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Disodium Benzodipyrrole Sulfonate as Neutral Hole-Transporting Materials for Perovskite Solar Cells

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Supporting Information

ABSTRACT: Hole-transporting material (HTM) is an indispensable constituent in organic electronic devices, generally comprising a donor/dopant combination. We report that a disodium salt of substituted benzo[1,2-*b*:4,5-*b′*]dipyrrole bearing two racemic alkanediylsulfonate anion side chains (BDPSOs) serves as a neutral, nonhygroscopic, dopant-free HTM for lead perovskite (MAPbI$_3$) solar cells. These organic/inorganic hybrid molecules are useful for tunable orbital level and controllable solubility. A fluorinated BDPSO has an energy level matched with MAPbI$_3$, affording an inverted-structure solar cell that performs with 17.2% efficiency with minimal hysteresis. The solar cell devices fabricated using BDPSOs showed remarkable storage and operational stability.

Printable solar cells[1] continue to attract interest in industry and academia. They consist of a photoactive layer sandwiched between charge-transporting layers,[2] whose properties much affect the performance and stability of the device.[3] Hole-transporting material (HTM) generally comprises a donor/dopant combination as in poly(3,4-ethylenedioxythiophene):poly(styrenesulfonate) (PEDOT:PSS),[4] an aqueous gel coated on an indium tin oxide (ITO) anode. PEDOT is a donor polymer and PSS is a strongly acidic dopant.[5] Such a donor/dopant combination is a standard HTM configuration, where the dopant is either acidic[6] or oxidative,[7] that causes side effects. The HOMO levels of PEDOT:PSS is difficult to control. Small molecules are intrinsically more controllable than polymers. Recently developed triarylamine[8] and thiophene[9] HTMs, however, still are open to further improvements as to their electronic tunability, doping, and solvent compatibility. Having long focused on small molecules for organic electronics,[10] we considered that a hybrid of a heteroaromatic organic group[11] and an inorganic salt would serve as a useful HTM. Here we report on a new class of organic/inorganic hybrid molecules, a disodium salt of 2,3,6,7-tetraarylbenzo[1,2-*b*:4,5-*b′*]dipyrrol-1,5-yl alkanediylsulfonates (BDPSOs), in particular, **3-F-br-4C** possessing fluorine atoms[12] and racemic side chains (Figure 1b), as HTM for lead perovskite-based (e.g., CH$_3$NH$_3$PbI$_3$ or MAPbI$_3$) solar cells (PVSCs)[13] of inverted structure (Figure 1a).[14] BDPSOs feature neutrality, transparency, film uniformity, stability in air, nonhygroscopicity, structural variety, tunable HOMO level, and compatibility with the perovskite (PV) fabrication conditions. A PVSC device using **3-F-br-4C** without doping performs with a power conversion efficiency (PCE) of 17.2% with minimal hysteresis, performance better than PEDOT:PSS and comparably to the state-of-the-art polymer, poly[bis(4-phenyl)(2,4,6-trimethylphenyl)amine] (PTAA).[7a] The branched side chains used as a diastereomeric mixture prevent crystallization and hence ensure film homogeneity. The device without encapsulation endures 40-day storage, and with encapsulation retains >90% of the initial PCE after 1300 h at maximum power point (MPP) under continuous light soaking at 35 °C.

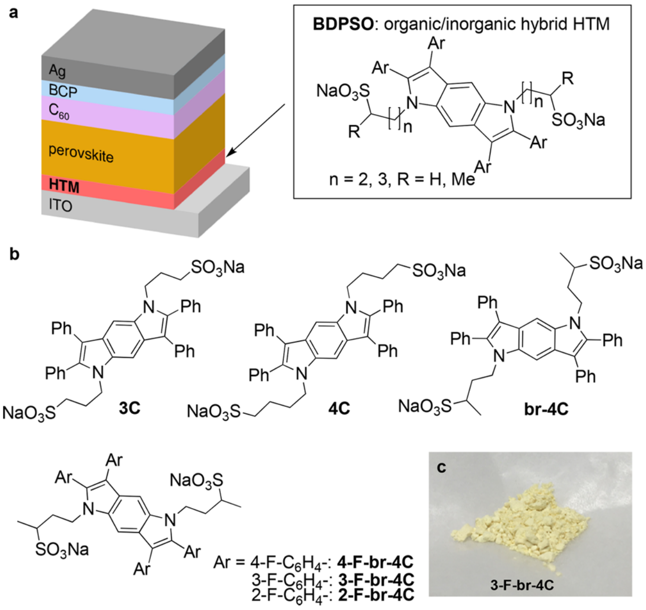

Figure 1. BDPSO as HTM for PVSCs. (a) Planar p-i-n PVSC using BDPSO. (b) BDPSOs investigated (c) Photograph of **3-F-br-4C**.

