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Supporting Information

Perovskite White Light-Emitting Diodes Based on a Molecular Blended Perovskite Emissive Layer

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1. EXPERIMENTAL SECTION

1.1 Materials.

Tris(4-bromophenyl)amine, *tetrakis*(triphenylphosphine)palladium(0) Pd(PPh₃)₄, and malononitrile were obtained from Sigma-Aldrich Co. and used without further purification. Pyridine, THF and toluene were dried and purified according to the known techniques and then used as a solvent. Synthesis of 5,5-dimethyl-2-phenyl-2-[5-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-2-thienyl]-1,3-dioxane (**II**) [1] was described previously. All reactions, unless stated otherwise, were carried out under an inert atmosphere.

1.2 Synthesis of compound 1.

Synthesis of compound **2** was described previously.[2] The general strategy for preparation of compound **1** is similar to those elaborated for the star-shaped molecules with alkyl- and phenyldicyanovilyl DCV groups,[3] and is outlined on Scheme S1. First, 4-*tris*(4-bromophenyl)amine (**I**) was reacted with compound **II** under Suzuki conditions to give a star-shaped precursor, *tris*{4-[5-(5,5-dimethyl-2-phenyl-1,3-dioxan-2-yl)-2-thienyl]phenyl}amine (**III**), in 82% isolated yield. In the next step, a solution of ketal **III** in THF was treated with 1M HCl to remove protecting 5,5-dimethyl-1,3-dioxane groups, resulting in the [nitrilotris(4,1-phenylenethiene-5,2-diyl)]tris(phenylmethanone) (**IV**) in 90% yield. Finally, Knoevenagel condensation of trifunctional ketone **IV** with malononitrile in pyridine under a microwave heating afforded the desired *tris*(4-{5-[dicyano(phenyl)methyl]-2-thienyl}phenyl)amine compound **1** in 70% isolated yield.

¹H and ¹³C NMR spectroscopy, elemental analysis, and mass-spectrometry were used to characterize the structure of the precursors and the final compound (see Figure S4-S9 of the Supplementary Information).



Scheme S1. Synthesis of compound 1. (a) Pd(PPh)₃, aq. 2M Na₂CO₃, toluene/ethanol, reflux, 8h; (b) 1M HCl, THF, reflux, 4h; (c) CH₂(CN)₂, pyridine, microwave heating, reflux, 24h.

1.3 Synthetic procedures for the synthesis of compound 1.

tris{4-[5-(5,5-dimethyl-2-phenyl-1,3-dioxan-2-yl)-2-thienyl]phenyl}amine (III). In an inert atmosphere, degassed solutions of tris(4-bromophenyl)amine (I, 1.3 g, 2.7 mmol) and 5,5dimethyl-2-phenyl-2-[5-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-2-thienyl]-1,3-dioxane (II, 3.9 g, 9.7 mmol) in toluene/ethanol mixture (50/5 mL) and 2M solution of aq. Na₂CO₃ (6.3 mL) were added to Pd(PPh₃)₄ (280 mg, 0.2 mmol). The reaction mixture was stirred at reflux for 8 h, and then it was cooled to room temperature and poured into 75 mL of water and 100 mL of toluene. The organic phase was separated, washed with water, dried over sodium sulfate and filtered. The solvent was evaporated in vacuum and the residue was dried at 1 Torr. The product was purified by column chromatography on silica gel (eluent toluene) to give pure compound III (2.35 g, 82%) as yellow solid. M.p. = 111-113 °C. ¹H NMR (250 MHz, CDCl₃): δ [ppm] 0.90 (s, 9H), 1.16 (s, 9H), 3.60 (d, 6H, J=11.0 Hz), 3.71 (d, 6H, J = 11.0 Hz), 6.70 (d, 3H, J = 3.7 Hz), 7.00 (d, 3H, J=3.7 Hz), 7.03–7.09 (overlapping peaks, 6H), 7.30-7.47 (overlapping peaks, 15H), 7.57–7.63 (overlapping peaks, 6H). ¹³C NMR (125 MHz, CDCl₃): δ [ppm] 22.27, 22.68, 30.04, 72.45, 99.69, 121.73, 124.24, 126.68, 126.90, 127.01, 128.29, 128.46, 129.24, 140.25, 144.59, 145.78, 146.47. Calcd (%) for C₆₆H₆₃NO₆S₃: C, 74.62; H, 5.98; S, 9.05; N, 1.32. Found: C, 74.76; H, 6.14; S, 9.21; N, 1.26. MALDI-MS: found m/z 1062.99; calculated for [M]⁺ 1062.43.

