

Prompting power conversion efficiency of perovskite solar cells to 17.7% with Indolo[3,2-b]carbazole dopant-free hole transporting material by improving its spatial configuration

Bin Cai^a, Xichuan Yang^{*a},
Xiaoqing Jiang^a, Ze Yu^{*a}, Anders Hagfeldt^b and Licheng Sun^{ac}

^a State Key Laboratory of Fine Chemicals, Institute of Artificial Photosynthesis, DUT–KTH Joint Education and Research Center on Molecular Devices, Dalian University of Technology (DUT), Dalian 116024, China. E-mail: yangxc@dlut.edu.cn; ze.yu@dlut.edu.cn.

^b Laboratory of Photomolecular Science, Institute of Chemical Sciences and Engineering, École Polytechnique Fédérale de Lausanne, CH-1015-Lausanne, Switzerland.

^c Department of Chemistry, School of Chemical Science and Engineering, KTH Royal Institute of Technology, 100 44 Stockholm, Sweden.

1. General information

Materials and measurements

The starting materials for C201 and C202 synthesis were all commercially available from Energy Chemical. PbI₂, PbBr₂, 4-tert-butylpyridine (t-BP), tris(2-(1H-pyrazol-1-yl)-4-tert-butylpyridine)- cobalt (III) tris(bis(trifluoromethylsulfonyl)imide) (FK209) and bis(trifluoromethane) sulfonimide lithium salt (LiTFSI) were purchased from Sigma-Aldrich. N, N-dimethylformamide (DMF), dimethyl sulphoxide (DMSO) and chlorobenzene (CB) were purchased from J&K. Methylammonium bromide (MABr), methylammonium iodide (MAI) and formamidinium iodide (FAI) were purchased from Xi'an Polymer Light Technology Corp. Spiro-OMeTAD was purchased from Dalian HeptaChroma SolarTech Co., Ltd. All the chemicals were directly used without further purification.

¹H-NMR spectrum was recorded on a Varian INOVA 400NMR apparatus. Chemical shifts were calibrated against TMS as an internal standard. UV-vis absorption spectra were measured by Agilent 8453 spectrophotometer. Cyclic voltammetry measurements were performed with CHI 630 Electrochemistry work station. The first oxidation potentials of C201 and C202 were conducted in the dichloromethane solution with 0.1M TBAPF₆ as the supporting electrolyte. The three electrodes consist of a glassy carbon as working electrode, a platinum wire as counter electrode and an Ag/AgCl electrode as the reference electrode. The redox potential was calibrated by the Fc/Fc⁺ as the internal reference.

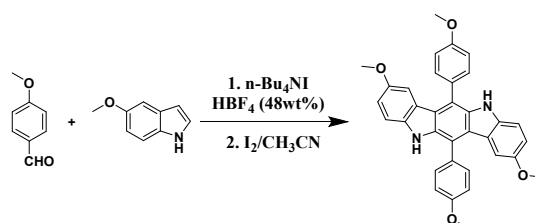
Hole mobility was measured by fabricating the hole-only device: ITO/PEDOT:PSS/HTM/Au. And the results were obtained by the Mott-Gurney's equation, $J = 9\varepsilon_r\varepsilon_0\mu_h V^2/8L^3$, where ε_r is the relative dielectric constant of the transport medium, normally $\varepsilon_r = 3$ for organic materials; ε_0 is permittivity of the free space; L is the thickness of the film; μ_h is the hole mobility; and V is the applied voltage. C201 and C202 are 100 °C hot-cast above the PEDOT:PSS, and their thicknesses are ~ 100 nm.

Scan electron microscopy was conducted with FEI (Field Emission Instruments: Nova Nano SEM 450), USA. The surface morphology of C201 and C201 films were characterized by atomic force microscopy (Dimension ICON, Bruker, Germany). *J-V* characteristics were carried out at the Keithley 2400 meter under the simulated sunlight of AM 1.5G, and calibrated with a standard silicon solar cell (SER. No:

506/0358). A black mask with a circular aperture (0.05 cm²) was applied on the top of the cell. The J-V curves are recorded at a scan rate of 10 mV s⁻¹. The incident photon-to-current conversion efficiency (IPCE) spectra were obtained by a Hypermono-light (SM-25, Jasco Co. Ltd., Japan). A standard silicon solar cell was used as reference before the measurement. Steady-state photoluminescence (PL) measurements were performed with Spectro fluorometer (Horiba Jobin Yvon, Fluorolog-3) and the time resolved PL decay spectra were measured with the Edinburgh LP920.