BDPSOs as a disodium salt were synthesized by simple and scalable routes (Figure 2a) in minimum two steps from commercial compounds. The 2,3,6,7-tetraphenylbenzo[1,2-*b*:4,5-*b′*]dipyrrole core (BDP) is accessible in one step through a classical reaction between *p*-phenylenediamine and benzoin,[15] or a palladium-catalyzed Larock-cyclization.[16] BDPs deproto-

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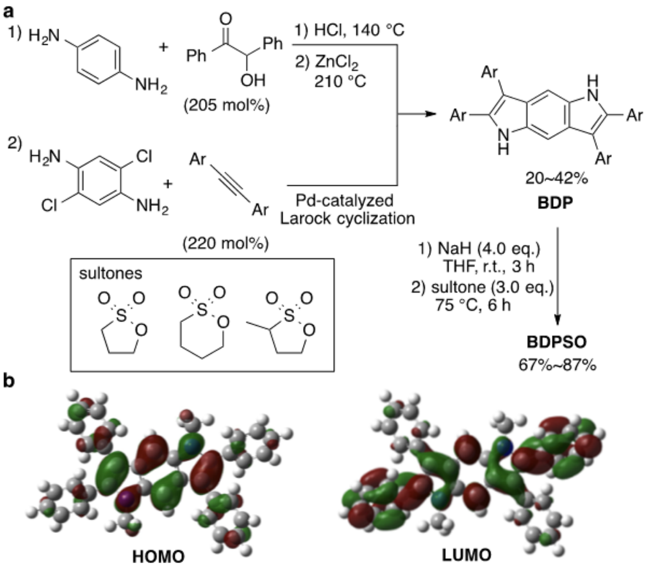

Figure 2. Synthesis and structures of BDPSOs. (a) Two synthetic routes to BDPSOs. (b) HOMO and LUMO of BDP, determined by B3LYP/6-31G(d).

nated with sodium hydride were *N*-alkylated in situ with sultone to obtain the BDPSO disodium salts as yellow solids (Figure 1c). The fluorinated compounds were synthesized by the second method. BDPSOs are poorly soluble in common solvents (e.g., dichloromethane, chlorobenzene, tetrahydrofuran, acetone, and water), but soluble in an acetone/water mixture, which we used for device fabrication. Disodium BDPSOs are heat stable decomposing at >400 °C. They are nonhygroscopic and stable under air for four years as confirmed by ^1H NMR.[17]

All BDPSOs show similar UV–vis absorption and emission spectra in a dilute *N*-methyl pyrrolidone (NMP) solution, as illustrated for **br-4C** and **3-F-br-4C** in Figure 3a (see SI for all six compounds). They show two absorption maxima (λ_{max} = 320 and 380 nm) and one emission maximum (λ_{max} ~ 450 nm). The absorption onsets range between 410 and 430 nm, indicating an optical band gap of 2.90–3.00 eV, values suitable for efficiently blocking electrons in PVSC applications.

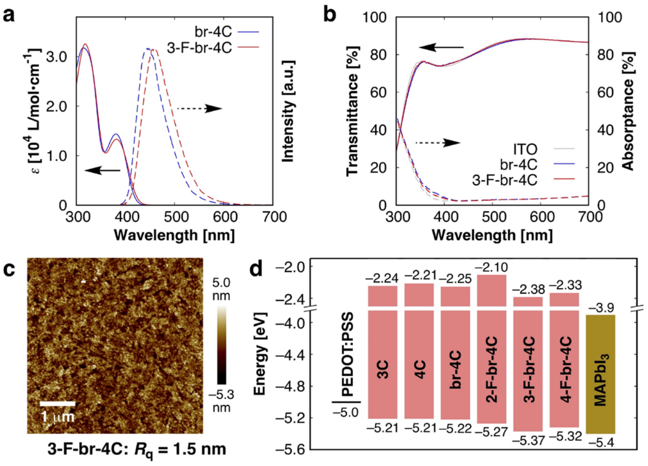

Figure 3. Photophysical properties of BDPSOs. (a) UV–vis absorption and emission spectra. (b) UV–vis transmittance and absorbance of thin films on ITO. (c) AFM height image of **3-F-br-4C** film on ITO. (d) IP of films formed on ITO, measured by PYS.

