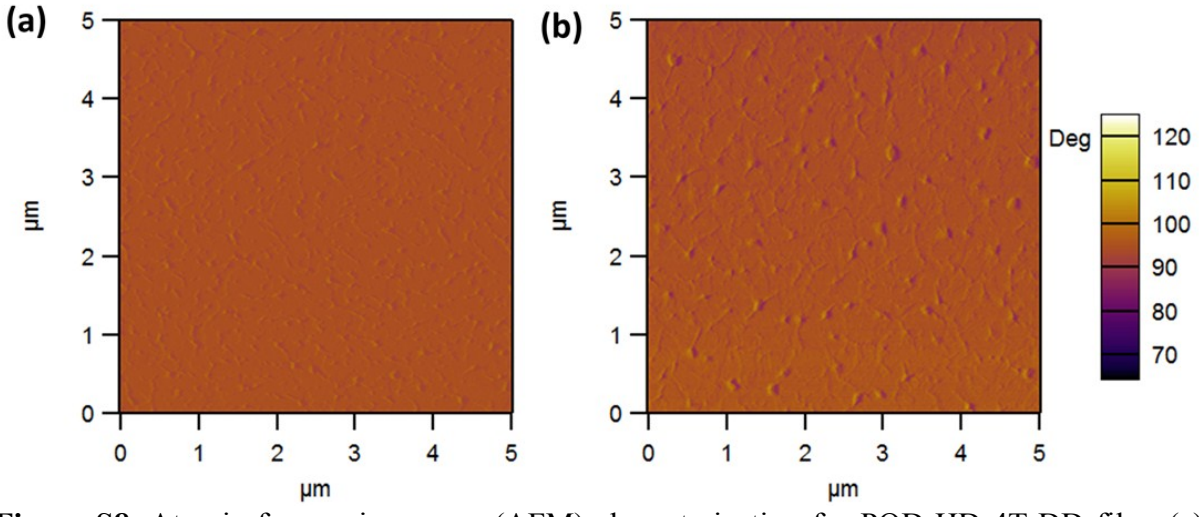



**Figure S8.** Atomic force microscopy (AFM) characterization for PQD-HD-4T-DD film. (a) Phase image of Figure 4(a) and (b) Figure 4(b).

