Progress in D–A–D-type Small Molecule Hole-Transport Materials for Perovskite Solar Cells

Yajie Fu,^{a,c} Muhammad Sohail,^b Aaqib Khurshid,^b and Derong Cao^{*,a}

^a State Key Laboratory of Luminescent Materials and Devices, School of Chemistry and Chemical Engineering, South China University of Technology, Guangzhou, Guangdong 510641, China

^b Department of Chemistry, Faculty of Chemistry, University of Sargodha Sub campus Bhakkar, Bhakkar 30000, Pakistan

^c School of Chemical Engineering, Qinghai University, Xining, Qinghai 810016, China

Email: drcao@scut.edu.cn (D. C.)

Abstract As one of the key components of perovskite solar cells (PSCs), hole transport materials (HTMs) effectively improve the performance and stability of the devices and greatly promote the development of PSCs. At present, due to the advantages of flexible structure design, simple synthesis, low-cost and abundant raw materials, organic small molecule HTMs have been studied extensively by researchers. Among them, small molecule HTMs with donor–acceptor (D–A) type structures for PSCs have received great attention in the last few years because of their high hole mobility due to strong dipolar intermolecular interactions, minimizing ohmic losses of the contact, good stability, and high solubility. In this review, we mainly introduce some representative D–A–D-type small molecule HTMs, summarize and comment on their properties, and discuss the relationship between molecular structure and performance parameters of devices. Finally, based on the current research, the future design of new efficient HTMs is prospected.

Keywords perovskite solar cells, hole transport materials, power conversion efficiency, small molecule, D–A–D-type

Introduction

With the rapid growth of population and the development of society, the traditional fossil energy will soon be exhausted. Therefore, people use solar energy to solve the increasingly serious energy and environmental problems. Solar cell is a kind of common semiconductor photovoltaic device, which directly converts solar energy into electric energy. After decades of development, the types of solar cells have developed from traditional crystalline silicon cells to all kinds of new solar cells, including semiconductor thin film cells, organic thin film cells, dye-sensitized cells, and perovskite solar cells (PSCs). PSCs with high extinction coefficient and excellent double carrier transport properties of perovskite crystalline $\text{CH}_3\text{NH}_3\text{PbX}_3$ (X is halogen) as the light absorption layer have attracted extensive attention of researchers in particular.^[1–7] At present, the power conversion efficiency (PCE) of perovskite solar cells has exceeded 25%,^[8] which has become one of the research hotspots in the field of new solar cells.

Perovskite is named because it has a similar molecular configuration as CaTiO_3 , and its crystal structure is simple, generally represented by ABX_3 , where X represents anions (usually halogen ions Cl^- , Br^- and I^-), A and B are cations of different sizes (A is larger than B), A is generally an organic cation such as CH_3NH_3^+ (MA), $\text{CH}_2(\text{NH}_2)^{2+}$ (FA), etc., B is generally a divalent transition metal ion, such as Pb^{2+} , etc. As shown in Figure 1, in a three-dimensionally symmetric crystal structure, the B cation at the center of the cube is surrounded by X anions located on the six face centers to form a coordinated regular octahedral structure BX_6 , and then the BX_6 regular octahedron passes through the vertex X extending in the three-dimensional direction, the A cation is in the interstitial

Figure 1 Crystal structure of cubic perovskite.

space created by the eight adjacent octahedrons in the three-dimensional structure to maintain the charge balance. The photoelectric properties of ABX_3 perovskite materials can be adjusted by changing the A, B, X ions.^[9–11] $\text{CH}_3\text{NH}_3\text{PbX}_3$ is an efficient light absorbing material for solar cells, which has many excellent properties: strong absorption in the visible region and near infrared region of 280–820 nm;^[12,13] ultra-long effective diffusion length of carriers; unique bipolar transmission characteristics, which can transport both electrons and holes.^[14,15] In addition, perovskite materials have good film-forming property, simple preparation process and low cost. Uniform films can be prepared by solution coating and heating at room temperature, so they are widely used in solar cells with different structures.

