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Indeno[1,2-b]carbazole as Methoxy-Free Donor Group to Construct Efficient and Stable Hole-Transporting Materials for Perovskite Solar Cells

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Abstract: With perovskite-based solar cells (PSCs) now reaching efficiencies >20%, the stability of PSCs devices has become a critical challenge for commercialization. However, most efficient hole-transporting materials (HTMs) thus far still rely on the state-of-the-art methoxy triphenylamine (MOTPA) donor unit in which methoxy groups usually reduce the device stability. Herein, a carbazole-fluorene hybrid has been employed as methoxy-free donor to construct organic HTMs. The indeno[1,2-b]carbazole group not only inherits the characteristics of carbazole and fluorene, but also exhibits additional advantages arising from bulky planar structure. Consequently, M129 endowed with indeno[1,2-b]carbazole simultaneously exhibits a promising efficiency of over 20% and superior long-term stability. The hybrid strategy toward the methoxy-free donor opens a new avenue for developing efficient and stable HTMs.

Perovskite solar cells (PSCs) have attracted considerable research interest due to their outstanding optoelectronic properties.^[1] The performance of PSC highly depends on the HTMs, which facilitates hole extraction and electron blocking.^[2] Spiro-OMeTAD is famous for high efficiency, but it suffers from high cost and low hole conductivity. To developing alternative HTMs toward PSCs with an n-i-p device structure, small organic compounds,^[3-24] conjugated polymers,^[25,26] porphyrins^[27] and phthalocyanines^[28,29] have been developed.

How to construct efficient small organic HTMs? The most commonly used strategy is combination of highly conjugated cores such as pyrene,^[8] tetrathienylethene,^[9]

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indacenodithiophene,^[10] anthanthrone,^[11] tetrathienoanthracene, ^[12] and dithieno[3,2-b:2',3'-d]pyrrole (DTP)^[13,14] with the peripheral MOTPA. Methoxy groups in the MOTPA provide a hole-transfer pathway due to the molecular interaction between the HTM and the perovskite methylammonium^[5]. In addition, methoxy groups make HTMs easier to oxidize and thus leads to a high hole mobility.^[30] However, the widely used methoxy group is not always perfect. Strong electron-donating capability of methoxy groups could decrease the oxidation potential of HTM, thus leading to a loss in open-circuit voltage (Voc).[4] In addition, the panisole in MOTPA usually results in a limited T_{a} , which is associated with severe degradation of PSCs under thermal stress.^[31] To make matters worse, the presence of methoxy groups in MOTPA notoriously increases the hydrophilicity of HTM layer, which deleteriously affect the device stability. In short, methoxy groups cause a dilemma between efficiency and stability. Nevertheless, methoxy-free arylamines, in particular the ones with higher performance as compared to MOTPA, have been rarely reported. This indicates that seeking methoxy-free arylamines that simultaneously have high performance and stability is highly challenging.



Figure 1. Schematic illustration of the molecular design of M127-129.

In this work, the methoxy-free building block 11,11-dimethyl-5propyl-5,11-dihydroindeno[1,2-b]carbazole was introduced as electron donor to construct HTM M129 (Figure 1). Our results clearly demonstrated that indeno[1,2-b]carbazole outperformed MOTPA in terms of the efficiency and stability. To deeply understand how the hybrid donor improves the performance of HTM, we synthesized two reference HTMs, M127 and M128, using carbazole and fluorene as donor, respectively. Interestingly, the indeno[1,2-b]carbazole group not only inherits the favorable characteristics from carbazole and fluorene, but also exhibits additionally merits arising from the bulky planar structure. As results, M129 exhibits multitudinous advantages in T_g, hole mobility, HOMO level, morphology uniformity, and processability. The M129 with indeno[1,2-b]carbazole donor was found to be capable of generating a PCE of 20.35% and 17.50% in doped and dopant-free PSCs, respectively. The results compare favorably with those measured for M130 (Figure 2a) and Spiro-OMeTAD under the same experimental conditions. The results make the

M127

M128 M129

- M130

-30 nm

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Temperature / °C

Figure 2. a) The structure of M130. b) Energy levels diagram of studied PSCs. c) Hole mobility measurements for doped M127-130. d) DSC curves of M127-130 at a heating rate of 10 °C min⁻¹. e) AFM images of doped M127-130 coated on perovskite. methoxy-free Indeno[1,2-b]carbazole a promising arylamine improves hole-transporting properties. This observation can be

donor toward highly efficient and stable HTMs.

