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ELECTRONIC SUPPLEMENTARY INFORMATION

for

Introducing pyridyl into electron transport materials plays a key role in improving electron mobility and interface property for inverted perovskite solar cells

Rui Zhu, Quan-Song Li*, Ze-Sheng Li*

Key Laboratory of Cluster Science of Ministry of Education, Beijing Key Laboratory of Photoelectronic/Electrophotonic Conversion Materials, School of Chemistry and Chemical Engineering, Beijing Institute of Technology, 100081 Beijing, China

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Computational details

The hooping mode was chosen to evaluate the charge transport processes because it is more suitable for organic semiconductor systems, where the orientation and stacking pattern of organic molecules are affected by the weak van der Waals forces.[1] The hopping motions are homogeneous random walk, and the hopping drift mobility μ was calculated based on the Einstein relation:[2]

$$\mu = \frac{eD}{k_B T}$$

where e, k_B, and T represent the elementary charge, Bolztmann's constants, and temperature, respectively. D is the diffusion coefficient for charge-carriers derived by a random walk through the kinetic Monte Carlo simulation:[3]

$$D = \frac{1}{2n}\lim_{t\to\infty}\frac{(r^2)}{t} \approx \frac{1}{2n}\sum_{mn} r_{mn}^2 W_{mn} P_{mn}$$

here n is the spatial dimensionality, r^2 is the mean-square displacement, and t is the diffusion time.

An arbitrary molecule (m) is chosen as the starting point, and 15 Å is used as the threshold value of nearest distance between hopping molecules to build transport network. Then the charge transfer rate k_{mn} was calculated in the framework of Marcus equation. The charge is only allowed to hop to the nearest neighboring molecules with a probability $P_{mn} = k_{mn} / \sum_{mn} k_{mn}$ (n is the hopping path). At each step, a random number r is uniformly generated between 0 and 1. If $\sum_{\beta=1}^{\alpha-1} p_\beta^{(m)} < r < \sum_{\beta=1}^{\alpha} p_\beta^{(m)}$, the charge then goes to the neighbor in the αth direction with a hopping time $\tau = 1/k_{mn}$. 2000 simulations were performed and averaged out to get a linear relationship between root mean-square displacement and the simulation time, then we can get the D.

The charge transfer rate k_{mn} was expressed by the Marcus formulation:[4]

$$k_{mn} = \frac{4\pi^2 v^2}{h}\frac{1}{\sqrt{4\pi\lambda k_B T}}\exp\left(-\frac{\lambda}{4k_B T}\right)$$

here, h is the Planck constants, T was set to 300 K, λ is the reorganization energy, and v is the transfer integral.

The inner reorganization energy was estimated by the adiabatic potential energy surface approach,[5, 6]

$$\lambda = \lambda_1 + \lambda_2 = E_\pm(Q_N) - E_\pm(Q_\pm) + E_N(Q_\pm) - E_N(Q_N)$$

where the subscripts N, +, and − denote neutral, cationic, and anionic electronic state, respectively.

The transfer integral (v) measures the strength of electronic coupling between adjacent molecules, and can be estimated by the site-energy corrected approach,[7]

$$v_{mn} = \frac{v_{mn}^{0} - \frac{1}{2}(e_m + e_n)S_{mn}}{1 - S_{mn}^{2}}$$

where $e_{m(n)} = <\Phi_{m(n)}|H|\Phi_{m(n)}>$, $v_{mn} = <\Phi_m|H|\Phi_n>$, and $S_{mn} = <\Phi_m|S|\Phi_n>$, in which $\Phi_{m(n)}$ is the frontier molecular orbital of monomer m(n) in the dimer. H and S are the dimer Hamiltonian and the overlap matrices, respectively. The above calculations were done by using Gaussian and MOMAP software packages.[8, 9]

The polymorph module in Materials Studio 5.5 software package was used to predict the crystal structures of the studied compounds.[10] Firstly, the single molecules were optimized in Dmol3 with accuracy setting in fine, at the same time the electrostatic potential and population analysis were carried out. Next the crystal structure prediction was carried out by employing the Perdew-Burke-Ernzerhof (PBE) exchange–correlation energy functional and the Dreiding force field. The polymorph predictor simulation was restricted to the five most popular space groups $P2_1/C$, P1, $P2_12_1$, $P2_1$ and P2/c.[11, 12] Based on the obtained crystal structures, the charge transfer integral calculation was performed at PW91PW91/6-31G(d) level, which gave the results very close to the experimental ones.[13]

In the calculations about the $MAPbI_3$/ETM interface, we chose the widely used 110-perovskite surface in tetragonal phase of $MAPbI_3$ to compare our results on **TDTP** derivatives with previous reported results on **TDTP**. [14] Both PbI_2 and MA terminals have been considered. Our slab models have a 2 × 2 periodicity in-plane, and a 20 Å vacuum region was added. The calculations were carried out with the GGA-PBE functional[15] on VASP software.[16] The vdw-DF2 functional for the exchange correlation was employed, because van der Waals interactions play a major role on the stability of the interface. [17] The valence wave functions were expanded by plane waves with a cutoff energy of 400 eV. Geometries were relaxed until the residual force less than 0.05 eV/Å per atom.

