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Electronic Supplementary Information

A new polytriarylamine derivative for dopant-free high-efficiency perovskite solar cells

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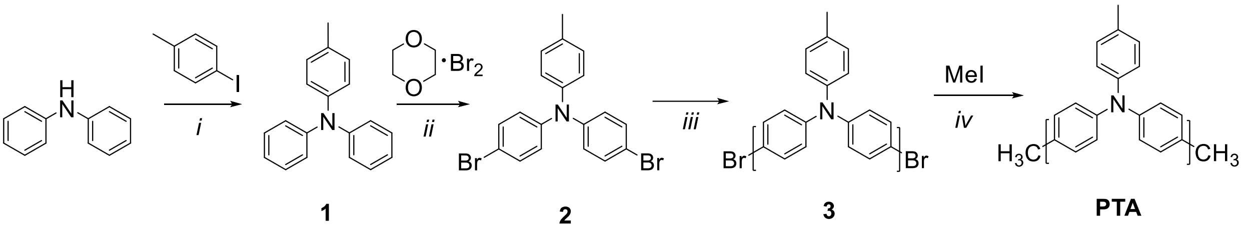
Synthesis of PTA

The polymer was synthesized according to Scheme 1.



i: Cu powder, K_2CO_3, nitrobenzene
ii: diethyl ether, -10°C
iii: Ni(dppp)Cl_2, potassium, $MgCl_2$, THF
iv: Ni(dppp)Cl_2, Mg, THF

Scheme 1. Synthesis of PTA

Synthesis of 4-methyltriphenylamine 1

A mixture of 4-iodotoluene (66.68 g, 30.6 mol), diphenylamine (43.94 g, 0.26 mol), anhydrous K_2CO_3 (41.4 g, 0.3 mol) and Cu powder (2.0 g) in nitrobenzene was refluxed overnight. After cooling to room temperature the crude mixture was filtered and washed with benzene (100 ml). The product was purified from nitrobenzene and 4-iodotoluene by evaporation under reduced pressure. The fraction with boiling point 180-200°C (3 mm Hg) was further purified with Al_2O_3 column chromatography (benzene: hexane 1:1) to yield a white solid (47.2 g, yield 70.1 %); m.p. = 68°C.

Synthesis of 4,4'-dibromo-(4''-methyl)triphenylamine 2

Bromine-1,4-dioxane complex (55 g, 0.22 mol) was slowly added to the solution of **1** (28.72g, 0.11 mol) in diethyl ether (140 ml) at -10°C. The temperature was maintained for 3h, after then, the reaction mixture was stirred overnight at room temperature. The crude solution was extracted with 20% NaOH, the organic fraction was washed with 5% acetic acid, and then the solvent was evaporated in vacuum. Purification by Al_2O_3 column chromatography (benzene : hexane 1:4) and further recrystallization from 90% acetic acid afforded a white solid (38.2 g, 82.6 %); m.p. = 107°C; Elem. Anal. % Calcd: C 57.71, H 3.62, Br 38.31; found: C 57.37, H 3.69, Br: 38.31

Synthesis of poly-[4,4'-dibromo-(4''-methyl)triphenylamine] 3

Potassium (5.21g, 0.133 mol) was added slowly to the solution of $MgCl_2$ (5.54 g, 0.058 mol) in anhydrous THF (300 ml) under argon atmosphere. The solution was refluxed for two hours and then cooled to the room temperature. A solution of **2** (24.52 g, 0.059 mol) in anhydrous THF (50 ml) was added dropwise. After 3 hours stirring at room temperature Ni(dppp)Cl_2 (0.35 g, 0.65 mmol) was added and the mixture was further heated at reflux for 2 hours. After cooling to room temperature, the crude mixture was poured into ethanol. Solid yellow-brown product was filtered and washed with four portions of hydrochloric acid (2% solution, 100 ml each portion) and then with water until neutral pH was reached. The crude product was redissolved in toluene (60ml) and the solid residue was filtered out. The solution was then poured into hexane (350 ml) to yield the yellow solid (6.35g, 39%); m.p. = 183-187°C; Elem. Anal. % Calcd: C 82.29, H 5.45, N 5.05, Br 7.20; found: C 82.18, H 4.87, N 5.15, Br: 7.03.