PSCs are generally composed of fluorine doped tin oxide (FTO), electron transport material (ETM), perovskite light

Figure 2 Three typical device structures of perovskite solar cells: (a) mesoscopic sensitization structure; (b) regular planar heterojunction structure; (c) inverted planar heterojunction structure.

absorption layer, hole transport material (HTM) and metal electrode (Au, Ag, Al, etc.). PSCs originated from dye-sensitized solar cells (DSSCs). The initial structure is mesoscopic sensitized solar cells evolved from DSSCs, as shown in Figure 2a. After development, the existing PSCs can be divided into mesoscopic sensitized structure and planar heterojunction structure according to whether there is mesoporous TiO_2 or not. According to the hole transport layer or electron transport layer in contact with the conductive substrate, the planar heterojunction PSCs can be further divided into regular structure and inverted structure, as shown in Figures 2b and 2c.

As the key material of PSCs, HTMs not only increase the stability of the devices, but also improve the PCE of devices, which brings new opportunities for the development of PSCs.^[16-24] At present, the reported HTMs are mainly divided into three categories: inorganic HTMs, organic polymer HTMs and organic small molecule HTMs. Inorganic HTMs, including CuI,^[25] CuSCN,^[26-28] NiO,^[29] PbS^[30] and CuInS₂,^[31] have good conductivity and low manufacturing cost. However, PSCs based on inorganic HTMs have poor stability, and their performance is not as good as those based on organic HTMs, and the range of materials available is narrow, which limits their applications. Similarly, organic polymer HTMs are also faced with certain limitations due to their complicated purification process, low solubility, difficult to identify molecular weight characterization, and poor permeability in nanostructured materials. In contrast, organic small molecule hole-transport materials (SM-HTMs) can be flexibly designed to adjust energy level matching and surface properties. Besides, they have the characteristics of simple synthesis, low cost, and abundant raw materials. Among them, donor-acceptor-donor (D-A-D) molecules with donor-acceptor (D-A) scaffold have been demonstrated as efficient organic HTMs because their low-lying highest occupied molecular orbital (HOMO) energy levels, and impressive hole mobility.^[32-35] Indeed, the use of D-A type structures have been proven to be one of the major design strategies to prepare high performance HTMs because their high charge carrier mobility due to strong dipolar intermolecular interactions, minimizing ohmic losses of the contact, good stability, and high solubility.^[36] This review article is specifically focused on D-A-D-type SM-HTMs being developed in PSCs.

D-A-D-type SM-HTMs

Donor (D)-acceptor (A)-donor (D) molecules have been widely demonstrated as efficient HTMs due to their

intramolecular charge transfer (ICT) character and high dipole moment, which could induce self-doping and built-in potential to boost charge extraction.^[37-40] Besides, the HOMO and lowest unoccupied molecular orbital (LUMO) of the D-A-D molecules can be readily tuned by adopting appropriate D and A building blocks. Usually, strong intramolecular charge transfer characteristic is presented in D-A-D-type molecules, which not only affects their band-gap and optical properties but also may enhance the intermolecular packing in the thin film as well as the charge carrier mobility.^[37-41]

D-A-D-type SM-HTMs based on benzothiadiazole

Since benzothiadiazole (BTD) has a strong electron-withdrawing ability and has been extensively studied in dye sensitized solar cells and organic solar cells, the D-A-D-type hole transport materials based on BTD first attracted researchers' attention (Figure 3).

Choi and co-workers^[42] have designed and synthesized a novel symmetric oligomer HTM **1** incorporating 2,1,3-benzothiadiazole (BTD) core and applied in PSCs. The HOMO levels of **1** is measured to be -5.34 eV, which is deeper than 2,2',7,7'-tetrakis-*N,N*-di-*p*-methoxyphenylamine)-9,9'-spirobi-fluorene (spiro-OMeTAD) result in a higher average open-circuit voltage (V_{OC}). A relatively high PCE of 13.99% has been achieved by employing **1** with the electron withdrawing BTD unit as the core, which is comparable to that of the spiro-OMeTAD (14.55%).

