Electronic Supplementary Information

Suppressing Non-radiative Energy Loss of Organic Solar Cells by Embedding Nitroxide Radical Blocks in Wide Bandgap Conjugated Polymer Donors

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Experimental Section

Materials

The 2,6-bis(trimethylstannyl)-4,8-bis(5-(2-ethylhexyl)-4-fluorothiophen-2-yl)benzo[1,2-*b*:4,5-*b*′]dithiophene (BDT-FSn), 1,3-bis(5-bromothiophen-2-yl)-5,7-bis(2-ethylhexyl)benzo[1,2-*c*:4,5-*c*′]dithiophene-4,8-dione (BDDBr) and 2,5-dibromo-1,4-bis(4-oxy-2,2,6,6-tetramethylpiperidine-1-oxyl)phthalate (BTMP) were synthesized by following a previous report and characterized by ^{1}H NMR before use. PDINN was purchased from Solarmer Materials (Beijing) Inc. (China). Other reagents and solvents were purchased from commercial sources and used as received. Poly(3,4-ethylenedioxythiophene): polystyrene sulfonate (PEDOT: PSS, Clevios AI 4083) was purchased from Heraeus (Germany). Pre-patterned high-transmittance ITO-glass substrates (resistance ~ 12 Ω sq^{-1}, maximum transmittance ~ 94% at ~ 550 nm, size of 20 × 15 × 0.7 mm^3) were purchased from You Xuan Ltd. (China).

Synthesize of polymers

Polymerization for PM6-BTMP1

BDT-FSn (141.1 mg, 0.1500 mmol) and BDDBr (113.9 mg, 0.1485 mmol) were dissolved in 10 mL toluene and 1mL N, N-Dimethylformamide in a 25 ml double-neck round-bottom flask. Afterwards, 1 mL solution of the BTMP (0.95 mg, 0.0015 mmol) of 9.5 mg in 10 mL toluene was added to a round neck flask. And then $Pd_2(dba)_3$ (1.5mg), $P(o\text{-}tol)_3$ (2.5 mg) was added. After another flushing with argon for 20 min, the reactant was then heated to 110 ºC and stirred for 12 h. At the end of polymerization, the polymer was end-capped with 2-tributylstannylthiophene and 2-bromothiophene. At the end of the reaction, the mixture was dropped into 300 mL of anhydrous methanol and then filtered to obtain the crude product. The coarse polymer was purified by silica gel chromatography using toluene. The solution of the copolymer in toluene was condensed to 15 mL and then poured into methanol (300 mL). The precipitate was collected and dried under a vacuum overnight (Yield: 78%). M_n = 34800 g/mol, PDI = 2.5.

Polymerization for PM6-BTMP2

The PM6-BTMP2 was synthesized according to the procedure of the PM6-BTMP1, except that the polymerization was carried out with BDT-FSn (141.1 mg, 0.1500 mmol), BDDBr (112.7 mg,

0.1470 mmol), and 2 mL solution of BTMP (9.5 mg in 10 mL toluene, BTMP, 0.003mmol) was added to a round neck flask. The precipitate was collected and dried under a vacuum overnight (Yield: 74%). GPC: M_n = 36500 g/mol, PDI = 2.4.

Polymerization for PM6-BTMP5

The PM6-BTMP5 was synthesized according to the procedure of the PM6-BTMP1, except that the polymerization was carried out with BDT-FSn (141.1 mg, 0.1500 mmol), BDDBr (109.3 mg, 0.1425 mmol), and 5 mL solution of BTMP (9.5 mg in 10 mL toluene, BTMP, 0.0075mmol) was added to a round neck flask. The precipitate was collected and dried under a vacuum overnight (Yield: 76%). GPC: M_n = 45700 g/mol, PDI = 2.1.

General Method:

^{1}H NMR spectra were recorded on a Bruker DRX 400 spectrometer operating at 400 MHz. Film absorption spectra were obtained by using a UV-visible spectrophotometer (HITACHI, Japan). The thickness of the film was obtained by using a spectroscopic ellipsometer (J. A. Woollam, USA). Thermogravimetric analysis Analytical gel permeation chromatography (GPC) measurements (Waters GPC 2410) were performed in tetrahydrofuran (THF) relative to polystyrene standards. Electron paramagnetic resonance (EPR) measurements were taken using a Bruker A300-9 5/12 apparatus. Cyclic voltammetry (CV) analysis was performed on a CHI 600D electrochemical workstation (Shanghai Chenhua Co.) at a scan rate of 50 mV·s^{-1}. Film absorption spectra were obtained by using a UV-visible spectrophotometer (HITACHI, Japan). *J-V* characteristics were measured with programmed software developed by Ossila Ltd. (UK) and a source meter unit (2612B, Keithley, USA). Characterization of the EQE of the device on a 7-SCSpecIII external quantum efficiency measurement instrument (Seven Star Optical Instruments, Beijing, China).