Synthesis of (poly-(4,4'-(4''-methyl)triphenylamine) PTA

The mixture of Mg (4.13 g, 0.17 mol), methyl iodide (60 ml, 0.11 mol), Ni(dppp)Cl_2 (0.15 g, 0.28 mmol) and **3** (6.0 g, 0.003 mol) in THF (95 ml) was stirred overnight at room temperature and then heated at reflux for 2h. After cooling to room temperature the crude mixture was poured into 2% solution of hydrochloric acid (1500 ml). A yellow solid was consequently washed with hydrochloric acid, water, ammonia hydroxide, water and then dried in vacuum at 50°C. Purification by column chromatography on silica gel (toluene) afforded the desired PTA (3.47 g, 61.4%); m.p. = 206-210°C. The glass transition temperature t_g= 185°C was determined with differential thermal analysis. Elem. Anal.% Calcd: C 88.56, H 6.08, N 5.36, found: C 88.47, H 5.71, N 5.83; λ_{max} = 314 nm in chloroform.

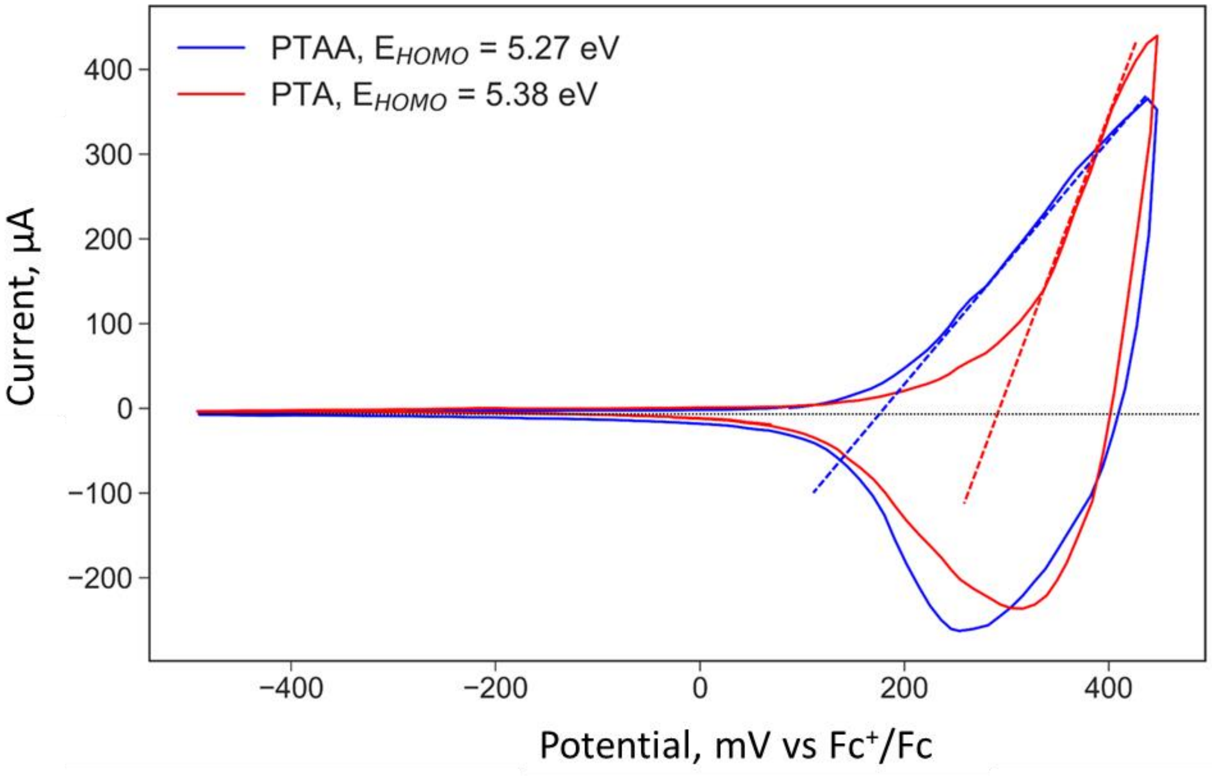


Figure S1. Cyclic voltammograms of PTA and PTAA films deposited on glassy carbon electrode