Wu et al.^[43] designed and synthesized HTM **2** with BTD unit as the core, and studied the effect of BTD electron-withdrawing center on the material properties. The results show that the planar BTD structure effectively enhances the interaction between molecules, thus increasing the charge transfer in HTM **2**. HTM **2** shows the energy level matching with perovskite layer, good hole mobility and thermal stability. The optimal PCE of PSC devices based on **2** (16.87%) is comparable to that of "state of art" spiro-OMeTAD (16.24%), which should be ascribed to their similar HOMO levels and good hole mobility. Then, based on HTM **2**, Wu and co-workers^[44] substituted mono-fluorine and difluorine on the benzothiadiazole cores to obtain HTMs **3** and **4**, respectively. Among them, the monofluorine-substituted **3** has more suitable energy level, better thermal stability, better hole extraction and transport ability. In addition, the surface morphology of **3** film is smooth. The PCE of the device based on **3** is 18.54%, and the filling factor is up to 81%. While the main reason for the inferior performance of difluorine-substituted **4** is its poor film forming ability.

Figure 3 The structures of D-A-D-type SM-HTMs based on benzothiadiazole.

Xu *et al.*^[39] synthesized a D-A-D-based HTM **5** based on BTD and applied it to PSCs. HTM **5** had low-lying HOMO levels and impressive hole mobility due to their D-A-D configuration. By introducing BTD onto HTM **5**, the PCE of the PSC device has amounted to 16.03%, which is comparable to that of the PSC fabricated with spiro-OMeTAD (17.80%).

Zhou and co-workers^[45] designed and synthesized two D-A-D typed dopant-free HTMs **6** and **7** with BTD acceptor unit by introducing electron-donating group alkoxy and electron-withdrawing group fluorine atoms as side group. The results show that both **6** and **7** have a low-lying HOMO energy level and high hole mobility. When two dopant-free HTMs were applied in PSCs, the higher hole mobility made the **7**, which the fluorine atoms on core acceptor got a PCE of 12.1%, while spiro-OMeTAD based dopant-free PSC only showed a PCE of 7.96%. Besides, **6**-based PSCs show an impressive long-term stability. This work demonstrates that the D-A-D typed HTMs have a good application prospect in the field of PSCs with the incorporation of appropriate side group. Recently, this group^[46] also designed and synthesized a new benzothiadiazole-based D-A-D HTM **8** with a more planar structure by introducing of thiophene bridges. The results indicate that the insertion of thiophene bridges can effectively reduce the dihedral angle between triphenylamine arms and the core acceptor, which makes the molecule more planar, and the hole mobility was thus greatly increased. The corresponding dopant-free **8**-based PSCs get a PCE of 13.5%, which is superior to that of dopant-free spiro-OMeTAD (7.8%).

More recently, Ye *et al.*^[41] successfully designed and synthesized a dopant-free SM-HTM **9** with excellent performance and low cost through the molecular configuration design of D-A- π -A-D, using fluorene with long alkyl chains as

the core π bridge, BTD as the acceptor unit, and triphenylamine as the terminal donor. The long alkyl chains on the π bridge in the middle of the molecule not only makes the molecule have good solubility and film quality, but also effectively optimizes the layered stacking arrangement of the molecule and extends the conjugate length of the molecule, which makes the molecule have excellent hole transport performance. In addition, the unique D-A- π -A-D configuration of the molecule effectively reduces the HOMO energy level and the energy barrier between the hole transport layer and the perovskite interface, which greatly improves the performance of hole extraction and transport at the interface. PSCs based on dopant-free **9** showed better performance than doped spiro-OMeTAD, with an amazing PCE of up to 21.5%.