Supporting Figures and Tables

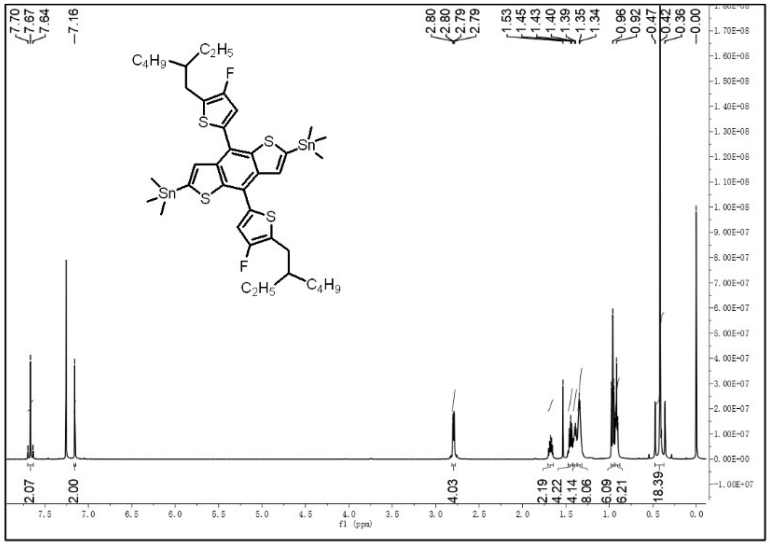

Fig. S1. ^{1}H NMR spectrum of 2,6-bis(trimethylstannyl)-4,8-bis(5-(2-ethylhexyl)-4-fluorothiophen-2-yl)benzo[1,2-*b*:4,5-*b*′]dithiophene (BDT-FSn) in $CDCl_3$.

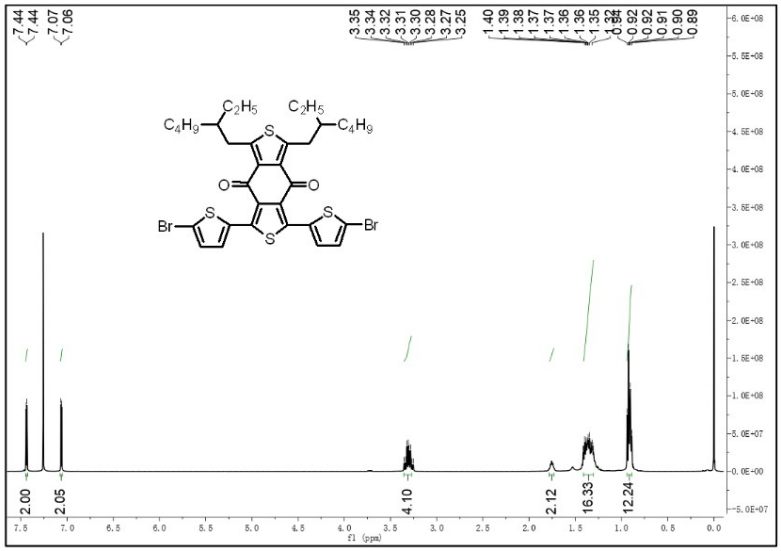

Fig. S2. ^{1}H NMR spectrum of 1,3-bis(5-bromothiophen-2-yl)-5,7-bis(2-ethylhexyl)benzo[1,2-*c*:4,5-*c*′]dithiophene-4,8-dione (BDDBr) in $CDCl_3$.