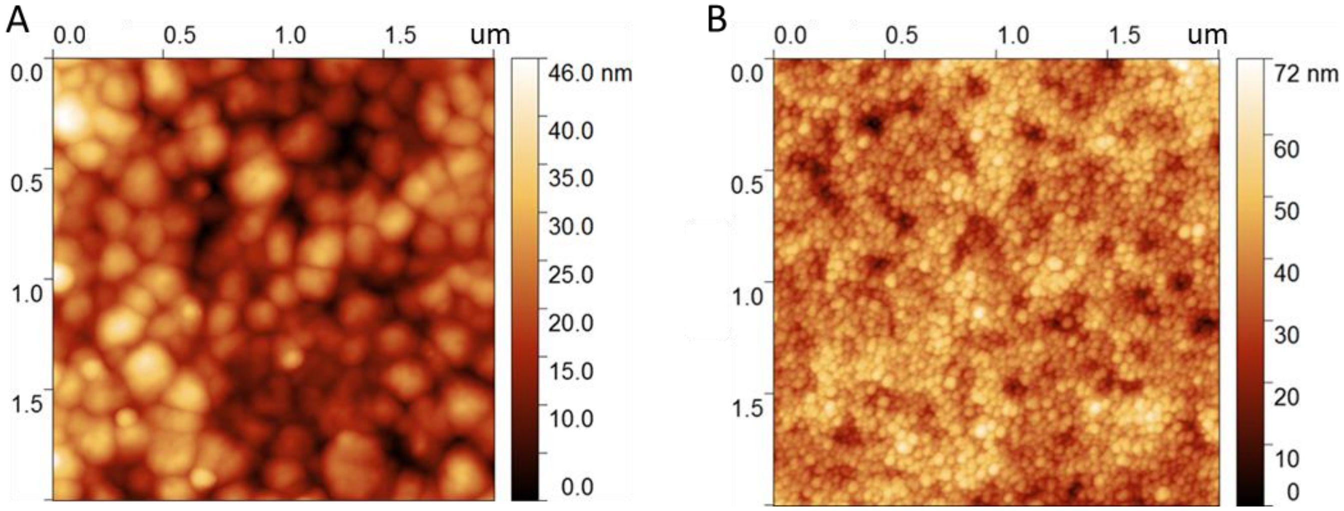


Figure S2. AFM topography images for A) ITO/SnO_2/$Cs_{0.15}FA_{0.85}PbI_{2.55}Br_{0.45}$/PTA and B) ITO/$SnO_2$/$Cs_{0.15}FA_{0.85}PbI_{2.55}Br_{0.45}$/PTA/$MoO_3$ stacks deposited following the procedure used for solar cell fabrication.

