Supporting Information

Synthesis and Photophysics of Monodisperse Co-oligomers Consisting of Alternating Thiophene and Perylene Bisimide

Yuchao Ma, Yi-Shi Wu, Yan-Xia Zhao, Hongbing Fu,* and Jiannian Yao**

Contribution from the Beijing National Laboratory for Molecular Sciences (BNLMS),

Institute of Chemistry, Chinese Academy of Sciences, Beijing 100190

*Corresponding authors (Tel&Fax: +86-10-82616517, E-mail: hongbing.fu@iccas.ac.cn, yswu@iccas.ac.cn, jnyao@iccas.ac.cn)

Synthesis of $(TP)_2T$, $(TP)_3T$, and $(TP)_6T$

N,*N*′-Di(2-ethylhexyl)-1,7-dibromoperylene-3,4,9,10-tetracarboxylic Acid Bisimide (**1**) (700mg, 0.91mmol), 2,5-Bis(tri-n-butylstannyl)thiophene (**2**) (601mg, 0.91mmol) and toluene (50ml) were added into a 100 mL three-neck round bottom flask. Then the flask was deoxygenated with argon for 15 min. After the deoxygenation, the catalytic amount of $Pd(PPh_3)_4$ was added. The mixture was stirred and heated to reflux for 24 hours under argon. When the system was cooled down to room temperature, a solution of KF (5 g) in water (10 mL) was added to the black solution generated in the reaction. Then the mixture was stirred at room temperature for 2 h to remove the tin impurity, extracted with dichloromethane (2 × 100 mL), washed with water (2 × 200 mL), and dried over anhydrous $NaSO_4$. After removal of the dichloromethane under vacuum, the resulting solid was purified by column chromatography using dichloromethane as eluent to give $(TP)_2T$ (134mg, 10.3%), $(TP)_3T$ (79mg, 6.1%) and $(TP)_6T$ (35mg , 2.7%) as black solid. The R_f data were 0.9, 0.7 and 0.1 for $(TP)_2T$, $(TP)_3T$ and $(TP)_6T$ respectively with dichloromethane as developing agent.

$(TP)_2T$: ^1H NMR 400 MHz ($CDCl_3$): =8.62(s, 2H, perylene-H), 8.46(s, 2H, perylene-H), 8.21-8.28(m, 6H, perylene-H), 7.91(m, 2H, perylene-H), 7.66(dd, 2H, thiophene-H), 7.45(dd, 2H, thiophene-H), 7.15-7.29(m, 4H, thiophene-H), 4.01-4.22(m, 8H, $-CH_2-N$), 1.84-1.95(m, 4H, -CH-), 1.28-1.42(m, 32H, $-CH_2-$), 0.88-0.96(m, 24H, $-CH_3$); ^{13}C NMR 100MH ($CDCl_3$): =163.597, 163.382, 146.657,

143.42, 134.265, 133.727, 133.458, 132.743, 132.073, 129.750, 129.100, 128.838, 127.802, 127.668, 122.552, 122.508, 122.277, 122.145, 44.591, 38.193, 38.050, 30.978, 30.864, 28.926, 28.841, 24.233, 24.131, 23.267, 23.204, 14.317, 14.237, 10.813, 10.737. MALDI-TOF MS (m/z) 1473.1 (m^+).

$(TP)_3T$: ^{1}H NMR 400 MHz ($CDCl_3$): =8.55-8.70 (m, 6H, perylene-H), 8.22-8.39 (m, 10H, perylene-H), 7.98(m, 2H, perylene-H), 7.47-7.56(m, 6H, thiophene-H), 7.17-7.28(m, 4H, thiophene-H), 3.9-4.1(m, 12H, -CH_2-N), 1.92(m, 6H, -CH-), 1.32-1.38(m, 48H, -CH_2-), 0.88-0.94(m, 36H, -CH_3); ^{13}C NMR 100MH ($CDCl_3$): =163.699, 163.527, 146.864, 143.493, 133.570, 133.234, 133.088, 132.038, 130.088, 129.813, 129.263, 129.182, 129.096, 128.058, 127.945, 122.673, 122.492, 122.208, 44.542, 38.147, 38.063, 30.926, 30.875, 29.844, 28.881, 24.195, 24.130, 23.233, 23.198, 14.277, 14.228, 10.783, 10.734. MALDI-TOF MS (m/z) 2168.3 (m^+).