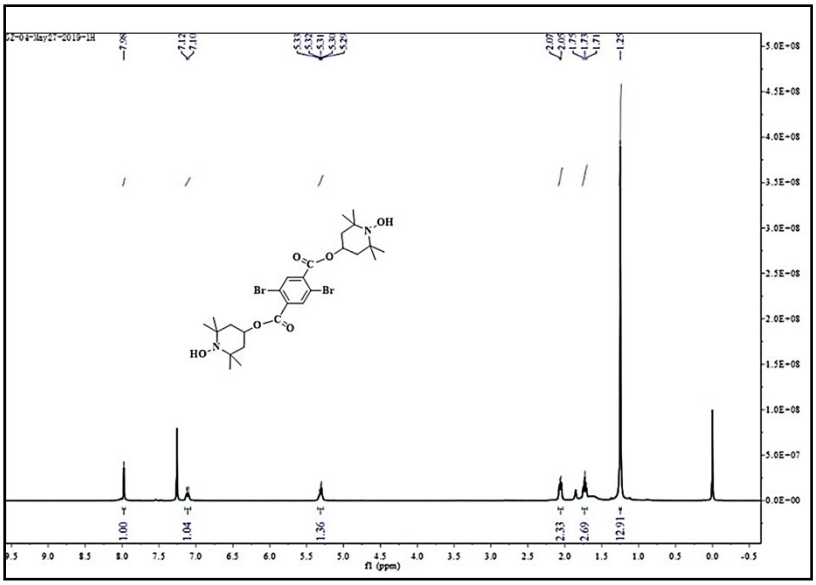

Fig. S3. ^{1}H NMR spectrum of 2,5-dibromo-1,4-bis(4-hydroxy-2,2,6,6-tetramethylpiperidine-1-yl)phthalate formed by reduction of BTMP after erythorbic acid in $CDCl_3$.

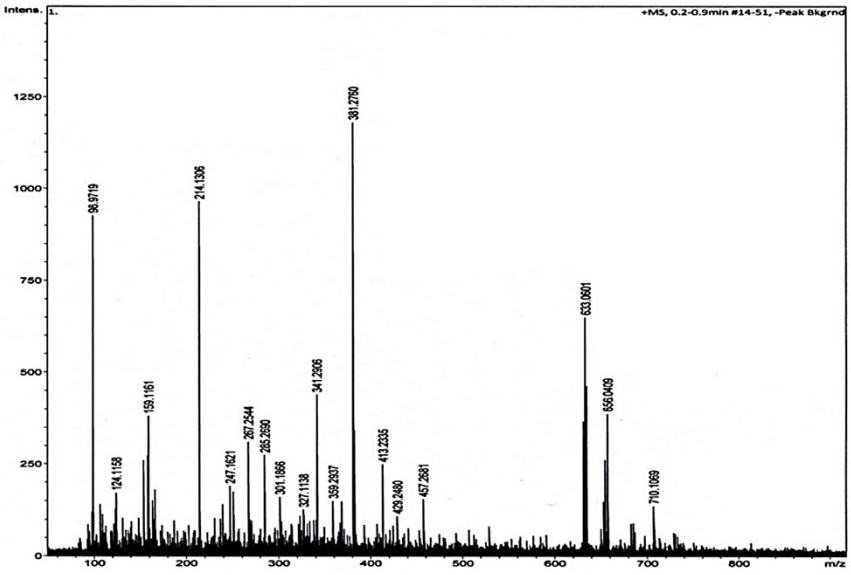

Fig. S4. Electro-spray ionization-time of flight mass spectrum of BTMP.

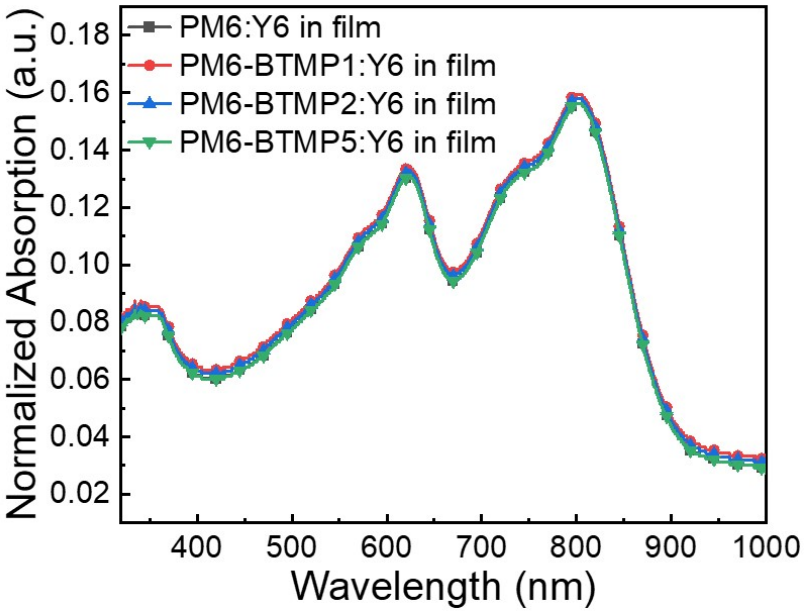

Fig. S5. Absorption of BTMP-modified PM6 polymers blends film with Y6.