Table ESI1 Absolute CCSD/6-31g (d, p) energies of the studied compounds optimized by B3LYP/6-31g (d, p) in dichloromethane

Molecules	Energy (au)
TDTP	− 2591.509
o-PDTP	− 1904.318
m-PDTP	− 1904.320
p-PDTP	− 1904.318

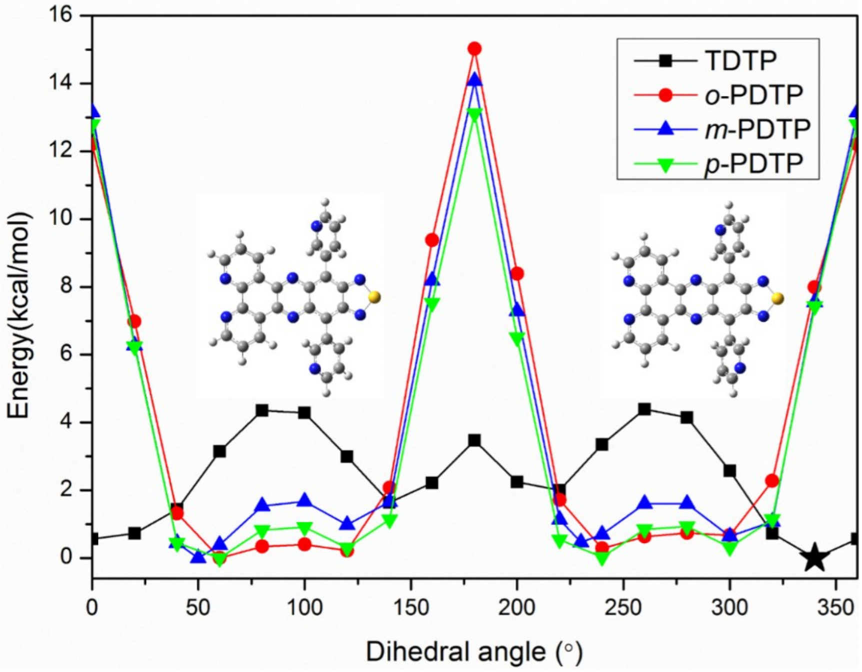
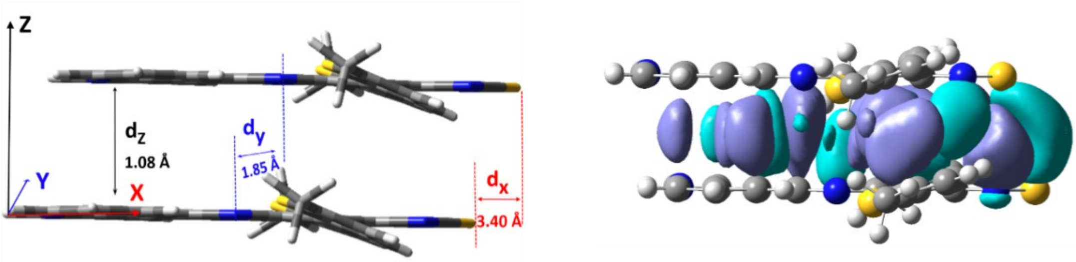
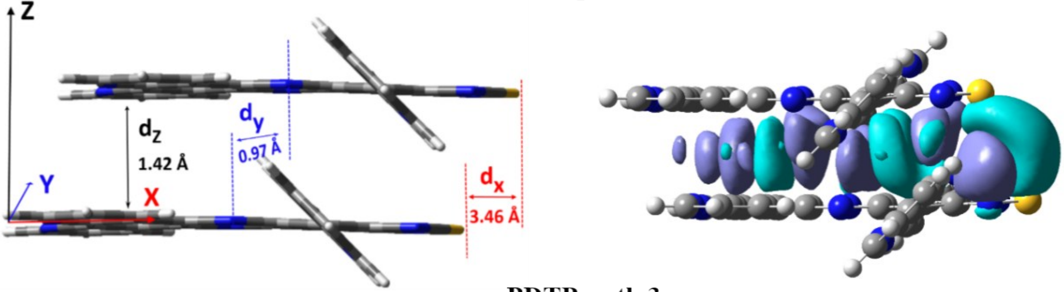