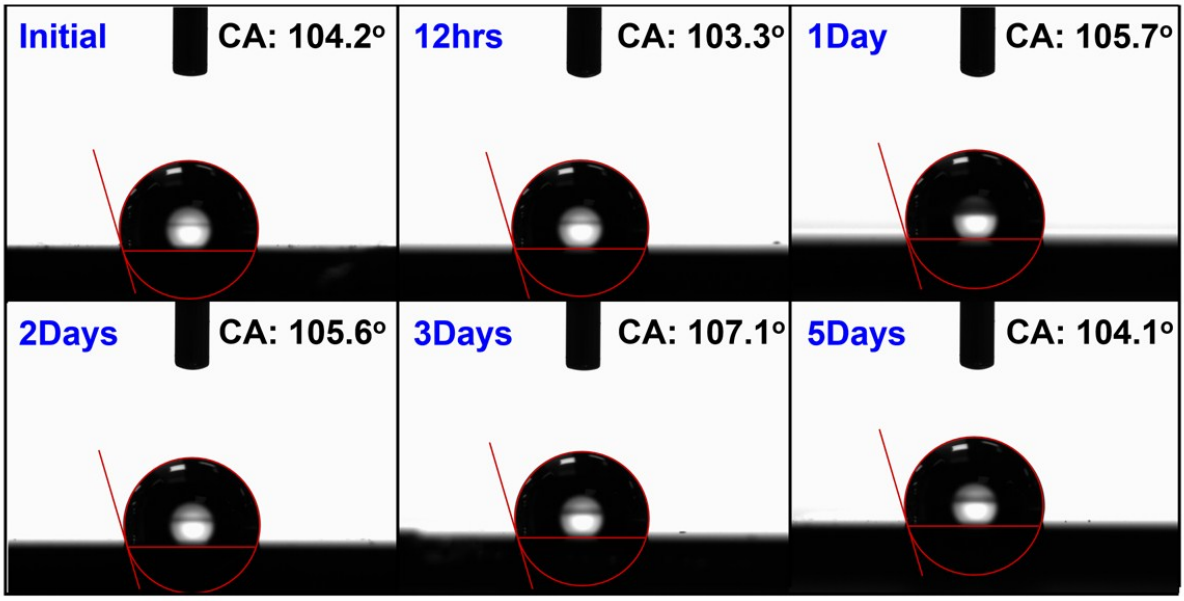



**Figure S9.** Water contact angle of PQD-HD-4T-DD films after immersing the film in DI water.

