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Step-saving synthesis of star-shaped holetransporting materials with carbazole or phenothiazine cores via optimized C-H/C-Br coupling reactions[†]

Jui-Heng Chen,^a Kun-Mu Lee,^{*b} Chang-Chieh Ting^a and Ching-Yuan Liu[®]*^a

In most research papers, synthesis of organic hole-transporting materials relies on a key-reaction: Stille cross-couplings. This requires tedious prefunctionalizations including the preparation and treatment of unstable organolithium and toxicity-concern organotin reagents. In contrast to traditional multistep synthesis, this work describes that a series of star-shaped small molecules with a carbazole or phenothiazine core can be efficiently synthesized through a shortcut using optimized direct C-H/C-Br cross-couplings as the key step, thus avoiding dealing with the highly reactive organolithium or the toxic organotin species. Device fabrication of perovskite solar cells employing these molecules (6-13) as holetransporting layers exhibit promising power conversion efficiencies of up to 17.57%.

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Introduction

Perovskite solar cells (PSCs) using organic molecules as holetransporting materials (HTMs) have attracted significant research interest because of their promising power conversion efficiencies (PCE).¹⁻¹³ Compared to π -conjugated polymers, oligomers possess several advantages including well-defined conjugation lengths, flexible molecular design and reproducible chemical synthesis with higher compound purities.¹⁴⁻²¹ By 2,2',7,7'-tetrakis(N,N-di-p-methoxyphenylamino)-9,9'-spifar. robifluorene (spiro-OMeTAD) is the most used organic HTM in perovskite-based solar cells.²² However, it was also stated that spiro-OMeTAD owns a number of drawbacks such as low conductivity, low hole-mobility, and high commercial price. Besides, synthetically speaking, accessing spiro-OMeTAD requires costly spirobifluorene as starting material. Therefore, present research attention has been switched to the development of non-spirolinked small molecules.23 Among various nonspiro-type building blocks, triphenylamine (TPA), carbazole (Cbz), and phenothiazine (PTZ) were very attractive to material scientists since they are inexpensive, readily available and usually exhibit remarkable PCEs while incorporated in PSCs as hole-transport layers.²⁴ Recently, we also demonstrated a series

of small-molecule HTMs incorporating TPA- or Cbz-derivatives as end-groups for efficient PSCs.25 However, we have noticed that the employment of Cbz or PTZ as core-moiety still remained less explored. Even though few examples were reported, synthetic approaches for these HTMs were neither stepeconomical nor optimized.24,26 Moreover, we envisaged that introduction of a carbazole or phenothiazine group as core for HTMs might further improve their hole-mobilities and the performance of PSCs. Therefore, we report herein, an efficient access to eight star-shaped new molecules with Cbz- or PTZ-



Fig. 1 Eight star-shaped HTMs with carbazole or phenothiazine cores: step-saving synthesis and application for perovskite solar cells.

^aDepartment of Chemical and Materials Engineering, National Central University, Jhongli District, Taoyuan 320, Taiwan, Republic of China. E-mail: cyliu0312@ncu. edu.tw

^bDepartment of Chemical and Materials Engineering, Chang Gung University, Department of Pediatrics, Chang Gung Memorial Hospital, Linkou, Taoyuan 333, Taiwan, Republic of China. E-mail: kmlee@mail.cgu.edu.tw

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cores (Cbz: carbazole for **6–9**; PTZ: phenothiazine for **10–13**) through a step-saving synthetic strategy under pre-optimized direct C–H arylation reaction conditions (Fig. 1). Property and photovoltaic performance of perovskite solar cells using these compounds as HTMs were also investigated.

Results and discussion

In Scheme 1, a comparison of two synthetic pathways to **JHC01– 08** was demonstrated. Traditionally, as shown in pathway A, the end-group molecules **3a–d**¹¹ underwent deprotonation with *n*butyl lithium at low temperature (usually –78 °C) to give unstable organolithium intermediates **4** which were subsequently transmetalated with trialkyltin chloride to afford organotin reagents **5**. The final products can be readily reached by performing Stille cross-coupling reactions of **5** with the core molecules (**1** or **2**), even though the preparation and treatment of organotin species is toxicity-concerned and time-consuming. On the other hand, in pathway B, we proposed a step-saving shortcut to **6–13** *via* direct C–H bond activation/arylation of **3a–d** with core **1** or **2**, by which the generation of organolithium and the contact of organotin compounds can be entirely avoided.