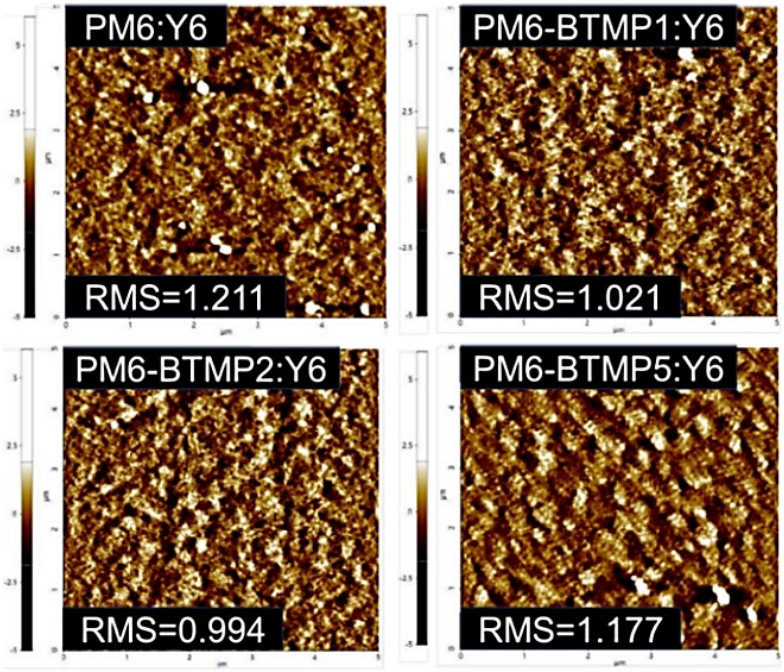

Fig. S6. AFM images of PM6:Y6 and BTMP-modified PM6 polymers with Y6.

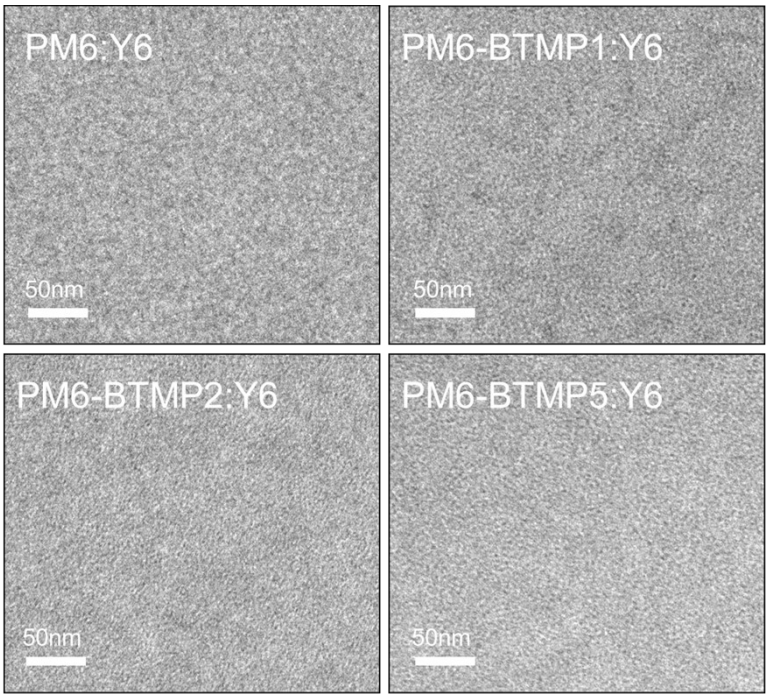

Fig. S7. TEM images of PM6:Y6 and BTMP-modified PM6 polymers with Y6.