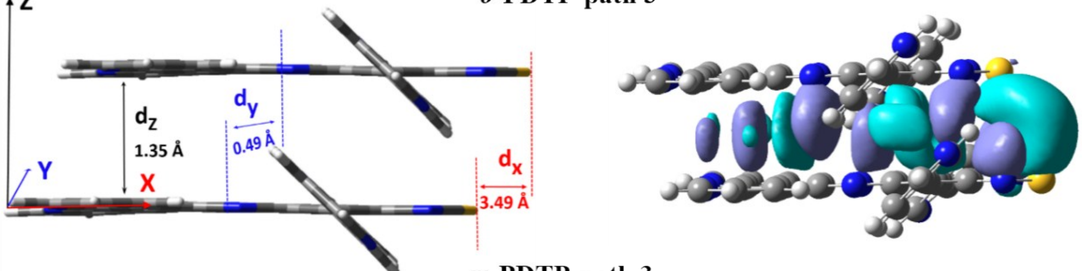
Fig. ESI1 Relative energies along the scan of the dihedral angle between the substituent groups and the molecular skeleton of the investigated molecules.



TDTP-path 3

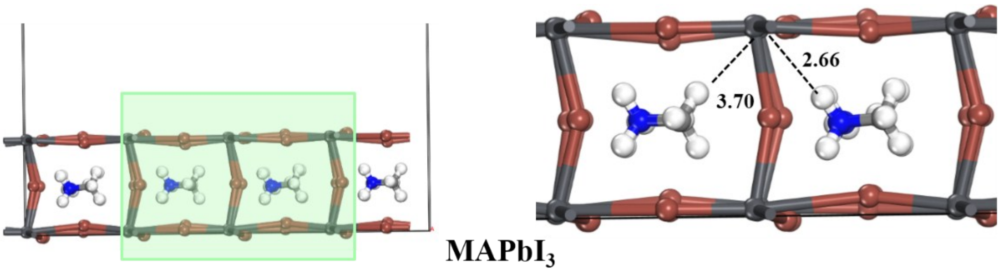


***o*-PDTP-path 3**

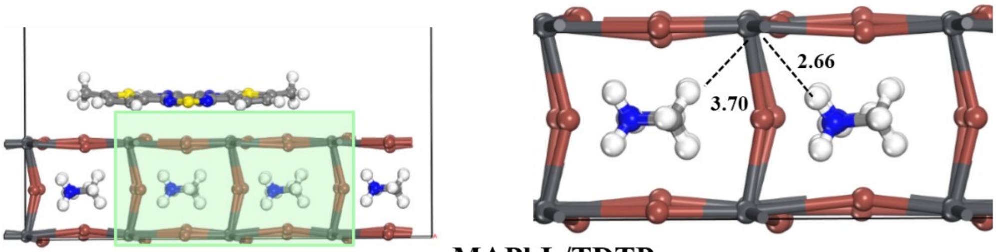


***m*-PDTP-path 3**

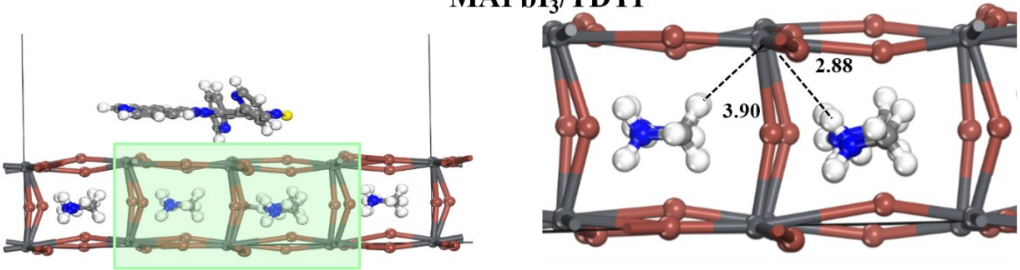
Fig. ESI2 Displacements and LUMO-LUMO overlap in dimers of TDTP, *o*-PDTP, and *m*-PDTP.