D-A-D-type SM-HTMs based on conjugated acceptors

It has been shown that the planar rigid conjugated core structures can effectively enhance intermolecular interactions and π - π stacking of HTMs to obtain dense film and improved hole mobility, which is helpful for the design of dopant-free HTMs. Therefore, some D-A-D-type dopant-free SM-HTMs based on conjugated acceptors have been designed and synthesized by researchers (Figure 4).

Pham *et al.*^[47] adopted a unique and novel anthanthrone (ANT) dye as a conjugated core building block to synthesize a new D-A-D-type HTM **10**. The synthesis of **10** was tactfully conducted in one-step *via* a simple coupling reaction using anthanthrone as the central core unit and diphenylamine as the end-capping unit. The results show that the HOMO energy level of **10** was estimated to be -5.46 eV, which was close to the valence band maximum (VBM) of the perovskite layer, assuring a high value for the V_{oc} and efficient hole extraction. When

Figure 4 The structures of D-A-D-type SM-HTMs based on conjugated acceptors.

evaluating dopant-free **10** as HTM in the PSCs, the highest PCE of 11.5% was achieved. Besides, the PSC devices based on **10** exhibit significantly high environmental stability, which is attribute to the hydrophobic nature and good surface morphology of **10**. Subsequently, other two new D-A-D-type dopant-free HTMs **11** and **12** based on an innovative anthanthrone dye as a core have been successfully designed and synthesized by Pham and his co-workers.^[48] The synthesis of both HTMs were also conducted *via* a simple coupling protocol using a common anthanthrone dye as a central core and two different triphenylamine and acenaphthylene end-capping units. By comparing the photoelectric properties of **11** and **12**-based PSCs in detail, it is found that the HOMO level of **11** is close to the maximum valence band of perovskite for better hole transport. The performance of PSCs was evaluated by using undoped **11** and **12** as HTMs, and the highest PCE of 13% and 17.5% were obtained, respectively. The HTM **11**-based PSCs not only exhibit high performance showing optimal PCE of 17.5% and average PCE of 16% with increased reproducibility of PSCs as compared to spiro-OMeTAD-based PSCs but also show high environmental stability. These two works indicate that ANT dye

is a highly efficient conjugated acceptor structure for the construction of low-cost and high-efficiency D-A-D-type dopant-free HTMs.

In addition to ANT dye, Pham *et al.*^[49] also introduced a quinacridone (QA) dye as the core acceptor into D-A-D-type HTMs, and three novel small-molecule dopant-free HTMs **13**, **14**, and **15** based on a quinacridone dye were designed, synthesized, and characterized successfully. In comparison with PSCs based on standard doped spiro-OMeTAD (15.2%), PSCs based on newly developed HTMs **13**, **14**, and **15** achieved PCEs of 18.2%, 16.6%, and 15.5%, respectively. Besides, as a result of avoiding the use of hygroscopic additives, the stability of unencapsulated devices based on novel HTMs improved significantly with respect to that of doped spiro-OMeTAD under similar aging conditions. The champion devices based on **13** obtained the highest PCE and retained superior stability to that of other HTMs owing to their higher hole mobility and suitable energy levels. This outstanding result proves that the HTMs based on quinacridone dyes have great application potential in the construction of efficient and stable PSCs.

Zhang *et al.*^[50] developed an efficient cyclopenta[hi]ace-

anthrylene-based D–A–D-type dopant-free HTM **16** and applied it in organic–inorganic hybrid and all-inorganic PSCs. The **16**-based PSCs exhibit good conductivity and hole-extraction/transport ability, rendering the material suitable as an excellent dopant-free HTM for PSCs. The (FAPbI₃)_{0.85}(MAPbBr₃)_{0.15} and CsPbI₂Br PSCs based on dopant-free **16** achieve impressive PCEs of 18.84% and 12.05%, respectively, both of which are much higher than that of the doped spiro-OMeTAD-based PSCs (18.41% and 11.51%) under the same working conditions. Moreover, the **16**-based PSCs without encapsulation display good long-term stability, which most likely can be attributed to the absence of hygroscopic dopants and the smooth film formation of **16** acting as a moisture and oxygen barrier.