## $^{1}H$, $^{13}C\{^{1}H\}$ NMR and MALDI-TOF of synthesized compounds

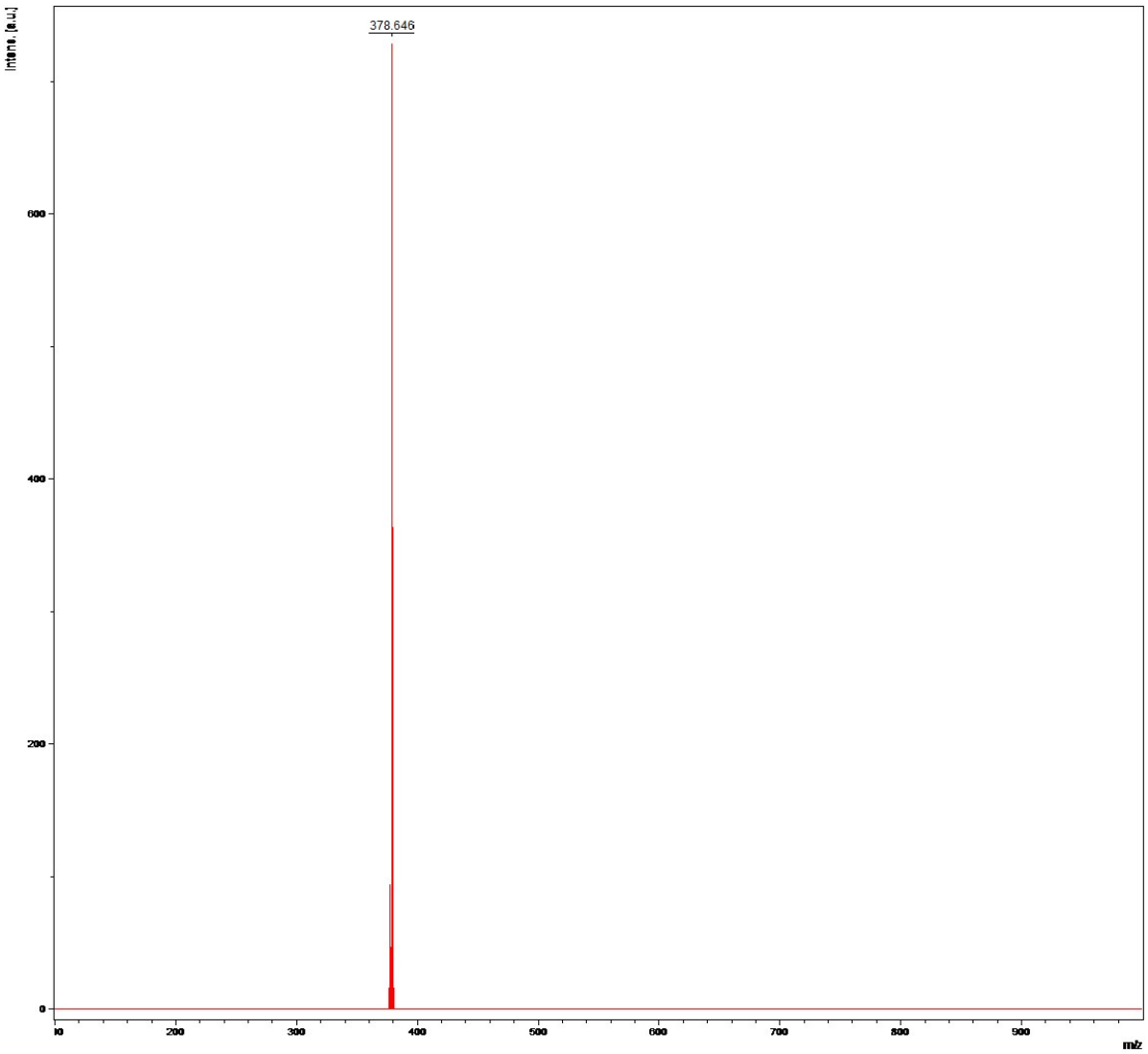



**Figure S10**. MALDI-TOF mass