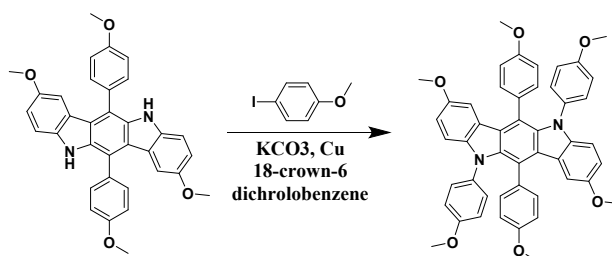
2. Synthetic procedures

All the reactions followed the reported papers.^{1,2}



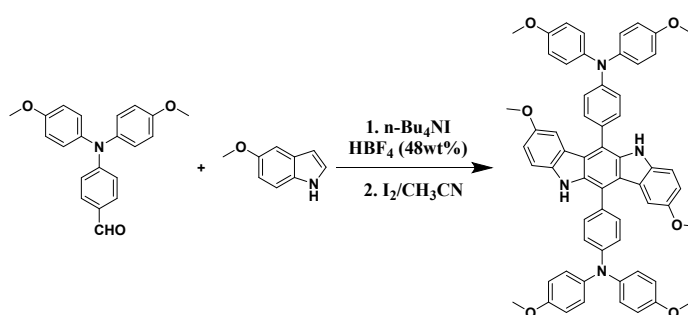
2,8-dimethoxy-6,12-bis(4-methoxyphenyl)-5,11-dihydroindolo[3,2-

b]carbazole: A solution of aqueous 48 (wt)% HBF₄ (5 mmol, 0.92 g) and n-Bu₄NI (5 mmol, 1.85 g) in acetonitrile (50 ml) was added to a solution of 5-methoxy-indole (20 mmol, 2.94 g) and the corresponding 4-methoxybenzaldehyde (20 mmol, 2.72 g) in acetonitrile (135 ml) on stirring at ice water bath. The resulting dark-blue reaction mixture was stirred for overnight at ambient temperature. After that, the solid was filtered off, and washed with acetonitrile (40 ml) and methanol (40 ml). The grey color crude products were then transferred to a round bottle added with iodine (1mmol, 0.25 g) and 25 ml acetonitrile, and reflux for 12h. the mixture purified by flash chromatography on silica gel with DCM as eluent. Light yellow powders were obtained after drying the solvent by rotation evaporation with a yield of 4.47 g (85%). C₃₄H₂₈N₂O₄ [M⁺], Exact Mass = 528.2049, MS(MALDI-TOF) = 528.2065.