The ionization potential (IP) of 3–14 nm-thick BDPSO films on ITO (thickness and atomic force microscopy (AFM) images in Figure S8) were determined by photoelectron yield spectroscopy (PYS)[18] to be between −5.21 and −5.37 eV (Figure 3d). These values agree with the trend (but not the absolute values) of the data estimated by differential pulse voltammetry in NMP solutions and by density functional theory (DFT) calculations (Figure S7). The HOMO is fully delocalized on the BDP ring (Figure 2b). We note a rather anomalously shallower HOMO of **2-F-br-4C** than that of the **3-F** and **4-F** counterparts, which may originate from an intramolecular dipole interaction between the 2-fluorine atom and the CH_2 group adjacent to nitrogen (cf. a marked difference of the CH_2 signals in ^1H NMR spectra in SI page 42). The **3-F-br-4C** film shows the lowest IP and hence best matches energetically with a $MAPbI_3$ film (Figure 3d). The hole-mobility of **3-F-br-4C** HTM is 4.0×10^{-5} cm^2/(V·s) using space-charge-limited-current method, which is similar to the hole mobility of a common HTM, spiro-MeOTAD (10^{-5} cm^2/(V·s) ~ 10^{-4} cm^2/(V·s)).

BDPSOs showed high affinity to the UV/ozone-cleaned surface of ITO, and a uniform film of 3–14 nm thickness formed after spin coating (4 mg/mL in acetone/water mixture). Racemic **3-F-br-4C** afforded a thin film with an average thickness of 8 nm and with a root-mean-square surface roughness (R_q) of 1.5 nm, as shown in Figure 3c. A thin film of BDPSOs on ITO absorbs only in the UV region (Figure 3b), and hence is suitable for inverted-structure PVSCs.

PVSC device fabrication commences with spin coating of an acetone/water solution of BDPSO on ITO, followed by annealing at 130 °C for 10 min under air and then for 10 min under nitrogen, which is necessary to achieve high performance. Compact $MAPbI_3$ layer atop BDPSOs was fabricated using chlorobenzene-washing method (see SI for details). The device fabrication was completed by vacuum deposition of C_{60} (30 nm), bathocuproine (BCP, 15 nm), and Ag electrode (100 nm). Scanning electron microscopy (SEM) analysis of the PV film fabricated atop **3-F-br-4C** revealed a thickness of ca. 280 nm, and a smooth and dense surface (Figure 4a,b). The UV–vis absorption spectrum of the PV film formed atop **3-F-br-4C** showed slightly higher intensity than the one atop **br-4C** (Figure 4c), suggesting a favorable influence of the fluorine substitution on the PV crystal growth. X-ray diffraction (XRD) also supported the homogeneity and crystallinity of the PV film formed on **br-4C** and **3-F-br-4C** (Figure 4d). Steady-state photoluminescence (PL) of a PV film on different HTM films revealed efficient charge extraction by **3-F-br-4C** and **br-4C** (Figure 4e). Superiority of **3-F-br-4C** for charge extraction compared with **br-4C** and PEDOT:PSS was corroborated by the fastest photocurrent decay (Figure 4f), and by the slowest photovoltage decay (Figure 4g). The BDPSO molecules may also exert passivation effects on the neighboring PV film.[8c]

Performances of 9.0 mm^2 devices fabricated under the identical conditions using various BDPSOs and PEDOT:PSS as reference are summarized for their average values and root-mean-square errors (RMSEs) in Table 1. The **3F-br-4C** device showed an average PCE of 16.9 ± 0.3% and the best PCE of 17.24% (Figure 5a). The average 12.5% performance of the PEDOT:PSS device is similar to a previously reported value (PCE = 12.7%) using a similar fabrication method.[19] As shown