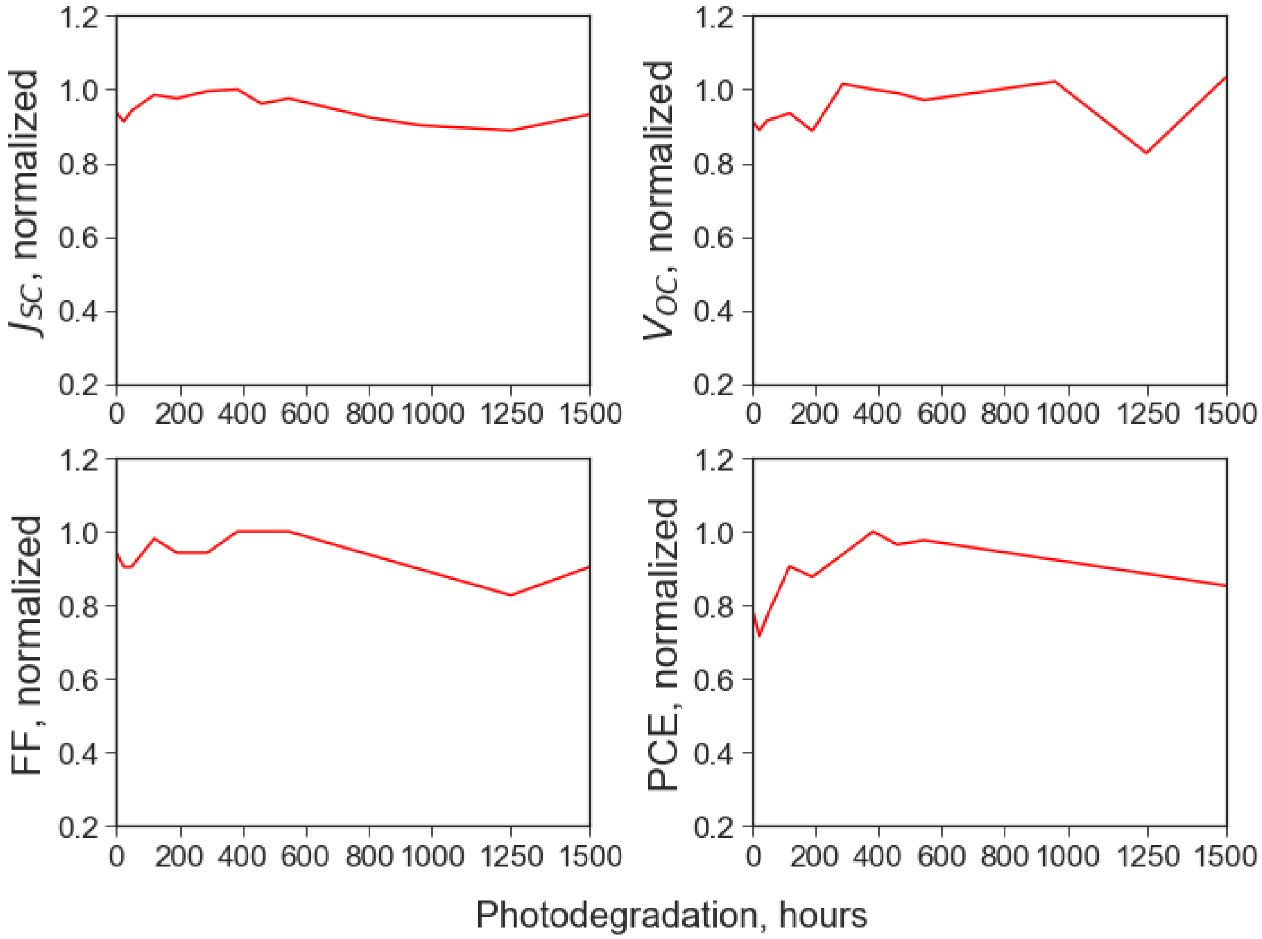


Figure S3. Evolution of PV parameters of ITO/SnO_2/$Cs_{0.15}FA_{0.85}PbI_{2.55}Br_{0.45}$ /PTA/MoO_3/Al cells (average across 4 cells) under continuous illumination (30 mW/cm^2, 45°C). UV portion of light was filtered.