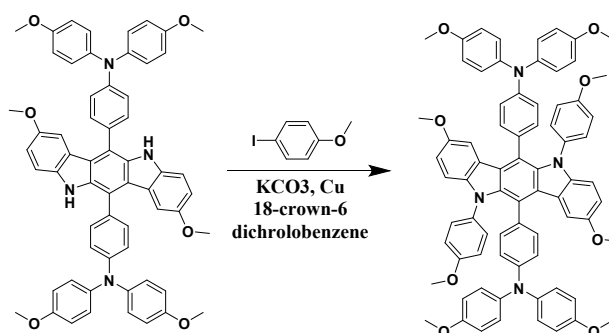


2,8-dimethoxy-5,6,11,12-tetrakis(4-methoxyphenyl)-5,11-

dihydroindolo[3,2-b]carbazole: The reaction mixtures consisting of 2,8-dimethoxy-6,12-bis(4-methoxyphenyl)-5,11-dihydroindolo[3,2-b]carbazole (1.00 g, 1.89mmol), potassium carbonate (1.56 g, 11.34 mmol), iodoanisole (2.21 g, 9.45 mmol), copper (0.73 g, 11.34mmol), 18-crown-6 (0.10 g, 0.38 mmol), and 1,2-dichlorobenzene (ca.15 mL) were stirred at reflux temperature for 24 h. The reaction mixtures were cooled down and filtrated, the solvent was distilled in a vacuum, and the crude product was subjected to silica gel column chromatography with dichloromethane as eluent. Yellow powders were obtained with a yield of 1.15 g (82%). ¹H-NMR (400 MHz, CDCl₃) δ 7.05 (s, 4H), 6.70 (t, J = 53.0 Hz, 14 H), 6.27 (s, 4H), 3.77 (s, 18 H). C₄₈H₄₀N₂O₆ [M⁺], Exact Mass = 740.2886, MS(MALDI-TOF) = 740.2875.



4,4'-(2,8-dimethoxy-5,11-dihydroindolo[3,2-b]carbazole-6,12-diyl)bis(N,N-bis(4-methoxyphenyl)aniline): A solution of aqueous 48 (wt)% HBF₄ (5 mmol, 0.92 g) and n-Bu₄NI (5 mmol, 1.85 g) in acetonitrile (50 ml) was added to a solution of 5-methoxyindole (20 mmol, 2.94 g) and the corresponding 4-[Bis(4-methoxyphenyl)amino]benzaldehyde (20 mmol, 6.66 g) in acetonitrile (135 ml) on stirring at ice water bath. The resulting dark-blue reaction mixture was stirred for overnight at ambient temperature. After that, the solid was filtered off, and washed with acetonitrile (40 ml) and methanol (40 ml). The grey color crude products were then transferred to a round bottle added with iodine (1mmol, 0.25 g) and 25 ml acetonitrile, and reflux for 12 h. the mixture purified by flash chromatography on silica gel with DCM as eluent. Light yellow powders were obtained after drying the solvent by rotation evaporation with a yield of 7.47 g (81%). C₆₀H₅₀N₄O₆ [M⁺], Exact Mass = 922.3730, MS(MALDI-TOF) = 922.3752.



4,4'-(2,8-dimethoxy-5,11-bis(4-methoxyphenyl)-5,11-dihydroindolo[3,2-b]carbazole-6,12-diyl)bis(N,N-bis(4-methoxyphenyl)aniline): The reaction mixtures consisting of 4,4'-(2,8-dimethoxy-5,11-dihydroindolo[3,2-b]carbazole-6,12-diyl)bis(N,N-bis(4-methoxyphenyl)aniline) (3.00 g, 3.25 mmol), potassium carbonate (2.70 g, 19.50 mmol), iodoanisole (3.80 g, 16.25 mmol), copper (1.25 g, 19.50 mmol), 18-crown-6 (0.17 g, 0.65 mmol), and 1,2-dichlorobenzene (ca.25 mL) were stirred at reflux temperature for 24 h. The reaction mixtures were cooled down and filtrated, the solvent was distilled in a vacuum, and the crude product was subjected to silica gel column chromatography. Yellow powders were obtained with a yield of 3.05 g (83%). ¹H-NMR (400 MHz, CDCl₃) δ 6.94 (d, J = 20.3 Hz, 18 H), 6.86 – 6.57 (m, 20 H), 6.42 (d, J = 26.0 Hz, 2 H), 3.79 (s, 24 H). C₇₄H₆₂N₄O₈ [M⁺], Exact Mass = 1134.4568, MS(MALDI-TOF) = 1134.4576.

3. Device fabrication

The PSC devices were fabricated according to previous reports³. the 25 mm × 15 mm fluorine-doped tin oxide (FTO) glass substrates were cleaned in an ultrasonic bath containing acetone, 2-propanol, and ethanol for 20 min in sequence. A compact TiO₂ thin film with thickness around 30 nm was deposited on cleaned FTO substrates by spray pyrolysis of the titanium precursor and annealed at 500 °C for 30 min in air. Then a layer of mesoporous TiO₂ around 120 nm were deposited by spin-coating method and sintered in the air at 500°C for 30 min in air.