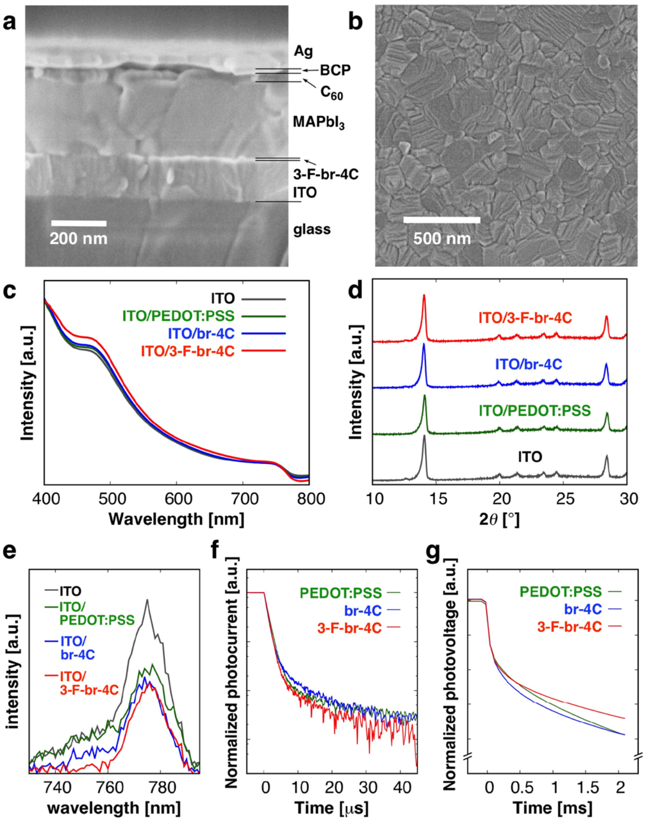

Figure 4. PVSCs fabricated using **3-F-br-4C**. (a) Cross-sectional and (b) top-view SEM images of PV film atop **3-F-br-4C** film. (c) UV−vis absorption spectra of PV films formed on different HTMs and ITO. (d) XRD spectra. (e) PL spectra. Ratio of integrated PL intensity from the top to bottom is 1:0.70:0.52:0.45. (f) Photocurrent decay. (g) Photovoltage decay.

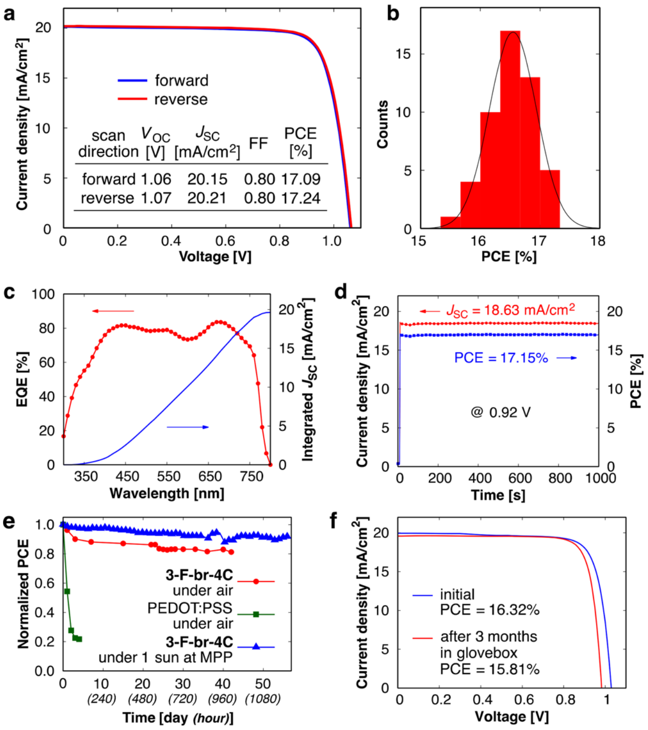

Figure 5. Photovoltaic properties and stability of PVSCs fabricated using **3-F-br-4C**. (a) *J*−*V* curves of the champion device (9.0 mm^2) under 100 mW·cm^{-2} AM 1.5 G solar illumination at scanning rate of 10 mV/30 ms. (b) Histogram of PCEs of 50 devices. (c) EQE profile of the best device. (d) Stabilized photocurrent measurement and power output. (e) Stability tests under storage condition and under light soaking (one sun, with UV cut, 35 °C) at MPP. (f) *J*−*V* curves of a **3-F-br-4C** device after aging in nitrogen glovebox for 90 days.

in Table 1, and in previous related work,[20] the PVSC fabricated using PEDOT:PSS as HTM suffers from the mismatched surface energy level (IP ~ 5.0 eV; Figure 3d), often reducing V_{oc} to <1.0 V. BDPSOs whose energy level matches better with that of PV (Figure 3d) uniformly showed higher V_{oc} values (0.91−1.04 V) than PEDOT:PSS (0.83 V), and **3-F-br-4C** having the best matched energy level showed the best performance (17.2%). The FF of the BDPSO devices were generally reaching 0.80, except **4C** possessing a longer alkyl side chain (FF = 0.77). The BDPSOs having branched (**br**) side chains as a diastereomeric mixture consistently showed higher J_{sc} values, probably because of resistance to crystallization and hence better contact with PV. A 16 mm^2 device on a larger glass substrate exhibited a PCE of 16.3%. We also examined PTAA as HTM, which is known for its advantage on V_{oc} and FF,[7a] using the same device architecture and the same PV film fabrication method. An optimized device using PTAA showed PCE of 17.1% with V_{oc} of 1.00 V, J_{sc} of 20.90 mA/cm^2, and FF of 0.82. BDPSO is thus comparable to PTAA for its performance, and has an advantage over polymers for ready tunability of chemical structures and physical properties.