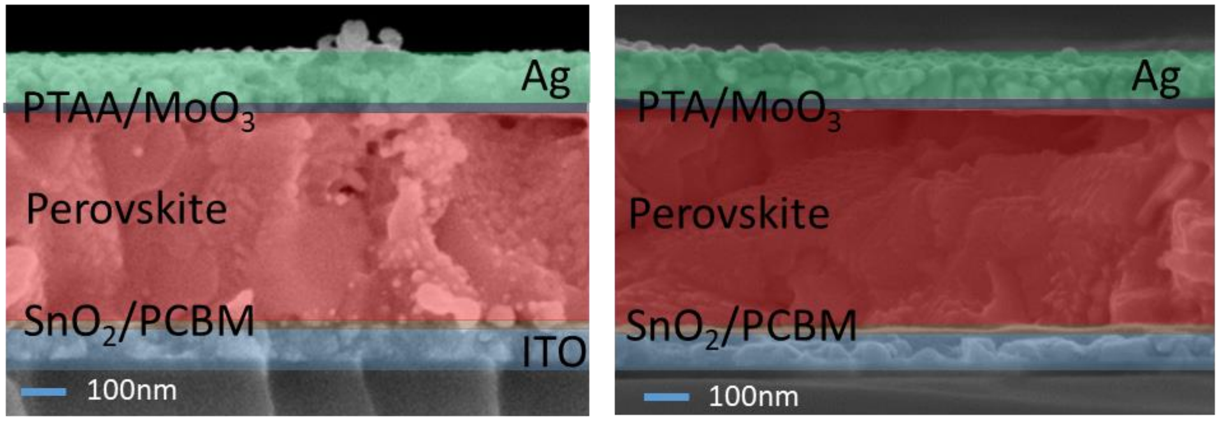


Figure S4. Cross-section SEM mages of solar cells assembled with PTAA (left) and PTA (right) hole transport materials. $MAPbI_3$ was used as the perovskite absorber layer

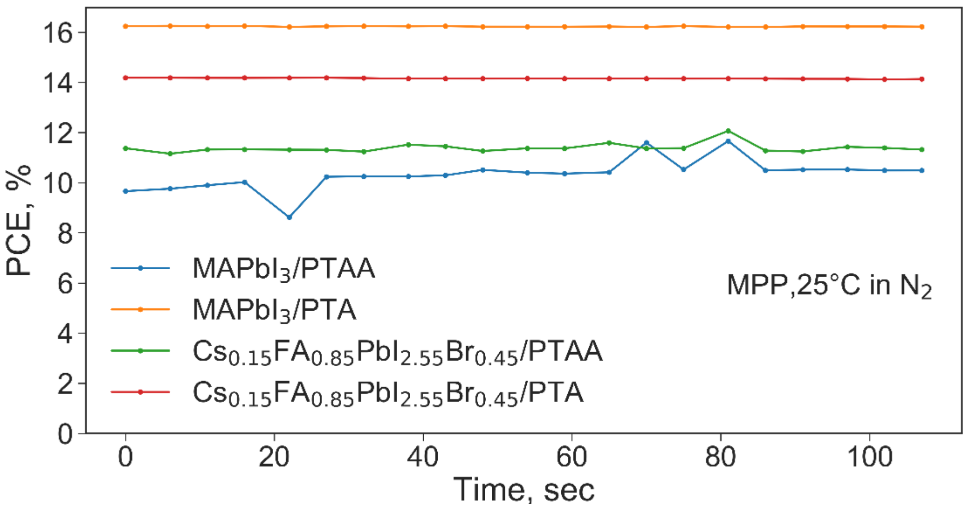


Figure S5. Evolution of the maximal power output of the solar cells fabricated using $Cs_{0.15}FA_{0.85}PbI_{2.55}Br_{0.45}$ and $MAPbI_3$ as light absorbers and PTAA or PTA as hole transport layer materials.

Table S1 Characteristics of the top ITO/SnO_2/PCBM/ $Cs_{0.15}FA_{0.85}PbI_{2.55}Br_{0.45}$/HTL/$MoO_3$/Ag solar cells. Cells were aged for 24 h in a nitrogen-filled glove box and measured with the voltage sweep rate of 10 mV/s in forward (FWD) and reverse (REV) directions.

HTL	Scan direction	V_{OC}, mV	J_{SC}, mA/cm^2	FF, %	η, %
PTA	FWD	1048	21.79	68.9	15.7
PTA	REV	1044	21.85	70.2	16.0
PTAA	FWD	1014	21.35	67.6	14.6
PTAA	REV	1008	21.38	68.9	14.9