spectrum of **PQD-2T**

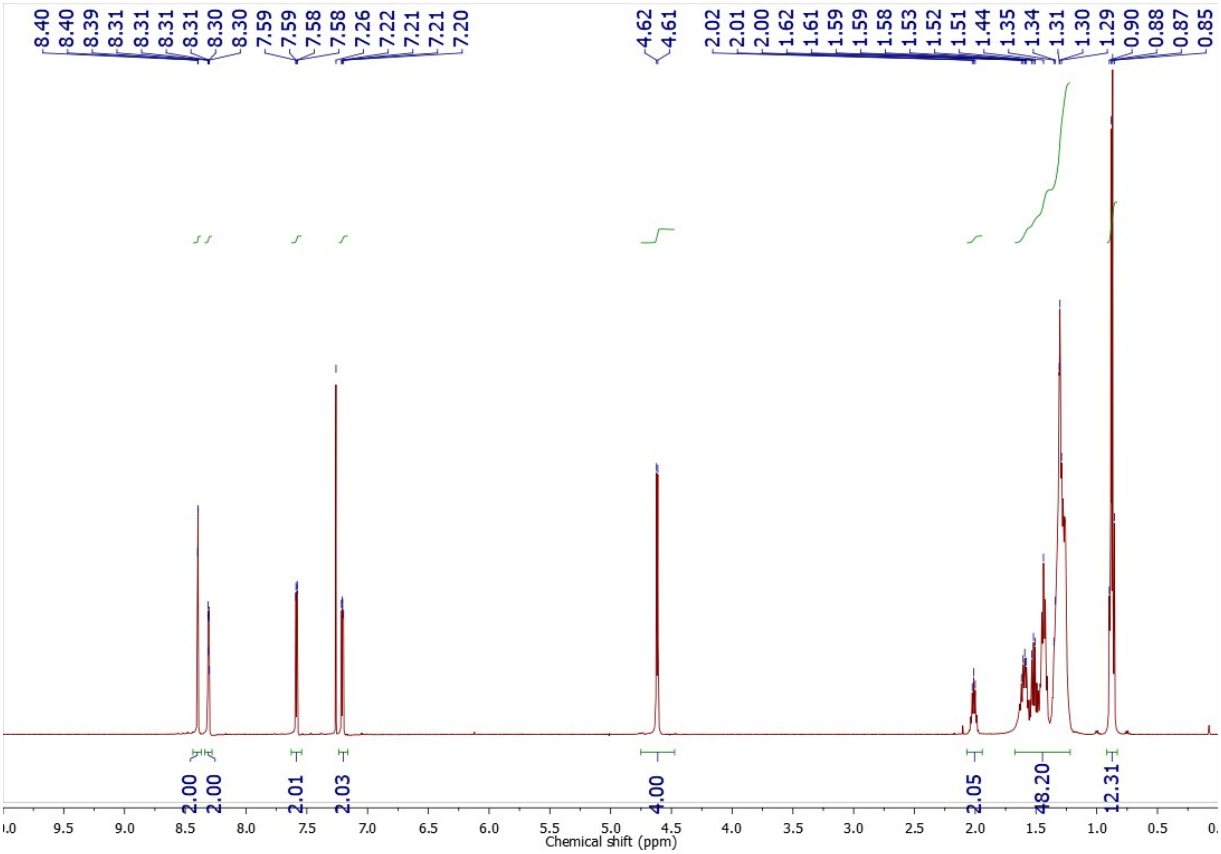



**Figure S11.** $^{1}H$ NMR spectrum (500 MHz) of **PQD-HD-2T** in $CDCl_3$.