The synthetic routes for preparing M127-130 are shown in Scheme S1-2 in the Supporting Information (SI). New compounds were fully characterized by NMR spectra (Figures S1-S15). The cost analysis of indeno[1,2-b]carbazole as well as M129 has been added in SI. Note that herein DTP was employed as the center for these HTMs due to the merits of fused heterocycle, such as strong conjugation effect, planar structure, and thiophene-iodine interaction.^[13,14] To estimate the relative energy levels of M127-130, square-wave voltammogram (SWV) was performed by using a CH₂Cl₂ solution of the HTMs (Figure S16). As illustrated in Figure 2b, the HOMO energy level for M130 (-5.08 eV) is higher than that of M129 (-5.15 eV) due to the stronger electron-donor character of methoxy. This suggests that M129 would be favorable for the hole transfer from perovskite and achieving high $V_{\rm oc}$. The HOMO energy level for M129 is slightly deeper than that of M127 (-5.13 eV). In addition, the absorption peak of M129 (406 nm) is somewhat closer to that of M127 (401 nm, Table S1). This finding indicates that the segment of carbazole in indeno[1,2b]carbazole governs the optical and electrochemical properties of M129. This conjecture is fully supported by calculation results. As shown in Figure S17, only the carbazole segment is involved in the electron transfer during oxidation since there is nearly no electron distribution of on the segment of fluorene in indeno[1,2b]carbazole.

The hole mobility (μ_0) of doped M127-130 were analyzed by the space-charge-limited currents (SCLCs) method. The fitted *J-V* curves of devices (ITO/PEDOT:PSS/HTM/Au) are shown in Figure 2c and the corresponding hole mobility are collected in Table S2. A lower hole mobility of 3.71 × 10⁻⁴ cm² V⁻¹ s⁻¹ was obtained for M130 in comparison to that of M129 (4.23 × 10⁻⁴ cm² V⁻¹ s⁻¹). On the other hand, M129 exhibited a much higher hole mobility than that of M128 (4.60 × 10⁻⁵ cm² V⁻¹ s⁻¹) and M127(1.11 × 10⁻⁴ cm² V⁻¹ s⁻¹), which means the combination of carbazole and fluorene favors the intermolecular stacking and therefore

improves hole-transporting properties. This observation can be attributed to the strong π -stacking as evidenced by absorption spectra measurements (Figure S18).^[8,10] M129 film displays a more bathochromic shift of 20 nm in comparison with its corresponding spectra in solution due to the bulky planar structure, while there is no shift for M130 due to its non-planar structure (Figure S19).

In addition, bulky planar-structured indeno[1,2-b]carbazole significantly increases the thermal stability of HTM. The decomposition temperatures (T_d , 5% mass loss, Figure S20) for M129 (432 °C) is much higher than that of M130 (412 °C), M127 (415 °C) and M128 (419 °C). Higher thermal stability for indeno[1,2-b]carbazole compared to MOTPA was further evidenced by the differential scanning calorimetry (DSC) measurements (Figure 2d). M130 with MOTPA donor exhibits a lower T_g of 101 °C. Encouragingly, M129 bearing the indeno[1,2-b]carbazole shows a marked increase in T_g , being 170 °C. This value is distinctively higher than most of organic HTMs including spiro-OMeTAD (125 °C).^[32] Importantly, enhanced T_g could effectively reduce the crystallization tendency, improving amorphous property and morphological stability in the film.