Based on pathway B, we carried out a facile synthesis of **6**-**13**. In order to find optimum reaction conditions, the direct C-H/C-Br cross-coupling was investigated using core **1** and end **3a** as model study focusing on ligand screening. First, as shown in Table 1, reaction of **3a** with tribromocarbazole was conducted under general C-H activation/arylation conditions: Pd(OAc)₂, PPh₃, PivOH, and K₂CO₃ in DMF (125 °C, 30 h), giving desired **6** in 38% (isolated yield, entry 1). Other triarylphosphine monodentate ligands were also examined to produce **6** in 29–57% yields (entries 2–4). *N*-Heterocyclic carbene (NHC) ligand such as IPr gave product in 38% (entry 5). The C-H arylation was then performed with three phosphine ligands bearing alkyl groups (entries 6–8), furnishing **6** Table 1 Ligand screening for the optimization of direct C–H arylations using core 1 and end $3a^{\alpha}$



Entry	Ligand	$\operatorname{Yield}^{b}(\%)$
1	PPh	38
2	$P(o-tolvl)_2$	57
3	$P(m-tolyl)_3$	29
4	Tris(o-methoxyphenyl)phosphine	53
5	IPr	38
6	$P(Cy)_3$	51
7	$P(adamantyl)_2(nBu)$	62
8	JohnPhos	35
9	dppe	20
10	dppp	23
11	Xantphos	21
12	DPEphos	18
13 ^c	$P(o-tolyl)_3$	70
14^c	$P(adamantyl)_2(nBu)$	67

^{*a*} Direct C-H arylation of **3a** (0.96 mmol) with **1** (0.30 mmol) was conducted under N₂ in the presence of Pd(OAc)₂ (15 mol%), ligand (30 mol%), pivalic acid (60 mol%), and K₂CO₃ (1.08 mmol) in DMF (3 mL) at 125 °C for 30 h. ^{*b*} Isolated yields. ^{*c*} 1 mL DMF was used.



 Pathway A: traditional multi-step synthesis
 vs.
 Pathway B: step-saving synthesis shortcut (This Work)

 Scheme 1
 Comparison of two synthetic pathways: multi-step versus step-saving synthesis of 6–13.

of up to 62% isolated yield. From entry 9 to 12, the bidentate phosphine ligands had also been tested. However, they were shown to be less efficient toward C–H/C–Br coupling reactions, providing 6 in only 18–23% yields.

According to above results, we selected $P(o-tolyl)_3$ (entry 2) and $P(adamantyl)_2(nBu)$ (entry 7) as the optimum ligands for additional examinations. In last two entries (13 and 14), the direct C–H arylations proceeded under a more concentrated condition (solvent reduced to 1 mL) and we were pleased to find the yield of **6** could be further improved (67–70%).

Therefore, in Scheme 2, we decided to use $P(o-toly)_3$ for the efficient synthesis of other HTM molecules (7–9 with a Cbz core; **10–13** with a PTZ core) because of its lower commercial price. In addition to the methoxy group (–OMe) that was often equipped with small-molecule HTMs, we also



Scheme 2 Synthesis of 7–13 under optimum reaction conditions.

explored other potential and previously used end-substituents¹¹ including *n*-hexyloxy group ($-OC_6H_{13}$), methyl sulfide group (-SMe) and tertiary-butyl group (-tBu). Reaction of **3b** ($R = OC_6H_{13}$) with either core-**1** (Cbz) or -**2** (PTZ) under optimum reaction conditions produced **7** or **11** in moderate isolated yields (62%; 65%). These two compounds exhibited fairly good solubility in common organic solvents owing to their longer alkyl chains, which might be beneficial to followup solution-based device fabrication and film formation through spin-coating techniques.