$(TP)_6T$: ^{1}H NMR 400 MHz ($CDCl_3$): = 8.20-8.43 (m, br, 22H, perylene-H), 8.57-8.71 (m, br, 12H, perylene-H), 8.00(m, 2H, perylene-H), 7.47-7.58(m, 12H, thiophene-H), 7.17-7.29(dd, 4H, thiophene-H), 4.11(m, 24H, -CH_2-N), 1.89(m, 12H, -CH-), 1.32(m, 96H, -CH_2-), 0.88-0.94(m, 72H, -CH_3); ^{13}C NMR 150MH ($CDCl_3$): =163.490, 163.381, 146.714, 146.301, 143.335, 135.696, 135.364, 134.490, 134.021, 133.427, 132.958, 132.117, 131.900, 129.860, 129.664, 129.128, 128.941, 128.432, 127.917, 127.553, 122.523, 122.058, 44.392, 37.985, 37.893, 37.398, 32.763, 31.926, 30.716, 30.036, 29.698, 29.361, 28.688, 27.977, 23.981, 23.076, 22.692, 19.731, 14.114, 10.593. MALDI-TOF MS (m/z) 4253.7 (m^+).

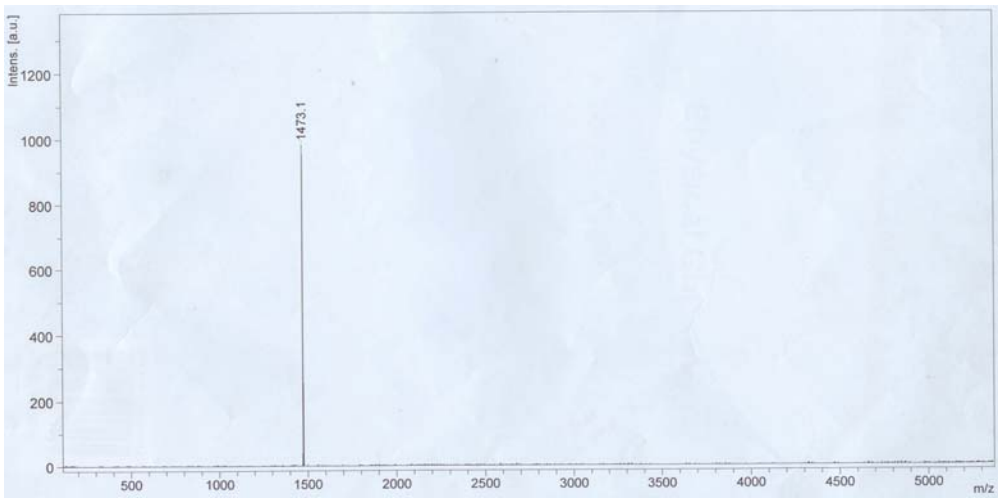

Figure S1. MS spectrum of **TP)$_2$T**.

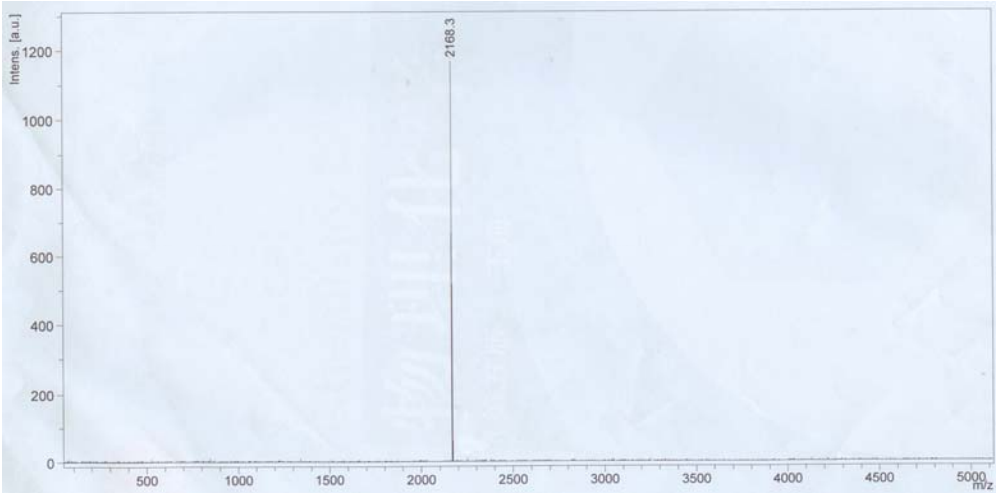

Figure S2. MS spectrum of $(\mathbf{TP})_3\mathbf{T}$.