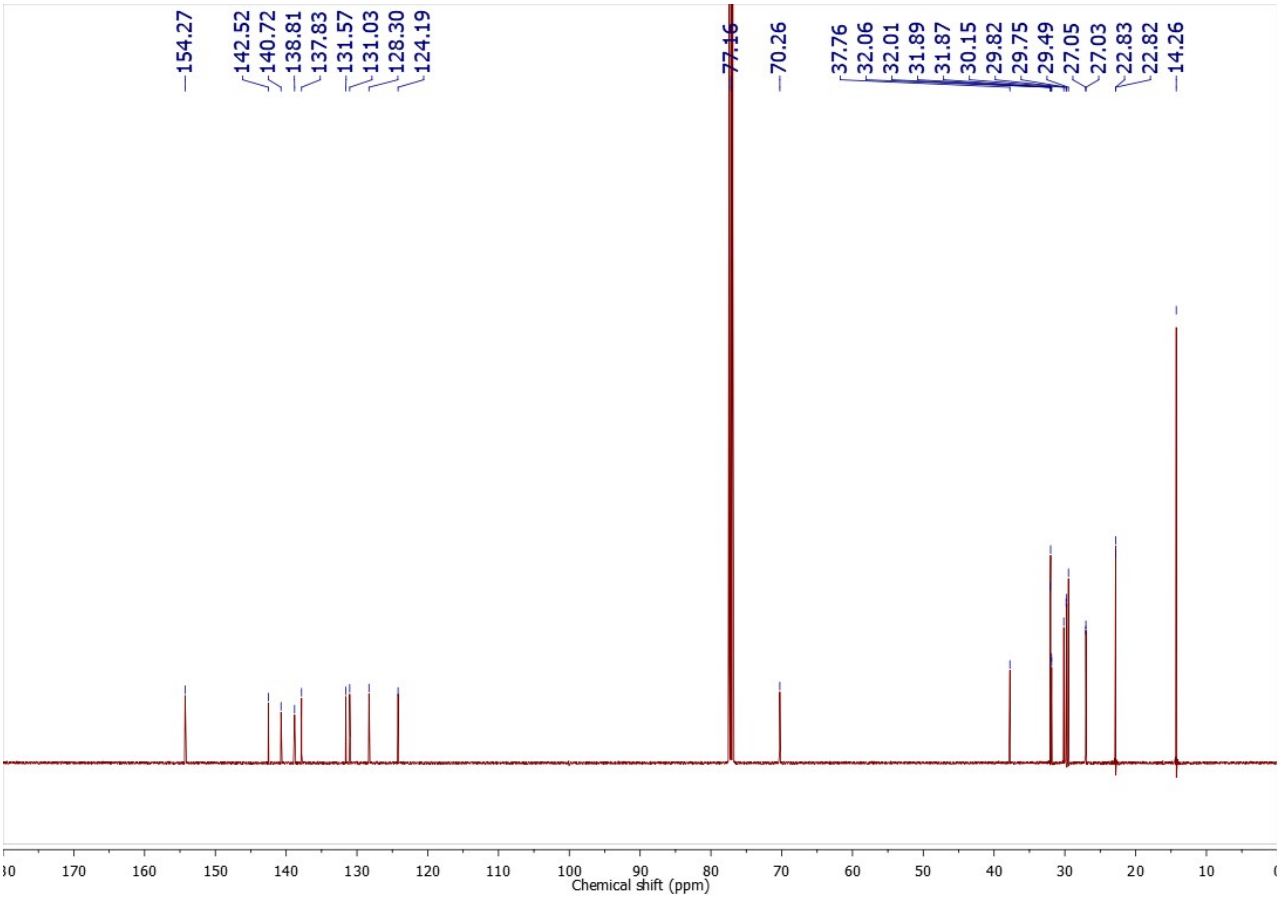



**Figure S12.** $^{13}C$ NMR spectrum (500 MHz) of **PQD-HD-2T** in $CDCl_3$.

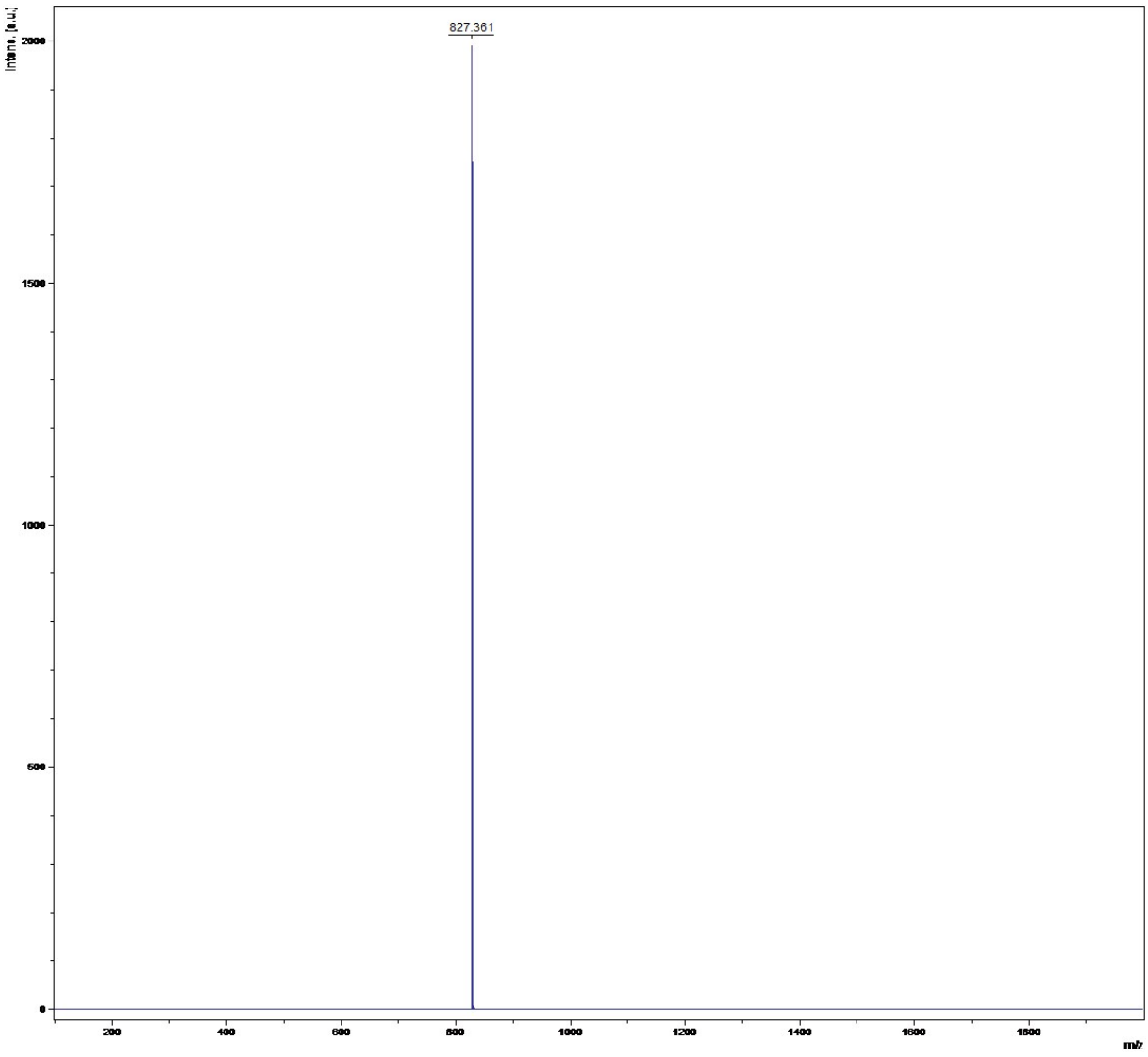