[nitrilotris(4,1-phenylenethiene-5,2-diyl)]tris(phenylmethanone) (IV). 1M HCl (6.2 mL) was added to a solution of compound **III** (2.2 g, 2.1 mmol) in THF (30 mL) and then the reaction mixture was stirred for 4 hours at reflux. During the reaction, the product was gradually formed as a precipitate. After completion of the reaction the organic phase was separated using diethyl ether, washed with water and filtered off to give pure compound give pure compound **IV** (1.5 g, 90%) as red powder. M.p. = 127-130°C. ¹H NMR (250 MHz, CDCl₃): δ [ppm] 7.16-7.21 (overlapping peaks, 6H), 7.29 (d, 3H, *J* = 4.1 Hz), 7.46-7.65 (overlapping peaks, 18H), 7.82-7.91 (overlapping peaks, 6H). ¹³C NMR (125 MHz, CDCl₃): δ [ppm] 123.34, 124.60, 127.49, 128.42, 128.59, 129.05, 132.14, 136.13, 138.11, 141.82, 147.37, 152.68, 187.89. Calcd (%) for C₅₁H₃₃NO₃S₃: C, 76.19; H, 4.14; N, 1.74; S, 11.96. Found: C, 76.31; H, 4.27; N, 1.62; S, 11.81. MALDI-MS: found m/z 803.93; calculated for [M]⁺ 804.03.

tris(4-{5-[dicyano(phenyl)methyl]-2-thienyl}phenyl)amine (compound 1). Compound IV (1.31 g, 1.6 mmol), malononitrile (0.86 g, 13.0 mmol) and dry pyridine (19.0 mL) were placed in a reaction vessel and stirred under argon atmosphere for 24 hours at reflux using a microwave heating. After completeness of the reaction, the pyridine was evaporated in vacuum and the residue was dried at 1 Torr. This crude product was purified by column chromatography on

silica gel (eluent dichloromethane). Further purification included precipitation of the product from its THF solution with toluene and hexane to give pure product as a black solid (1.09 g, 70%). M.p. = 209 °C. ¹H NMR (250 MHz, CDCl₃): δ [ppm] 7.11–7.68 (overlapping peaks, 6H), 7.34 (d, 3H, J = 4.3 Hz), 7.43–7.63 (overlapping peaks, 21H), 7.65 (d, 3H, J = 4.3 Hz). ¹³C NMR (125 MHz, CDCl₃): δ [ppm] 76.29, 114.10, 114.77, 124.34, 124.66, 127.76, 127.92, 128.79, 129.38, 131.62, 135.97, 136.85, 138.61, 147.62, 154.89, 164.14. Calcd (%) for C₆₀H₃₃N₇S₃: C, 76.01; H, 3.51; N, 10.34; S, 10.15. Found: C, 76.11; H, 3.52; N, 10.29; S, 10.11. MALDI-MS: found m/z 948.73; calculated for [M]⁺ 948.17.

1.4 General.

¹H NMR spectra were recorded in a "Bruker WP-250 SY" spectrometer, working at a frequency of 250.13 MHz and utilizing CDCl₃ signal (7.25 ppm) as the internal standard. ¹³C NMR spectra were recorded using a "Bruker Avance II 300" spectrometer at 75 MHz. In the case of ¹H NMR spectroscopy, the compounds to be analyzed were taken in the form of 1% solutions in CDCl₃. In the case of ¹³C NMR spectroscopy, the compounds to be analyzed were taken in the form of 5% solutions in CDCl₃. The spectra were then processed on the computer using the ACD Labs software. In the case of column chromatography, silica gel 60 ("Merck") was taken.

Mass-spectra (MALDI) was registered on the Autoflex II Bruker (resolution FWHM 18000), equipped with a nitrogen laser (work wavelength 337 nm) and time-of-flight massdetector working in reflections mode. The accelerating voltage was 20 kV. Samples were applied to a polished stainless steel substrate. Spectrum was recorded in the positive ion mode. The resulting spectrum was the sum of 300 spectra obtained at different points of the sample. 2,5-Dihydroxybenzoic acid (DHB) (Acros, 99%) and α -cyano-4-hydroxycinnamic acid (HCCA) (Acros, 99%) were used as matrices. Elemental analysis of C and H elements was carried out using CHN automatic analyzer CE 1106 (Italy). The settling titration using BaCl₂ was applied to analyze sulphur. Experimental error for elemental analysis is 0.30-0.50%. The Knövenagel condensation was carried out in the microwave "Discovery", (CEM Corporation, USA), using a standard method with the open vessel option, 50 watts.



Figure S1. The solubility tests. The DMF solution of a) MAPbBr₃ and b) MAPb(Br_{0.6}Cl_{0.4})₃. The MAPbBr₃ perovskite solution blended with c) Ir(dpm)PQ2, d) Rubrene, e) PO-01-TB, and f) Hex-Ir(piq)3. The MAPbBr₃ perovskite DMF solution blended with g) Compound **1**, and h) Compound **2**. The MAPb(Br_{0.6}Cl_{0.4})₃ perovskite solution blended with i) Compound **1**, and j) Compound **2**.



b				
	The weight of the	The weight of the	The weight of	The concentration
	organic powder	perovskite DMF	residuals	of the saturated
		solution		solution
Ir(dpm)PQ ₂	2.8 mg	280 mg	0.7 mg	0.750 wt%
PO-01-TB	5.8 mg	580 mg	1.4 mg	0.759 wt%
Hex-Ir(piq)₃	4.6 mg	460 mg	4.1 mg	0.110 wt%
rubrene	3.6 mg	360 mg	3.0 mg	0.167 wt%

Figure S2. a) A photograph shows the residuals in bottles after withdrawing the supernatant. The residuals in the bottles were dried up to estimate the exact weight of residuals. b) The amount of organic materials and perovskite DMF solution used to calculate the concentrations of the saturated solutions.