Atomic force microscopy (AFM) measurements (Figure 2e) shows that M129 exhibits a lower roughness than M130, leading to a better morphology uniformity. The enhanced morphology uniformity was also observed in the case of M128, which displays the lowest roughness among these HTMs. This finding suggests that the dimethylfluoren could significantly contribute to the morphology uniformity of HTM. Apparently, the morphology uniformity of M129 is governed by dimethylfluoren rather than carbazole. Morphology uniformity is very important for efficient PSCs because high quality film not only reduces the charge recombination losses at the perovskite-HTM interface, but also enhances the stability of device.^[33] X-ray diffraction (XRD) results suggest the amorphous phase of M128- and M129-based films (Figure S21).

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To evaluate the photovoltaic performance of PSCs, we fabricated n-i-p PSCs with a configuration of ITO/SnO₂/ Cs_{0.05}(FA_{0.83}MA_{0.17})_{0.95}Pb(Br_{0.17}I_{0.83})₃/HTMs/Au (Figure 3a).[34] Current-voltage (J-V) curves of the PSC devices were recorded by applying a forward bias with a scan rate of 10 mV S⁻¹ under the AM 1.5G solar irradiation, and the device parameters are summarized in Table 1. A small hysteresis (Figure S22) was observed for all devices based on M127, M129 and M130 (Hysteresis indexes are around 0.02, Table S3), expect for M128. As presented in Figure 3b, the doped M129 exhibits a promising PCE of 20.35%, with a V_{oc} of 1.12 V, a short-circuit photocurrent (J_{sc}) of 23.30 mA cm⁻², and a fill factor (FF) of 0.78. In contrast, the devices employing M130 yield much lower PCEs with an optimal efficiency of 18.59%. The significantly improved PCE of M129 clearly emphasizes the superior performance of the methoxy-free indeno[1,2-b]carbazole donor. The best PCE value achieved for M127, M128 and spiro-OMeTAD is 18.27%, 5.75% and 19.62%, respectively. M128 shows rather poor performance due to inferior hole mobility, lower conductivity (Figure S23) and higher charge recombination (Figure S24). The measured PCE for M129 is further confirmed by testing the steady-state photocurrent (Figure 3c) at a constant bias of 0.89 V for 150 s. The current loss for the best-performing device is less than 3% (the steady J_{sc} is 22.68 mA cm⁻²) after 150 s of consecutive operation, leading to a reliable high performance with a steady PCE of over 20%. Besides, the M129-based devices exhibit a narrower PCE distribution than other HTMs, as revealed by the histogram of efficiency statistics based on 20 devices fabricated using the optimized conditions (Figure 3d).



Figure 3. a) Cross-sectional SEM image of the device based on doped M129. b) The reverse scanning *J*–V curves for the best performing devices based on doped HTMs. c) Stabilized photocurrent of the best devices under a voltage bias near the maxima power point (0.88, 0.59, 0.87 and 0.89 V for doped M127, M128, M129 and M130, respectively). d) Box plots of the PCEs measured at 20 devices with doped M127-130.

To further demonstrate the merit of M129, dopant-free PSCs were tested in PSCs with the same architecture as shown above (Figure S25). M129 exhibits a highest PCE of 17.50% without using any passivation layer (Figure 4a and Table S4). The PCEs for dopant-free PSCs increased in the order of M128 (9.19%) < M127 (12.35%) < M130 (14.30%) < M129 (17.50%), which is consistent with the sequence of PCEs in doped devices. Nevertheless, contrary to M129, Spiro-OMeTAD is heavily reliant

on dopants since it showed a poor performance (12.64%). It is noteworthy that M129 is the first demonstration of methoxy-free HTM simultaneously with high performance for doped and dopant-free PSCs (Table S5), although they have different the mechanism of hole conduction. In the case of doped device, lithium and cobalt salts facilitate the generation of oxidized HTM radical cation and improve hole mobility, while the hole transport is expected to occur via a charge-hopping mechanism^[35] for the dopant-free M129.