Huang and co-workers^[51] designed and synthesized two D–A–D-type dopant-free HTMs **17** and **18** with fused dithienopyrrolobenzotriazole (DTBT) core to link two electron-donor units (alkoxylate triphenylamine). Both HTMs show high conductivity and hole mobility, high hole extraction efficiency and good photovoltaic performance, which may be ascribed to their positive HOMO value and large planar structure of DTBT. Systematical investigation reveals that the different alkoxyl chain length on triphenylamine has a minor influence on the photo-physical and electro-chemical properties, but a significant effect on the conductivity, hole mobility, hole extraction efficiency, and photovoltaic performance. Besides, the dopant-free **18**-based PSCs obtained a PCE of 13.22%, which was superior to that of spiro-OMeTAD (10.41%). When two HTMs were doped with additives, **18**-based PSC obtained a PCE of 15.77%, which was even superior to that of doped spiro-OMeTAD PSC (14.94%).

Recently, Wang *et al.*^[52] developed a series of D–A–D-type HTMs **19**, **20**, and **21** based on the dithienopyrrolobenzothiadiazole (DTPBT) units, which were distinguished by alkyl chains of different lengths grafted on the DTPBT unit. The incorporation of the DTPBT core units is beneficial for not only carrier transporting but also potential defects passivation *via* Pb–N/S interactions. Moreover, the alkyl chains of different lengths attached to the DTPBT are found critical for the structural planarity and device performance. The extended D–A–D conjugated structure and the suitable energy level of **19** are believed critical for the improved interfacial hole extraction and transfer, which is expected to improve device performance. The PSCs based on **19** with the *n*-butyl side chains obtain the optimal PCE of 22.76% and can maintain over 96% of the initial PCE after 120 days. The improved stability is attributed to the restraint of the generation of δ -phase perovskite as supported by the grazing incidence wide-angle X-ray scattering (GIWAXS) analyses.

Based on the identified molecular design principles, Guo *et al.*^[53] rationally developed two novel D–A–D-type HTMs **22** and **23** with phenylamine groups as the donor units and imide-functionalized thiophene derivatives as the acceptor units. Both HTMs show similar photophysical and electrochemical properties but greatly different molecular configuration and film morphological properties. Due to suitable energy level, appropriate hole-transporting ability, and most importantly, the excellent film morphology (high thermal stability, smooth surface, increased hydrophobicity, and improved passivation effect), the **23**-based PSC exhibits an excellent PCE of 21.17%, while the **22**-based PSC achieves a lower PCE of 17.20%. Besides, the **23**-based device exhibited wonderful long-term stability. This work indicates that the molecular structure and the resulting film morphology also play a critical role in determining perovskite film growth on top and interfacial interactions, which is vital for developing efficient dopant-free HTMs in PSCs.

Recently, our group^[36] have successfully designed and synthesized three D–A–D-type dopant-free HTMs **24**, **25**, and **26** with triphenylamine as a donor and fused dithienobenzochalcogenadiazole (DTBX, X = O, S, and Se) unit as an acceptor for applications in PSCs. The influence of the chalcogen atom variation of the three HTMs on optical and electronic properties and their devices performance was systematically investigated. The PSC based on selenium-containing HTM **26** affords a PCE value of 15.09% without any dopants, comparable to that of the device fabricated with doped spiro-OMeTAD (17.62%). Moreover, **26**-based PSCs exhibit much better long-term stability than spiro-OMeTAD due to their superior hydrophobicity and good film-forming ability.