The mixed-ion perovskite precursor solution of (FAPbI₃)_{0.85}(MAPbBr₃)_{0.15} was prepared by dissolving the FAI (1 M), MABr (0.2 M), PbI₂ (1.1 M) and PbBr₂ (0.2 M) in a mixed solvent of dimethyl formamide (DMF) and dimethyl sulfoxide (DMSO) (4:1, v/v). The perovskite solution was spin coated in a two-steps program at 1000 and 6000 rpm for 10 and 30 s, respectively. During the second step, 120 μL of chlorobenzene was poured on the spinning substrate 15 s prior to the end of the program. The substrates were then annealed at 100 °C for 1 h. After the perovskite cooled down to room temperature, the respective HTMs spiro-OMeTAD (72.3 mg ml⁻¹ in chlorobenzene with 28.8 μl t-BP, 17.5 μl 520 mg ml⁻¹ LiTFSI, 30 μl 300 mg ml⁻¹ FK209), C201 (10 mg ml⁻¹ in chlorobenzene) and C202 (10 mg ml⁻¹ in chlorobenzene) were spin coated at 3000 rpm for 30 s. Finally, 80 nm of gold top electrode was thermally evaporated under high vacuum. All the procedures were completed in the ambient environment with relative humidity below 20%.

4. Characterization

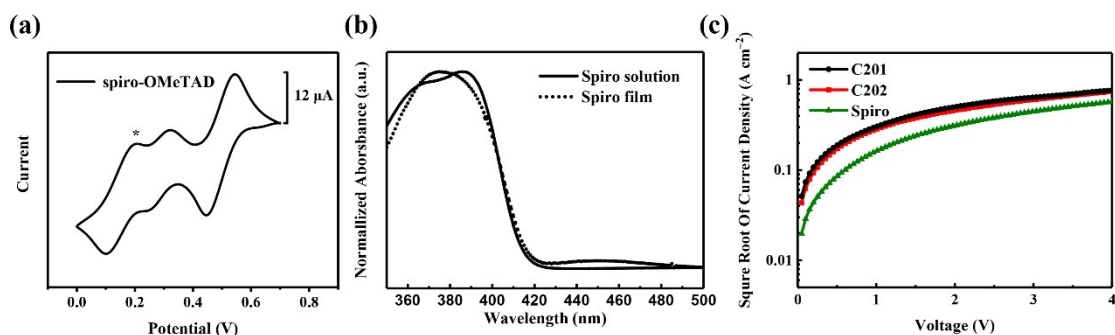


Fig. S1 a) Cyclic voltammety of spiro-OMeTAD measured in dichloromethane with 0.1 M TBAPF6 as supporting electrolyte, the peak marked by star is attributed to Fe/Fe^+ . b) UV-vis absorption spectra of the spiro-OMeTAD in dichloromethane solution and in thin films. c) Square root of current density–voltage curves for C201, C202 and spiro-OMeTAD, measured by hole-only devices.