Next, we investigated the optical, electrochemical, electrical and thermal properties of synthesized 6-13 and the results were summarized in Table 2 (relevant spectra were provided in ESI[†]). In general, the PTZ core-based 10-13 possess smaller optical bandgaps ($\Delta E_g = 2.56-2.57$ eV) than Cbz core-based 6–9 ($\Delta E_g = 2.73$ –2.81 eV). Based on the electrochemical measurements and calculations, we obtained each E_{HOMO} (the highest occupied molecular orbital) of eight HTM molecules, all of which were located between the E_{HOMO} of perovskite layer (MAPbI₃, $E_{HOMO} = -5.43$ eV) and Ag electrode ($E_{HOMO} = -4.20$ eV), revealing that 6-13 had appropriate energy levels to serve as potential hole-transport materials. In addition, the hole-mobility (μ_h) of 6-13 was evaluated by measuring their current density-voltage (I - V)in the region of space-charge limited current (SCLC). It was found that, HTMs bearing -tBu groups (9 and 13) exhibited outstanding hole mobilities ($\mu_{\rm h}$ = 6.46 \times 10^{-4} and 7.53 \times 10^{-4} cm² V⁻¹ s⁻¹) that are close to the $\mu_{\rm h}$ of **spiro-OMeTAD** $(8.38 \times 10^{-4} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1})$. Among all HTMs, the molecules with -SMe groups (8 and 12) showed the lowest hole mobilities ($\mu_{\rm h} = 1.35 \times 10^{-4}$ and 6.68 $\times 10^{-5}$ cm² V⁻¹ s⁻¹), which implied that -SMe might not be a suitable substituent for the design of small-molecule HTMs. We also obtained the thermal analysis data of all HTMs. It is interesting to note that, except for hole mobilities, 9 and 13 (with tBu groups) also showed superior decomposition temperature (T_d = 426 °C; 415 °C) and glass transition temperature ($T_g = 223$ °C; 228 °C) than those of other HTM molecules. Among eight

Table 2 Summary of the optical, electrochemical, electrical and thermal properties of $6{-}13$

HTMs	$\Delta E_{\rm g}^{\ a} [{\rm eV}]$	$E_{\rm HOMO}^{b} [\rm eV]$	$E_{\text{LUMO}}^{c} [\text{eV}]$	Hole mobility $(cm^2 V^{-1} s^{-1})$	$T_{\rm d} \left[^{\circ} { m C} ight]$	$T_{\rm g} \left[^{\circ} {\rm C}\right]$
6	2.76	-5.21	-2.45	$1.71 imes 10^{-4}$	370	177
7	2.73	-5.20	-2.47	1.59×10^{-4}	396	88
8	2.81	-5.25	-2.46	$1.35 imes10^{-4}$	406	192
9	2.78	-5.21	-2.43	6.46×10^{-4}	426	223
10	2.57	-5.16	-2.59	$2.34 imes10^{-4}$	406	184
11	2.56	-5.20	-2.64	4.10×10^{-4}	382	91
12	2.57	-5.22	-2.65	6.68×10^{-5}	387	192
13	2.56	-5.20	-2.64	7.53×10^{-4}	415	228

^{*a*} Δ*E*_g was calculated based on the spectra of UV/vis absorption and photoluminescence (measurements performed in CH₂Cl₂). ^{*b*} *E*_{HOMO} = $-[E_{1/2}$ (*vs.* Ag/AgCl_{sat'd}) + 0.197 (*vs.* NHE) + 4.500] eV (the electrochemical experiments were performed in CH₂Cl₂). ^{*c*} *E*_{LUMO} = $E_{HOMO} + \Delta E_{g}$.



Fig. 2 The steady-state photoluminescence spectra of devices fabricated as: glass/MAPbl₃ (perovskite layer)/6-13 (hole-transport layer).

HTMs, 7 and 11 carrying long alkoxyl groups $(-OC_6H_{13})$ demonstrated obviously lower T_g (88–91 °C), presumably resulting from the thermally caused motion of alkyl chains.27,28 Furthermore, we studied the hole-extraction

capability of eight molecules by conducting the experiments of steady-state photoluminescence (PL). The required devices were fabricated as glass/MAPbI₃/6-13, respectively. The spectra provided in Fig. 2 revealed that 9 & 13 (tBu groups) had remarkable PL quenching abilities. This implied they could extract holes efficiently from the interface between perovskite- and hole-transport layers, whereas the 8 & 12 (-SMe groups) showed poor hole-extraction capabilities.²⁹ We speculated this might be attributed to the inferior coordination of methyl sulfide groups to the perovskite layer.

Device fabrication of perovskite solar cells using 6-13 as hole-transporting layers was detailed in ESI.[†] In general, 6-13 was each dissolved in chlorobenzene and the solutions were heated to 90-100 °C to ensure the HTM molecule was completely dissolved. Each solution was then doped with lithium bis(trifluoromethane)sulfonimide (Li-TFSI) and 4tert-butylpyridine (TBP). After the PSC devices were obtained via spin-coating techniques, we evaluated their photovoltaic performances and the data were summarized in Table 3. It is interesting to note that PSCs based on 9 and 13 (with tBugroups) showed exceptional power conversion efficiencies (PCEs = 17.51%, 17.57%) regardless of the variation of their core molecules (Cbz or PTZ), which is comparable to the PCE of reference cells (spiro-OMeTAD, PCE = 17.65%). Based on the high T_{g} of 9 and 13 shown in last section (Table 2), we speculated that PSC devices incorporating 9- or 13 as holetransporting layer might possess more stable film morphology at high operational temperature, thus leading to higher PCEs. In addition, we found that there was no significant difference in PCEs of the solar cells fabricated with HTM molecules bearing either –OMe groups (6 & 10) or the longer $-OC_6H_{13}$ chains (7 & 11), all of which demonstrated excellent PCEs of 15.28-17.10%. PSCs with 8 & 12 (-SMe groups), as expected, displayed relatively poor PCEs