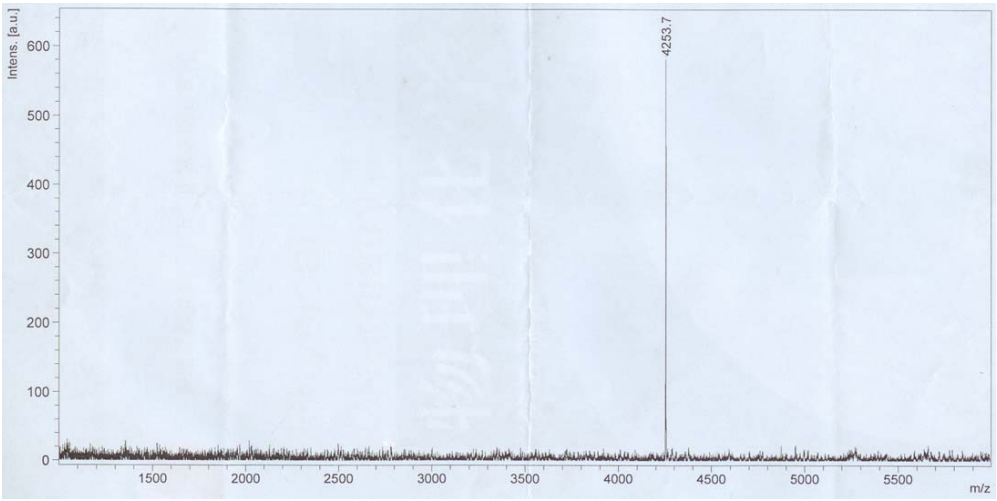

Figure S3. MS spectrum of **(TP)$_6$T**.

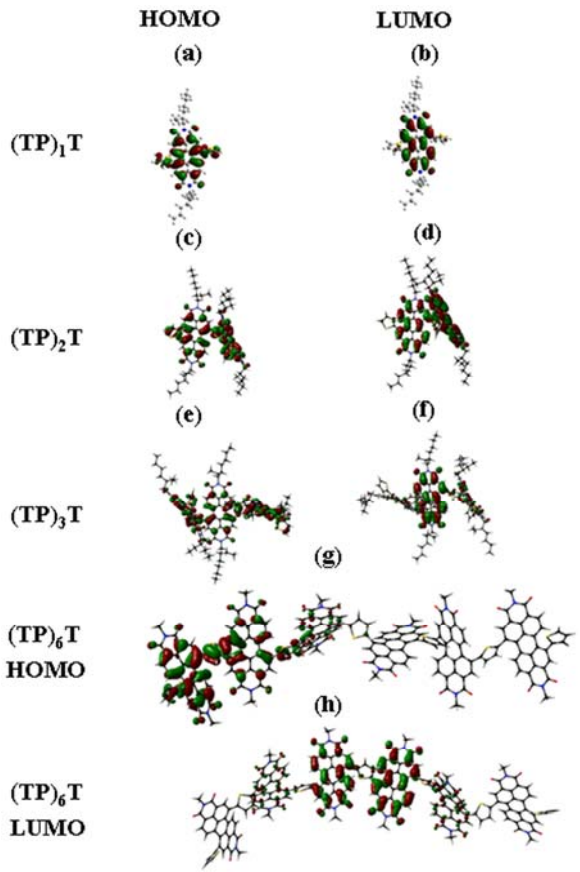

Figure S4. Optimized HOMOs and LUMOs obtained by DFT methods at the B3LYP/6-31G level for (**TP)$_1$T, TP)$_2$T,** (**TP)$_3$T,** and (**TP)$_6$T**, respectively.