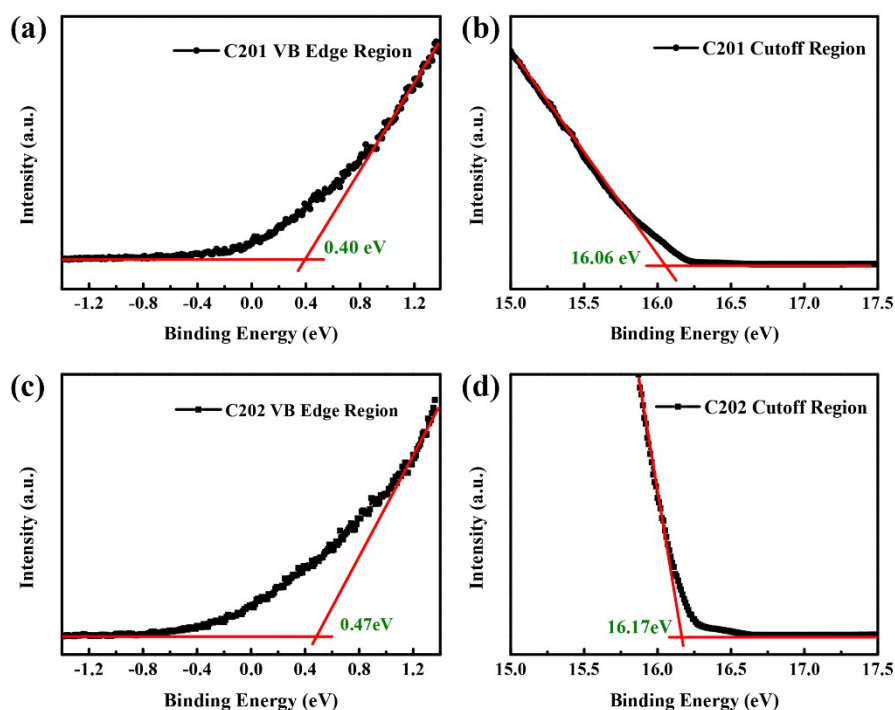


Fig. S2 Ultraviolet Photoelectron Spectra of C201 and C202 deposited on FTO.

Table S1 Summary of the optical and electrochemical properties of HTMs

Samples	$\lambda_{\text{max,sol}}^{\text{a}}$ [nm]	$\lambda_{\text{max,fil}}^{\text{b}}$ [nm]	HOMO ^c [eV]	HOMO ^d [eV]	LUMO ^e [eV]	T _d [°C]	hole mobility [cm ² V ⁻¹ s ⁻¹]
C201	431	439	-5.27	-5.39	-2.50	371	1.8E-4
C202	433	436	-5.23	-5.31	-2.49	396	1.5E-4

^{a)} Absorption spectrum in dichloromethane. ^{b)} Absorption spectrum on glass film. ^{c)} HOMO level calculated from the first oxidation potential peak of the cyclic voltammetry. ^{d)} HOMO level calculated from the UPS on glass film. ^{e)} LUMO = HOMO + E_g. HOMO calculated from CV.

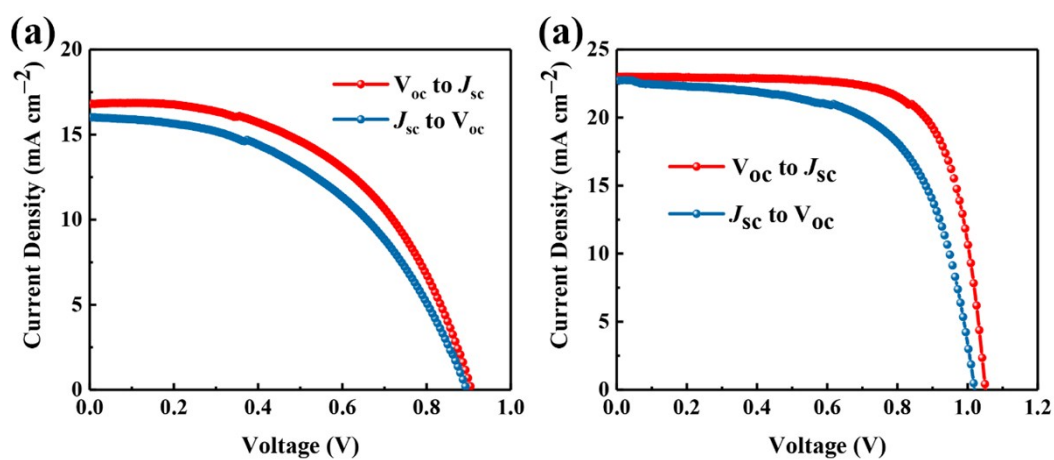
**Fig. S3** Current density-voltage characteristics based on a) C201 and b) C202 at forward scan and reverse scan under 100 mW cm⁻² illumination (AM 1.5G).

Table S2 Photovoltaic performance based on C201 and C202 at forward scan and reverse scan 100 mW cm⁻² illumination (AM 1.5G).