Figure S3. PL spectra and cross-sectional SEM images of the MAPbBr3 films blended with a) Ir(dpm)PQ₂, b) rubrene, c) PO-01-TB, and d) Hex-Ir(piq)₃.



Figure S4. The perovskite light-emitting diodes. The electroluminescence spectra of the device based on MAPbBr₃ blended with Ir(dpm)PQ2.



Figure S5. Scaled-up region (from 100 to 230 ^oC) of the first DSC heating scan for compound 1.

1. ¹H, ¹³C NMR Spectra



Figure S6. ¹H NMR spectrum of compound III in CDCl₃.





Figure S8. ¹H NMR spectrum of compound IV in CDCl₃.



Figure S9. ¹³C NMR spectrum of compound IV in CDCl₃.







Figure S12. Morphology of the perovskite films. The cross-section and top view scanning electron microscopy (SEM) images of the a),b), the MAPb(Br_{0.6}Cl_{0.4})₃ film, c),d), the MAPb(Br_{0.6}Cl_{0.4})₃ film blended with compound **1**, and e),f), the MAPb(Br_{0.6}Cl_{0.4})₃ film blended with compound **2**.



Figure S13. Surface morphology of the perovskite films. Low-magnification scanning electron microscopy top view images of a),b),c), the MAPbBr₃ film, d),e),f), the MAPb(Br_{0.6}Cl_{0.4})₃ film.



Figure S14. a) X-ray diffraction patterns in a logarithmic scale. b) X-ray diffraction pattern of perovskite films between 10° and 20°. c) The (200) reflection peaks of the pure and doped MAPb(Br_{0.6}Cl_{0.4})₃ films. The XRD pattern of MAPbBr₃ films was also shown.

а



Figure S15. Optical properties of the perovskite films. a) Absorption spectra and b) normalized photoluminescence spectra of the MAPb(Br_{0.6}Cl_{0.4})₃ films, the MAPb(Br_{0.6}Cl_{0.4})₃ film blended with compound **1**, and the MAPb(Br_{0.6}Cl_{0.4})₃ film blended with compound **2**. The PL spectra of the blended films were normalized to the peak in the red region. The PL spectrum of the as-prepared perovskite film was used as a reference and was normalized to its own peak.



Figure S16. Optical properties of the perovskite and organic materials. Photoluminescence spectra of the films of MAPbBr3, MAPb(Br0.6Cl0.4)3, compound **1**, and compound **2**.



Figure S17. Optical properties of the perovskite films. Confocal laser-scanning fluorescence microscope spectral images of a),b), the MAPb(Br_{0.6}Cl_{0.4})₃ films, c),d), the MAPb(Br_{0.6}Cl_{0.4})₃ film blended with compound **1**, and e),f), the MAPb(Br_{0.6}Cl_{0.4})₃ film blended with compound **2** in the wavelength range between a),c),e), 480 – 550 nm, and b),d),f), 600 – 750 nm.



Figure S18. Cross-sectional SEM images of a) MAPbBr₃, e) MAPbBr₃+compound 1, i) MAPbBr₃+compound 2. b),f),j),f),g),h),j),k),l) XPS mapping images of those perovskite films.



Figure S19. Micro-PL images and PL spectra.



Figure S20. Perovskite light-emitting diodes. a) Device structure. b) Energy band diagram.



Figure S21. The cross-sectional EM images of the perovskite light-emitting diodes with the emissive layer composed of perovskite. a) compound1 and b) compound 2.



Figure S22. Electrical properties of the perovskite light-emitting diode based on MAPbBr₃ film blended with compound **1**. a) Current density-voltage curve. b) Luminance-voltage curve. c) External quantum efficiency-voltage curve. d) Current efficiency-voltage curve.



Figure S23. Electrical properties of the perovskite light-emitting diode based on MAPb(Br_{0.6}Cl_{0.4})₃ film blended with compound **2**. a) Current density-voltage curve. b) Luminance-voltage curve. c) External quantum efficiency-voltage curve. d) Current efficiency-voltage curve. e) Radiance-voltage curve.



Figure S24. Perovskite light-emitting diodes. Normalized electroluminescence spectra of a) the device based on MAPbBr₃ film doped with compound **1**, and b) the device based on MAPb(Br_{0.6}Cl_{0.4})₃ film doped with compound **2**. The electroluminescence spectra are normalized to the peak with a short wavelength.

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