Other D–A–D-type SM-HTMs

The 2,1,3-benzoxadiazole (BOD) unit, as a relatively strong electron-withdrawing unit with similar structure to benzothiadiazole, has been employed as an acceptor in many D–A conjugated copolymers for organic photovoltaic applications (Figure 5). Wu *et al.*^[54] introduced the BOD unit for the first time to develop a novel D–A–D-type HTM **27** because of its high polarizability and good conjugation which can lead to significant intermolecular interactions such as π – π interactions. The best CH₃NH₃PbBr₃-based PSC with **27** exhibited a PCE (5.91%) compared to the PSC with spiro-OMeTAD (5.61%). Moreover, for the Cs_{0.05}(MA_{0.17}FA_{0.83})_{0.95}Pb(I_{0.83}Br_{0.17})₃-based PSC, **27** exhibited a much lower PCE (9.81%) compared with the cell with spiro-OMeTAD (13.2%), which is due to an energy difference, thus a small driving force, between the VB of the perovskite and the HOMO of **27**. Besides, PSCs with **27** exhibited good long-term stabilities based on both perovskite lead halide materials.

The quinoxaline unit has a moderately electron-withdrawing ability that can stabilize the HOMO level and improve the thermal-stabilities of organic HTMs. Zhang *et al.*^[40] designed and synthesized two D–A–D-type quinoxaline-based molecular HTMs **28** and **29** and applied them in PSCs. The results show that the structural change of the substituents on the quinoxaline core from phenyl (**28**) to thienyl (**29**) not only enhances the hole mobility and conductivity, but also shortens the hole extraction time. The **29**-based PSCs exhibit an optimal PCE of 19.62%, outperforming that of spiro-OMeTAD (18.54%) under the same conditions. In contrast, **28**-based PSC showed a moderate PCE (14.27%).

The thienopyrazine (TP) unit is an electron-withdrawing unit, which can enhance the ICT within the D–A–D organic molecules, thus improving the mobility. Xu and co-workers^[39] reported a novel D–A–D-based HTM **30** with triphenylamine as a donor and TP unit as an acceptor for application in PSCs. **30** shows a lower LUMO level than spiro-OMeTAD, which is due to the high electron affinity of the electron-deficient TP unit. The **30**-based PSC affords an impressive PCE value of 19.27%, which is superior to that of the PSC fabricated with spiro-OMeTAD (17.80%).

Considering that the electron-deficient nature of bipyridine might be able to adjust the energy levels of HTMs, Wu and co-workers^[55] reported two novel D–A–D structured HTMs **31** and **32** employing 2,2'- and 3,3'-bipyridine as the core structure, respectively. The introduction of the electron-deficient bipyridine core lowers the HOMO level of the new HTMs and enhances the *V*_{OC} of PSCs. The **32** with the better planarity has better conjugation in the whole molecule and the enhanced molecular interaction. As a result, **32** shows a champion PCE of 18.48%, surpass that of **31** (17.71%). The slightly higher PCE in the **32**-based PSC comes from the higher *V*_{OC} compared to the **31**-based device.

Figure 5 The structures of other D-A-D-type SM-HTMs.

Gong *et al.*^[56] designed and synthesized three D-A-D-type dopant-free SM-HTMs **33**, **34**, and **35** with different electron acceptor units. By varying the electron-withdrawing group from pyridine to pyrazine and diazine, their packing structure in single crystals, optical and electronic properties have exhibited a great difference. Three molecules were applied in PSCs as the dopant-free HTMs, and **33** achieved an improved PCE of 16.13% with minimal hysteresis and superior stability.

Zhu *et al.*^[57] designed two D-A-D-type HTMs, **36** and **37**, for the first time using benzoidone and bipyridone as core units. The electron-withdrawing core unit could enhance the interaction between molecules and promote the transfer of charge. Compared with **36**, **37** has lower HOMO energy level, better hole extraction and hole transporting ability, and higher hole mobility. The results show that the PSC based on **37** has a good PCE of 18.27% and shows almost no hysteresis effect. This work indicates that bipyridone is a suitable core group for the synthesis of D-A-D-type HTM.