The properties of the best **3-F-br-4C** device performing with 17.24% PCE are summarized in Figure 5a−d. Figure 5a shows the current density−voltage (*J*−*V*) curve under the standard AM 1.5 G illumination. The device showed minimal hysteresis upon forward and reverse scanning (Figure 5a), and showed V_{oc} of 1.07 V, J_{sc} of 20.21 mA/cm^2, and FF of 0.80. Reproducibility is illustrated for the **3-F-br-4C** device in Figure 5b, where the PCE histogram of 50 devices indicates that more than 90% of the devices showed PCE > 16%. High external quantum efficiency (EQE; Figure 5c) was obtained over a wide

Table 1. Performance Parameters of Thin-Film PVSCs using Different HTMs

HTM	V_{oc} (V)	J_{sc} mA cm^{-2}	FF	PCE (%)	R_s (Ω cm^2)	R_{sh} (kΩ cm^2)
3C	0.91 ± 0.04	17.5 ± 0.6	0.79 ± 0.02	12.9 ± 0.6	2.6 ± 0.5	3.2 ± 0.9
4C	0.90 ± 0.03	17.5 ± 0.6	0.77 ± 0.02	12.1 ± 0.2	2.7 ± 0.3	2.5 ± 0.7
br-4C	1.00 ± 0.01	19.5 ± 0.4	0.79 ± 0.01	15.6 ± 0.3	3.7 ± 0.4	3.1 ± 1.0
2-F-br-4C	0.94 ± 0.02	19.9 ± 0.4	0.79 ± 0.01	14.4 ± 0.6	3.6 ± 0.5	3.5 ± 1.5
3-F-br-4C	1.04 ± 0.02 (1.06)	19.8 ± 0.4 (20.2)	0.80 ± 0.01 (0.80)	16.9 ± 0.3 (17.2)	3.3 ± 0.3 (3.6)	4.2 ± 1.7 (11.4)
4-F-br-4C	0.98 ± 0.03	18.1 ± 0.4	0.80 ± 0.01	14.4 ± 0.4	3.2 ± 0.2	3.9 ± 1.4
PEDOT:PSS	0.83 ± 0.03	18.9 ± 0.7	0.79 ± 0.02	12.5 ± 0.7	2.9 ± 0.8	5.5 ± 1.5

[a] Data obtained by averaging five devices, RMSEs are shown in small font. The data in parentheses are for the best performing device.

range of the solar spectrum. The rather high EQE value between 400 and 460 nm may be not only due to the high absorption intensity of PV film but also to the emission of **3-F-br-4C** (Figure 3a). The integrated current density based on EQE was 19.63 mA/cm^2, which is consistent with the J_{sc} obtained from the J−V measurement (Table 1). Figure 5d shows the photocurrent density and PCE as a function of time at MPP (0.92 V). They remained stable for a 1000 s scan. A stable output PCE at the MPP over 17.15% is here demonstrated.

Figure 5e,f reports on storage and operational stability of 16 mm^2 devices. BDPSOs are nonhygroscopic, and hence the **3-F-br-4C** device without encapsulation exposed to air with a relative humidity of 40−50% retained >80% of the initial PCE after 40 days of storage (Figure 5e, red line), whereas a device made of PEDOT:PSS lost PCE and the PV dark color after 48 h under the same conditions because of the hygroscopicity of PEDOT:PSS[21] (green line). Similarly, an unencapsulated device of 16.3% PCE stored in nitrogen glovebox decreased only to 15.8% after 90 days under ambient light at ambient temperature (Figure 5f). Most importantly, a stability test on encapsulated 16 mm^2 devices working at MPP under continuous one sun illumination showed >90% retention of the initial PCE (15.6%) after 1300 h at 35 °C (blue line), suggesting that **3-F-br-4C** can intrinsically stabilize the PV device, a subject of further studies.

In summary, readily synthesizable BDPSO disodium salts, serve as a new class of neutral and dopant-free HTMs in PVSCs. An inverted **3-F-br-4C** PVSC device showed a PCE value of 17.2% with minimal hysteresis, and excellent storage and operational stability. Further modification of substituents and counter cations of BDPSO will allow us to achieve further tuning of properties for application to a variety of perovskite-type devices[22] and organic electronic devices.[10b]

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/jacs.8b01783.

Experimental procedures and physical properties of the compounds (PDF)

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Notes

The authors declare no competing financial interest.

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