**Figure S13**. MALDI-TOF mass spectrum of **PQD-HD-2T**

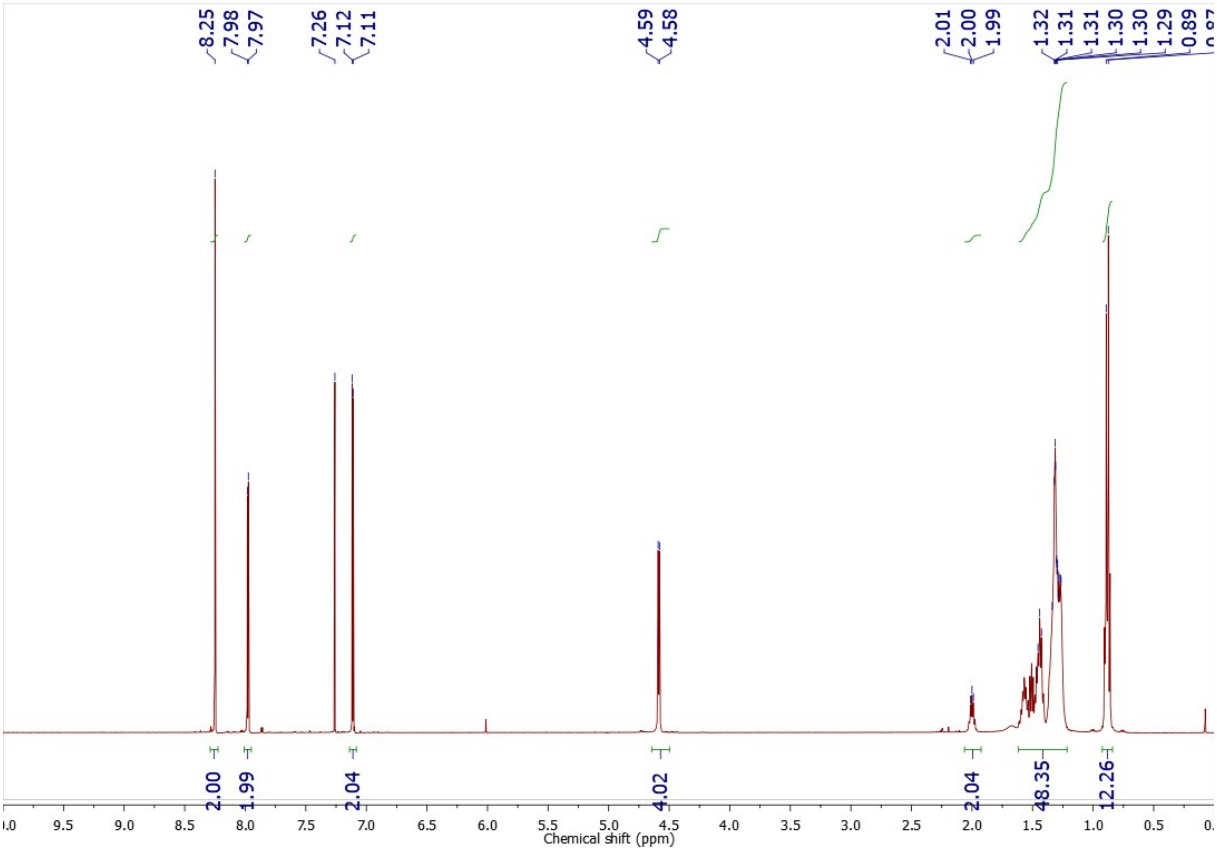



**Figure S14.