Besides, the M129-based dopant-free devices exhibit better reproducibility than the other HTMs (Figure S26). Steady-state photoluminescence (Figure 4b) and time-resolved photoluminescence (Figure 4c) measurements suggest that efficient hole extraction can be achieved by HTMs without the methoxy groups. Both samples with M129 and M130 show a high quenching ability of 91%, which is higher than that of M127 (83%). On the other hand, the difference in average lifetime (T_{avg}) between M129 (7.4 ns) and M130 (4.8 ns) is small (Table S6). For the doped HTMs, similar results were obtained (Figure S27 and Table S7). Therefore, we concluded that the hole-extraction capabilities were close for M129 and M130. The τ_{avg} decreased to 3.2 (dopant-free) and 4.1 (doped) ns for the M128-based film. reflecting the most efficient hole-extraction at the HTM/perovskite interface.

 Table 1. Summary of device parameters with doped (D) M127-130

нтм	V _{oc} [V]	J _{sc} [mA cm⁻²]	FF	PCE _{max} [%]	PCE _{ave} [%]
D M127	1.08	22.55	0.75	18.27	16.91
D M128	1.04	16.27	0.34	5.75	5.16
D M129	1.12	23.30	0.78	20.35	19.54
D M130	1.09	23.05	0.74	18.59	17.55
D spiro	1.10	23.16	0.77	19.62	18.05



Figure 4. a) The reverse scanning *J*–*V* curves for the best performing devices based on dopant-free (DF) HTMs. b) Steady-state PL spectra for dopant-free M127-130. c) Time-resolved PL spectra for dopant-free M127-130. d) Stability of the unsealed PSCs based on doped M129, M130 and Spiro-OMeTAD measured under ambient air with a humidity of 30-40% at room temperature.

The storage stability test of unsealed PSCs was carried out under ambient air with a humidity of 30% to 40% at 20–25 °C. The

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absence of methoxy groups and excellent film quality make the doped devices based on M129 more stable than M130 under ambient air. The M129 device can retain 94% of their original PCEs after 800 h with a humidity of 30% and the PCE slightly decreased to 82% of the initial value at 1000 h as the humidity increased to 40% (Figure 4d). In contrast, the M130 device dropped well below 65% of their original performance. The lower environmental stability of M130 could be attributed to the hydrophilicity of methoxy groups, which resulted in a smaller water contact angle of 73° with respect to M129 (84.3°, Figure S28). In addition, high T_a value of M129 is beneficial to the thermal stability of PSCs. The PCE of dopant-free M129 was maintained at 90% of the original value after thermal stress at 60 °C for 72 h under N₂ atmosphere (Figure S29). A slight degradation was observed after thermal stress at 70 °C. In contrast, the device made with doped Spiro-OMeTAD exhibited apparent degradation when thermal annealing was applied from 60° to 70°. This result can be ascribed to deformation of the Spiro-OMeTAD film arising from crystallization after thermal annealing at a high temperature.[4]

In summary, this work focuses on the HTM dilemma between achieving both high efficiency and stability. We constructed a methoxy-free donor alternative to MOTPA by fusing the fluorene into carbazole. Introduction of dimethylfluoren is found to improve the morphology uniformity and hole extraction. Moreover, expanding the donor raises the T_g of HTM by around 70 °C. Due to distinct advantages in T_{g} , hole mobility, film morphology and processability, M129 with the indeno[1,2-b]carbazole realized a high efficiency and stability simultaneously. The doped M129 exhibits a PCE exceeding 20% and the dopant-free device shows a PCE greater than 17%. The values are commensurate with current best results among doped and dopant-free organic HTMs for n-i-p structured PSCs. The hybrid strategy toward methoxyfree donor gets rid of the restriction of MOTPA as the electron donor in the designing efficient doped and dopant-free organic HTMs, opening a new avenue for developing efficient and stable PSCs.

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Keywords: hole-transporting materials • perovskites solar cells• methoxy-free donor • hybrid donor • indeno[1,2-b]carbazole

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High performance and stable methoxy-free donor: The indeno[1,2b]carbazole donor not only consolidates the merits of carbazole and fluorene, but also exhibits excellent thermal stability and high hole mobility due to bulky planar structure. HTM based on this methoxy-free donor realized a high efficiency and stability simultaneously, providing a promising strategy for developing efficient and stable PSCs.



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Indeno[1,2-b]carbazole as Methoxy-Free Donor Group to Construct Efficient and Stable Hole-Transporting Materials for Perovskite Solar Cells

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