Pham *et al.*^[58] developed a novel dopant-free HTM **38** based on an electron-deficient biphenylfumaronitrile (BPFN) unit as the core group and the triphenylamine (TPA) as end-capping group. The **38** with low-lying HOMO is employed as a dopant-free HTM in mesoporous PSCs yielding a best PCE of 18.4%, which is higher than that of doped spiro-OMeTAD (16.6%) under 1 sun condition. Moreover, **38**-based PSCs revealed improved stability over spiro-OMeTAD-based PSCs under similar aging condition without encapsulation.

Wang *et al.*^[59] designed and synthesized two D-n-A-n-D-structure organic small molecule HTMs **39** and **40** to investigate the effects of the introduction of different core acceptor groups on various properties of HTMs. Compared with **39**, the introduction of dicyanide with strong electron-withdraw-

ing ability lowers the LUMO level, enhances the intramolecular D-A interaction, and obtains the efficient HTM **40**. The PSC based on dopant-free **40** achieved the best performance, with the highest PCE of 16.8%, outperforming that of the PSC based on PEDOT:PSS (13.0%). In addition, the strong hydrophobic property of the **40** makes the long-term water-oxygen stability of the device much higher than that of the device using PEDOT:PSS as the hole transport layer.

Conclusions and Perspectives

As a key component of PSCs, HTMs greatly improve the efficiency and stability of devices. SM-HTMs have been the research hotspot in the field of optoelectronic materials because of their simple synthesis, easy structure modification and excellent performance. Among them, D-A-D-type HTMs have been extensively investigated in PSCs because their facile synthesis, low-lying HOMO energy levels, and impressive hole mobility. In this review, we introduced some representative D-A-D-type HTMs, and classify them by their structures. Through summarizing the molecular properties of these HTMs (Table 1), we can further understand the characteristics of efficient SM-HTMs, and inspire the following design of new HTMs. It can be concluded that D-A-D-type HTMs with good performance generally have the advantages of suitable energy level, high hole mobility, good solubility, and good thermal stability. Therefore, we should design and explore efficient HTMs from these aspects to improve the efficiency and stability of the PSCs. By summarizing previous studies, we can find that D-A-D-type HTMs based on conjugated acceptors generally have excellent performance and good stability without doping, and have good application prospects. Therefore, we can design