Sample		V_{oc} [V]	J_{sc} [mA cm ⁻²]	FF [%]	PCE [%]
C201	V_{oc} to J_{sc}	0.90	16.9	51.3	7.8
	J_{sc} to V_{oc}	0.89	16.1	47.4	6.8
C202	V_{oc} to J_{sc}	1.05	23.0	73.1	17.7
	J_{sc} to V_{oc}	1.02	22.7	62.9	14.6

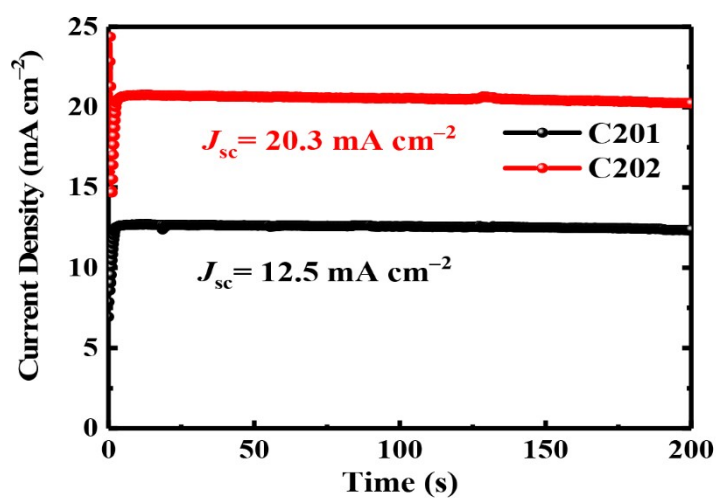


Fig. S4 Stabilized J_{sc} output at AM 1.5G simulated sunlight at the maximum power voltage, 0.61 V for C201, and 0.86 V for C202.

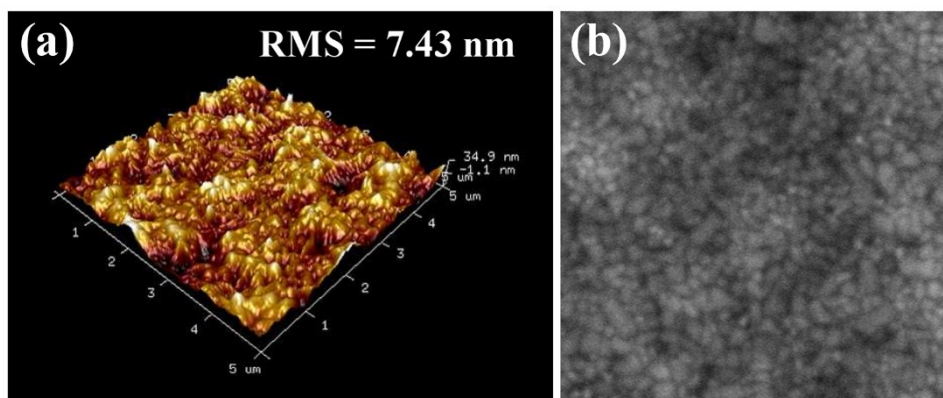


Fig. S5 a). Perovskite 3D AFM images covered with spiro-OMeTAD, $5.0 \mu\text{m} \times 5.0 \mu\text{m}$ b). Perovskite surface SEM images covered with spiro-OMeTAD, $5.0 \mu\text{m} \times 5.0 \mu\text{m}$.

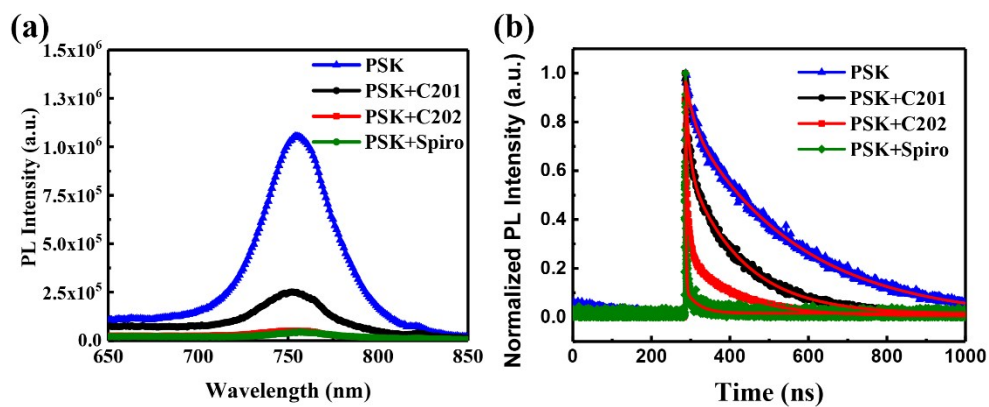


Fig.S6 a). Steady-state PL quenching, and b). time-resolved PL decay of bare perovskite, perovskite with C201, perovskite with C202 and perovskite with spiro-OMeTAD excited by 460 nm.