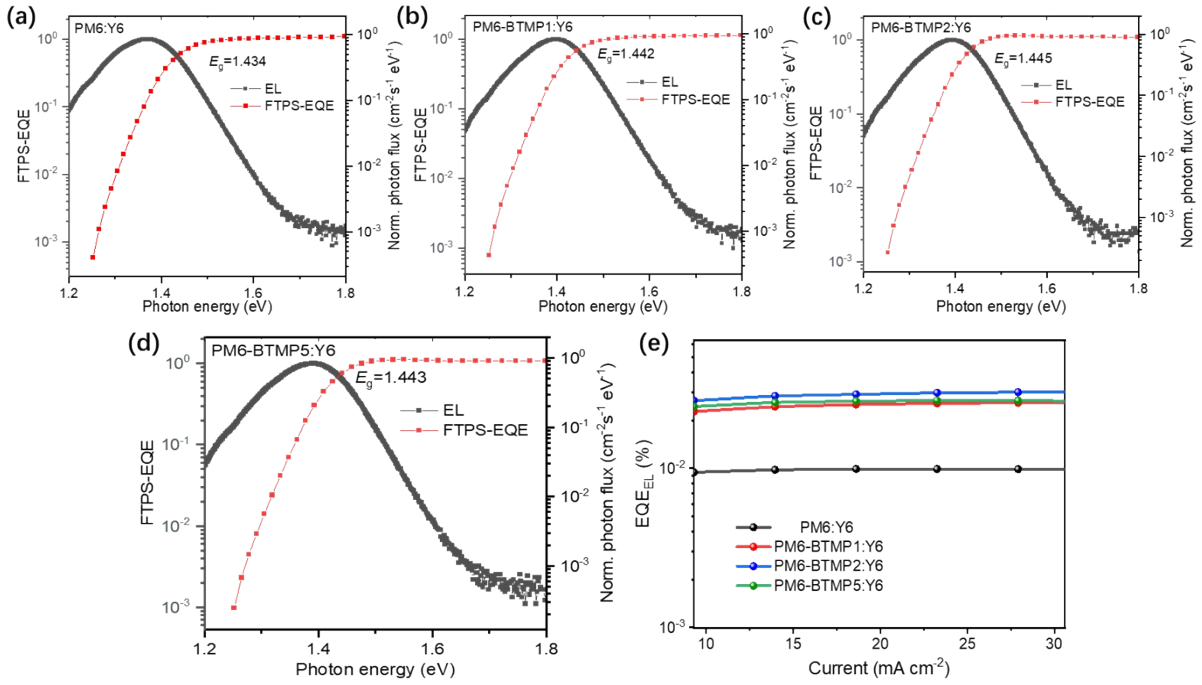

Fig. S8. EL, FTPS-EQE, and EQE_{EL} spectra of NFAs-OSCs based on the BTMP-modified PM6 polymers with Y6.

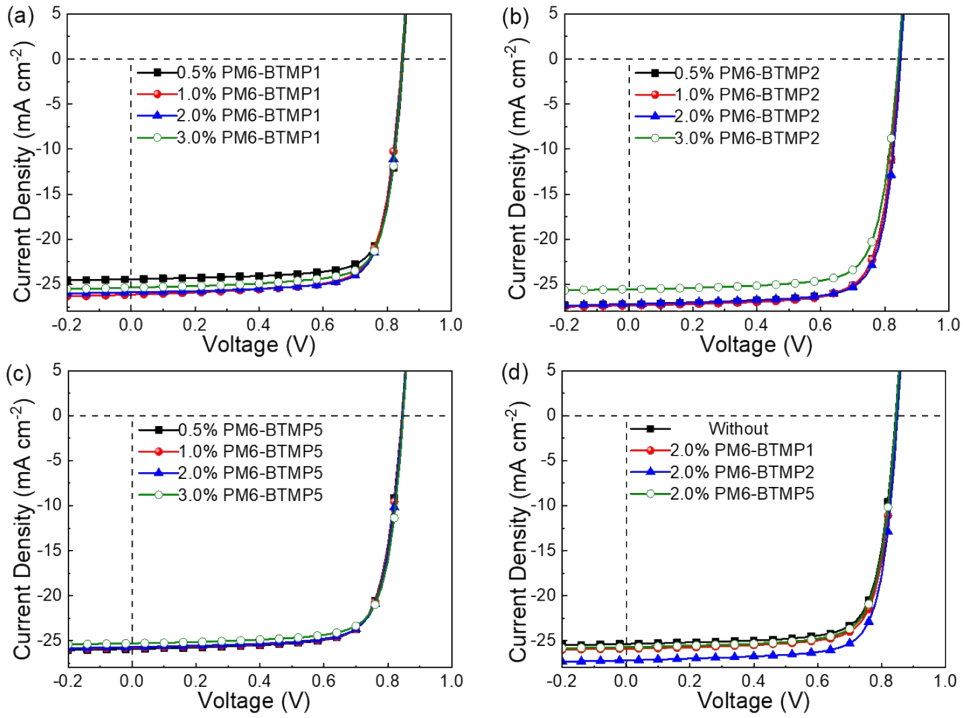

Fig. S9. *J-V* curves of the PM6:Y6-based NFAs-OSCs with different contents additives of BTMP-modified PM6 polymers.