Table 1 Photovoltaic properties and device stability of D–A–D-type SM-HTMs

HTM	Name	HOMO/eV	$J_{sc}/(mA \cdot cm^{-2})$	V_{oc}/V	FF/%	PCE/%	Stability ^a	Ref.
1	DPBTD-B[BMPDP] ₂	−5.34	20.96	0.951	70.2	13.99	—	[42]
2	JY5	−5.21	21.06	1.06	76	16.87	77.0%, 500 h, N ₂	[43]
3	JY6	−5.21	21.39	1.07	81	18.54	83.9%, 500 h, N ₂	[44]
4	JY7	−5.23	20.58	1.05	73	15.71	75.8%, 500 h, N ₂	[44]
5	YN1	−5.35	22.36	1.07	67	16.03	61.6%, 1000 h	[39]
6	B1	−5.23	16.96	0.90	44	6.95 (pristine)	90%, 10 days	[45]
7	B3	−5.27	20.90	0.91	64	12.1 (pristine)	79%, 10 days	[45]
8	DTBT	−5.18	21.5	0.906	69.3	13.50 (pristine)	83%, 15 days	[46]
9	DTB-FL	−5.18	23.8	1.14	79.1	21.5 (pristine)	76%, 600 h	[41]
10	DPA-ANT-DPA	−5.46	16.2	1.00	71	11.5 (pristine)	90%, 50 h	[47]
11	ACE-ANT-ACE	−5.32	18.7	1.03	67.1	13.1 (pristine)	70%, 200 h	[48]
12	TPA-ANT-TPA	−5.41	21.07	1.03	79.6	17.5 (pristine)	80%, 200 h	[48]
13	ACE-QA-ACE	−5.59	22.41	1.06	77.0	18.2 (pristine)	>80%, 30 days	[49]
14	TPA-QA-TPA	−5.41	22.40	0.99	75.1	16.6 (pristine)	>60%, 30 days	[49]
15	DPA-QA-DPA	−5.28	22.38	0.95	73.2	15.5 (pristine)	>60%, 30 days	[49]
16	YN3	−5.31	22.43	1.12	75	18.84 (pristine)	97%, 300 h (Inorganic PSCs) 92%, 300 h (Hybrid PSCs)	[50]
17	DT1	−5.12	19.78	0.95	57	10.73 (pristine)	90.8%, 300 h	[51]
18	DT2	−5.13	20.72	0.99	64	13.22 (pristine)	86.8%, 300 h	[51]
19	BDAD	−5.21	24.74	1.17	78.34	22.76	>96%, 120 days	[52]
20	ODAD	−5.21	24.06	1.06	75.98	19.19	—	[52]
21	DDAD	−5.21	23.88	0.89	76.79	16.18	—	[52]
22	MPA-BTI	−5.28	21.58	1.09	73.1	17.20 (pristine)	—	[53]
23	MPA-BTTI	−5.24	23.23	1.12	81.4	21.17 (pristine)	90%, 60 days 94%, 800 h, 80 °C, N ₂	[53]
24	DTBF	−5.03	22.48	0.95	62.3	13.31 (pristine)	—	[36]
25	DTBT	−5.00	22.20	0.93	52.1	11.65 (pristine)	—	[36]
26	DTBS	−5.05	22.78	0.96	69.1	15.09 (pristine)	77.8%, 30 days	[36]
27	BTPA-3	−5.42	19.9	0.925	53.4	9.81	—	[54]
28	TQ1	−5.32	21.79	1.09	60.16	14.27	70%, 100 h	[40]
29	TQ2	−5.30	22.55	1.12	77.67	19.62	86%, 100 h	[40]
30	YN2	−5.40	23.15	1.11	75	19.27	91.3%, 1000 h	[39]
31	F22	−5.27	21.26	1.05	79	17.71	77.4%, 500 h, N ₂	[55]
32	F33	−5.32	21.01	1.11	79	18.48	75%, 500 h, N ₂	[55]
33	TM2	−5.10	20.08	1.04	77.55	16.13	~80%, 500 h	[56]
34	TM3	−5.17	20.27	1.01	77.38	15.78	~80%, 500 h	[56]
35	TM4	−5.15	19.80	0.99	57.52	11.27	~80%, 500 h	[56]
36	BP-DC	−5.23	21.21	1.04	76	16.70	~80%, 30 days, N ₂	[57]
37	PT-DC	−5.29	21.70	1.06	79	18.27	~80%, 30 days, N ₂	[57]
38	TPA-BPFN-TPA	−5.47	22.70	1.04	78.0	18.40 (pristine)	76%, 100 h	[58]
39	1-OT	−4.91	17.21	1.08	77	14.4 (pristine)	—	[59]
40	1-OTCN	−4.96	20.13	1.09	78	16.8 (pristine)	75%, 10 days	[59]

^a The percentage of the retaining performance after the ageing test (unencapsulated devices).

new D–A–D-type HTMs based on conjugate acceptors to obtain efficient and stable PSCs. In addition, the key core acceptor units of many reported D–A–D-type HTMs are usually derived from organic optoelectronic materials in other research fields, such as organic solar cell or dye-sensitized solar cell fields. These acceptor groups have outstanding photoelectric properties, so they can be adopted as the core units of D–A–D-type HTMs after modification. Inspired by this, we should learn more about the research progress in the related photoelectric field, and introduce some novel, low-cost and conjugated structure core units into the HTMs after optimization, which may obtain efficient, dopant-free, and low-cost HTMs.

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Author Contributions

Following are the details of the contributions made by each of the authors for the manuscript: Prof. Dr. Derong Cao supervised and coordinated the organization of this review. Dr. Yajie Fu drafted and finalized this manuscript. All the authors revised this manuscript.

Conflict of Interest

The authors declare no conflict of interest.

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