Photovoltaic performance of perovskite solar cells using 6-13 as hole-transporting layers.^{*al*} Table 3

HTMs		$V_{ m oc}$ [V]	$J_{\rm sc} [{ m mA} \ { m cm}^{-2}]$	FF [%]	PCEs [%]
6	Best	1.05	21.41	75.50	16.96
	Average	1.02 ± 0.02	21.25 ± 0.42	73.40 ± 2.50	15.96 ± 0.92
7	Best	1.04	19.85	74.30	15.28
	Average	0.98 ± 0.04	19.73 ± 1.34	70.40 ± 5.50	13.61 ± 1.21
8	Best	0.87	19.99	22.80	3.95
	Average	0.60 ± 0.22	16.86 ± 3.36	30.90 ± 7.30	2.98 ± 0.93
9	Best	1.02	22.18	77.40	17.51
	Average	1.03 ± 0.01	22.00 ± 0.25	74.30 ± 2.20	16.82 ± 0.56
10	Best	1.06	21.37	73.30	16.61
	Average	1.02 ± 0.03	19.84 ± 1.39	74.30 ± 2.50	15.04 ± 1.04
11	Best	1.03	22.57	73.60	17.10
	Average	1.01 ± 0.01	22.07 ± 0.40	70.60 ± 6.80	15.82 ± 1.77
12	Best	0.87	14.68	61.00	7.78
	Average	0.81 ± 0.14	12.14 ± 1.63	66.00 ± 7.00	6.38 ± 1.24
13	Best	1.09	23.44	68.80	17.57
	Average	1.05 ± 0.02	22.20 ± 1.26	70.10 ± 1.00	16.42 ± 1.08
spiro-OMeTAD	Best	1.05	22.50	74.50	17.65
	Average	1.04 ± 0.01	21.59 ± 0.82	74.40 ± 1.60	16.77 ± 0.78
	e				

^a Reverse scans. ^b Statistical data were calculated based on 6-8 cells.

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(3.95%, 7.78%), which is consistent with the hole-mobility data acquired in Table 2.

Conclusions

Based on the optimized direct C-H arylation approach, we have efficiently synthesized eight new molecules bearing carbazole (6-9) or phenothiazine (10-13) cores in moderate to good isolated yields. Compared to traditional multistep synthesis, this step-saving synthetic methodology omitted previously required prefunctionalization steps such as deprotonative lithiation and transmetalation/stannylation. Perovskite solar cells fabrication using 6-13 as hole-transporting materials demonstrated power conversion efficiencies of 3.95-17.57%. Most noteworthy was that *t*-butyl substituted HTMs (9 and 13) exhibited exceptional hole-mobilities, thermal properties (high T_d and T_g), and the devices based on 9 or 13 displayed very promising power conversion efficiencies of 17.51-17.57%. Development of succinct synthetic routes combining direct C-H activation/ arylation reactions³⁰ for the facile preparation of new smallmolecule HTMs is currently underway in our laboratory.

Experimental

General procedure for the synthesis of 6-13

To a solution of $Pd(OAc)_2$ (15 mol%), $P(o-tolyl)_3$ (30 mol%), PivOH (60 mol%) and K₂CO₃ (3.60 equiv.) in DMF (3 mL) in a flame-dried Schlenk flask were added 3,6-dibromo-9-(4-bromophenyl)-9H-carbazole (1) or 3,7-dibromo-10-(4-bromophenyl)-10H-phenothiazine (2) (0.30 mmol) and the corresponding end-groups (3a-d) (0.96 mmol) under N₂. The reaction mixture was then heated at 125 $^\circ C$ under N_2 for 30 h. After the reaction mixture had cooled to room temperature, water (10 mL) was added. The mixture was extracted with dichloromethane (2 \times 20 mL), and the combined organic layers were washed with brine (50 mL), dried (Na₂SO₄) and concentrated in vacuo. Purification by flash chromatography afforded the desired products 6-13.

Conflicts of interest

There are no conflicts to declare.

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