** $^{1}$H NMR spectrum (500 MHz) of **PQD-HD-2T-2Br** in $CDCl_3$.

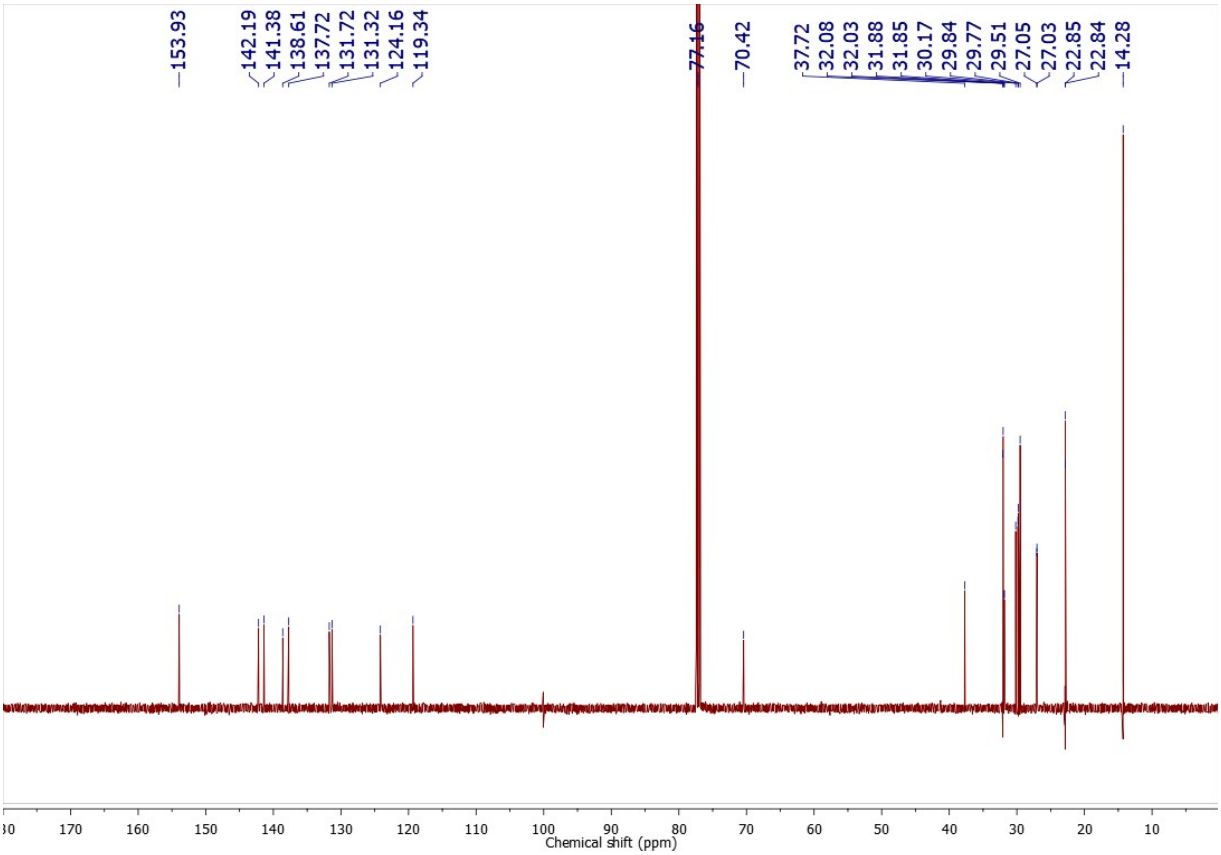



**Figure S15.** $^{13}$C NMR spectrum (500 