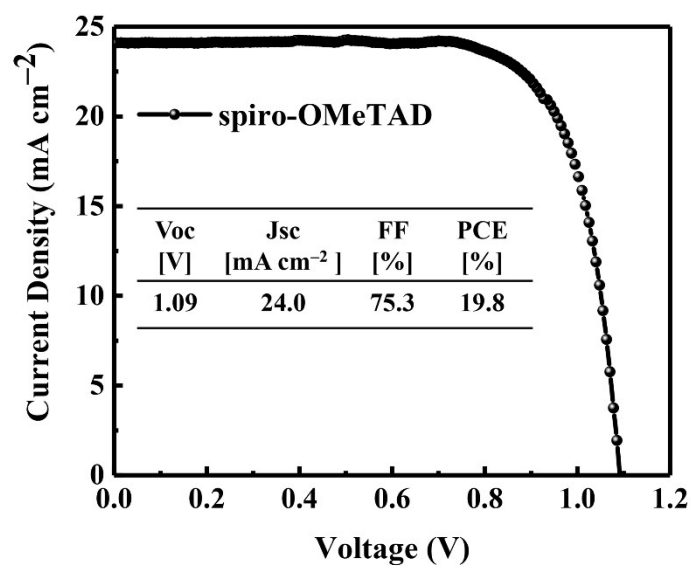


Fig. S7 Photovoltaic performance of the device based on doped spiro-OMeTAD at the same conditions for comparison.

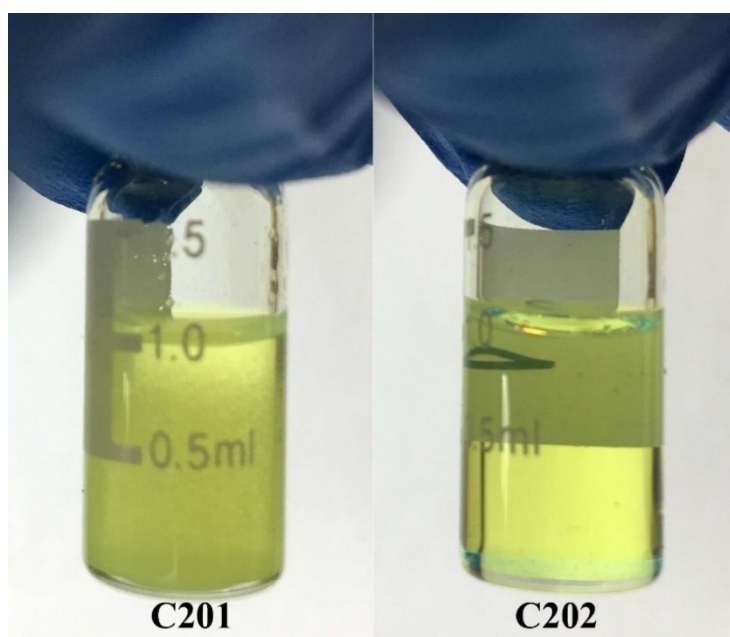


Fig. S8 the solubility of C201 and C202, both are 10mg ml⁻¹ in chlorobenzene.

1. R. A. Irgashev, A. Y. Teslenko, E. F. Zhilina, A. V. Schepochkin, O. S. El'tsov, G. L. Rusinov and V. N. Charushin, *Tetrahedron*, 2014, **70**, 4685–4696.
2. J. Simokaitiene, E. Stanislovaityte, J. V. Grazulevicius, V. Jankauskas, R. Gu, W. Dehaen, Y. C. Hung and C. P. Hsu, *J Org Chem*, 2012, **77**, 4924–4931.
3. X. Jiang, D. Wang, Z. Yu, W. Ma, H.-B. Li, X. Yang, F. Liu, A. Hagfeldt and L. Sun, *Adv Energy Mater*, 2019, **9**, 1803287.