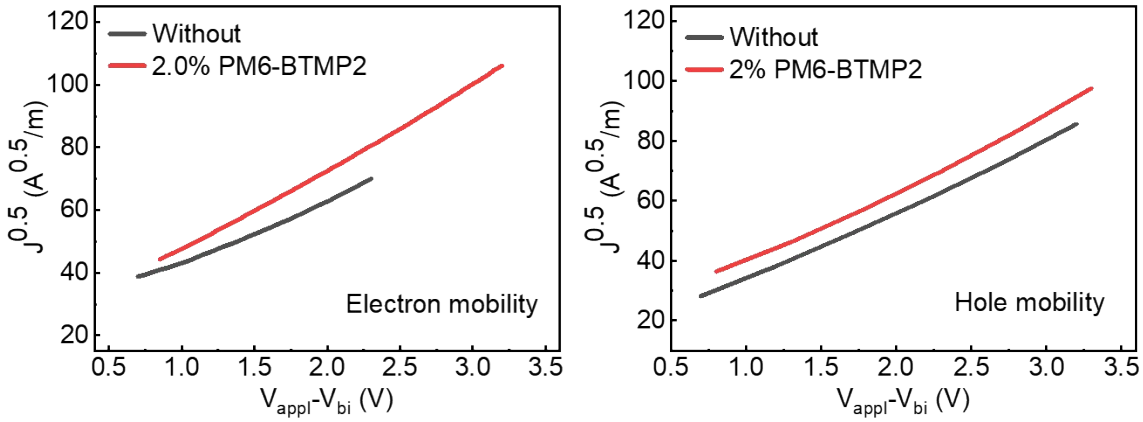

Fig. S10. Charge transport properties of the PM6:Y6 with 2% PM6-BTMP2 blend films obtained from SCLC: (a) electron mobility and (b) hole mobility.

Table S1. Electron mobility and hole mobility of BTMP-modified PM6 polymers with Y6 and PM6:Y6 blend film with 2 wt.% PM6-BTMP2 as additive.

Additive	Thickness (nm)	μ_h (cm^2 V^{-1} s^{-1})	μ_e (cm^2 V^{-1} s^{-1})	μ_h/μ_e
PM6:Y6	110	3.32×10^{-4}	4.59×10^{-4}	1.38
PM6-BTMP1:Y6	110	2.57×10^{-4}	1.28×10^{-4}	2.00
PM6-BTMP2:Y6	110	2.93×10^{-4}	1.13×10^{-4}	2.60
PM6-BTMP5:Y6	110	2.23×10^{-4}	1.06×10^{-4}	2.10
PM6:Y6 + 2.0 % PM6-BTMP2	110	3.76×10^{-4}	4.00×10^{-4}	0.94

Table S2. Photovoltaic parameters of various PM6:Y6-based NFAs-OSCs with different contents addition of BTMP-modified PM6 polymers with Y6.

Active layers	Additive	V_{OC} (V)	J_{SC} (mA/cm^2)	*FF* (%)	PCE (%)
PM6:Y6	Without	0.844	25.19	74.46	15.87
	0.5% PM6-BTMP1	0.850	24.42	77.73	16.13
	1.0% PM6-BTMP1	0.846	26.14	75.75	16.75
	2.0% PM6-BTMP1	0.847	25.90	77.20	16.93
	3.0% PM6-BTMP1	0. 848	25.37	77.08	16.58
	0.5% PM6-BTMP2	0.848	27.22	76.55	17.68
	1.0% PM6-BTMP2	0.846	27.34	76.32	17.66
	2.0% PM6-BTMP2	0.850	27.19	77.37	17.88
	3.0% PM6-BTMP2	0.844	25.54	76.19	16.40
	0.5% PM6-BTMP5	0.844	25.92	75.93	16.61
	1.0% PM6-BTMP5	0.844	25.75	76.54	16.64
	2.0% PM6-BTMP5	0.845	25.73	76.63	16.66
	3.0% PM6-BTMP5	0.848	25.30	76.78	16.47