MHz) of **PQD-HD-2T-2Br** in $CDCl_3$.

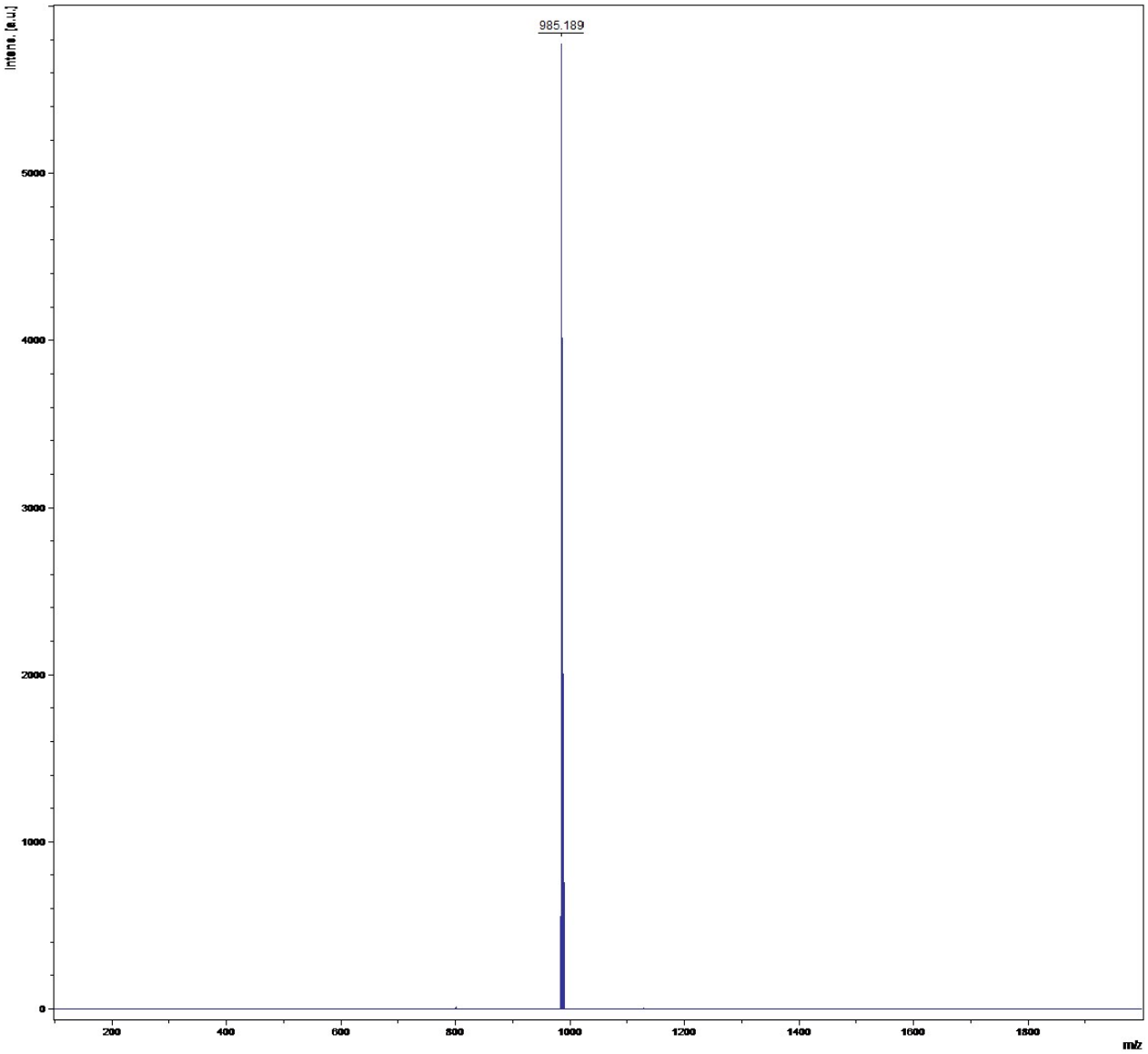



**Figure S16**. MALDI-TOF mass spectrum of **PQD-HD-2T-2Br**