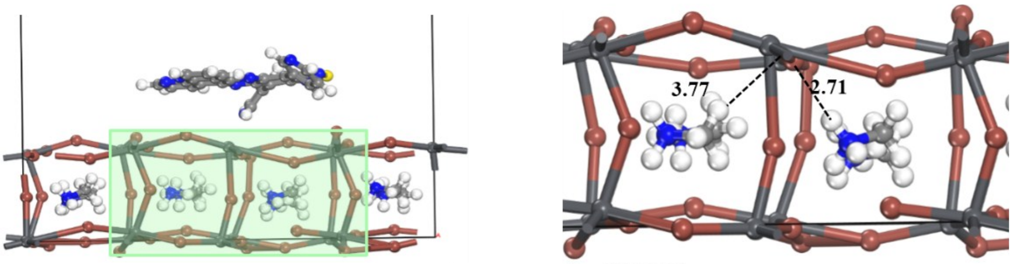
$MAPbI_3$



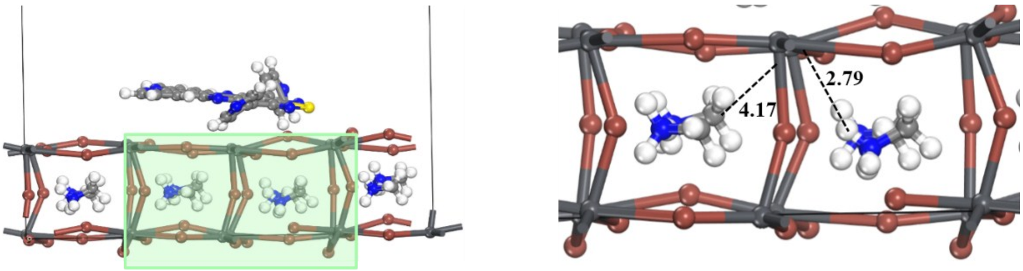
$MAPbI_3$/TDTP



$MAPbI_3$/*o*-PDTP

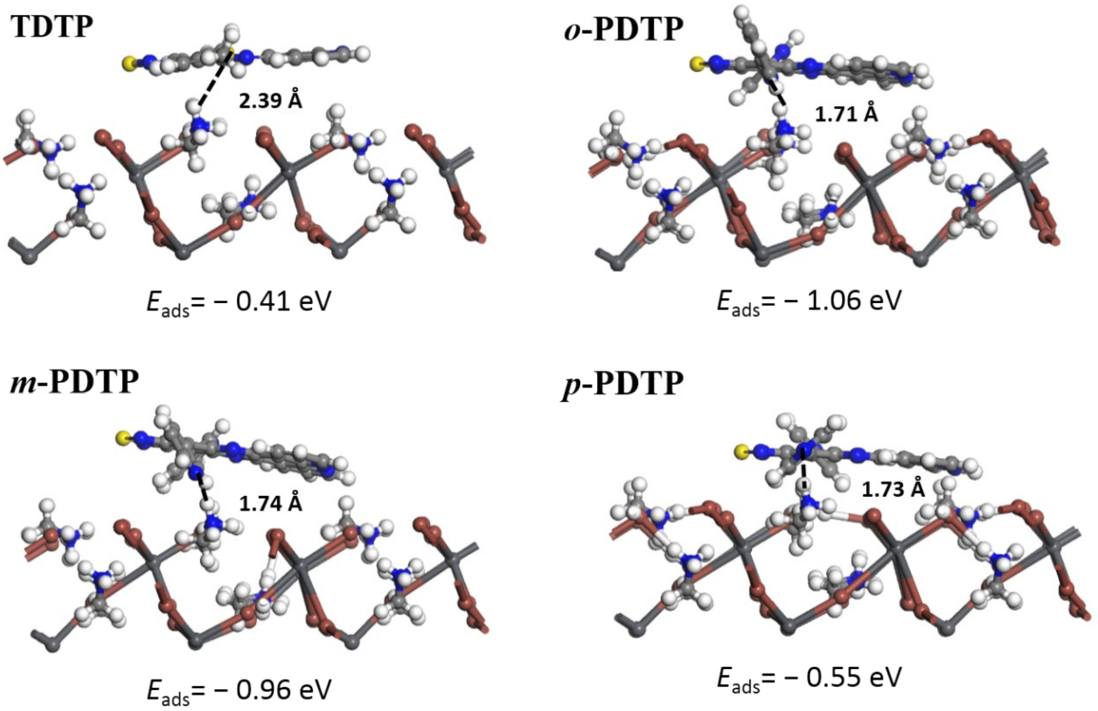


$MAPbI_3$/*m*-PDTP



$MAPbI_3$/*p*-PDTP

Fig. ESI3 The selected $H_{MA}\cdots I$ distances in $MAPbI_3$ with and without ETMs on the PbI_2-terminated $MAPbI_3$ (110) surface.



TDTP

$E_{ads} = -0.41$ eV

***o*-PDTP**

$E_{ads} = -1.06$ eV

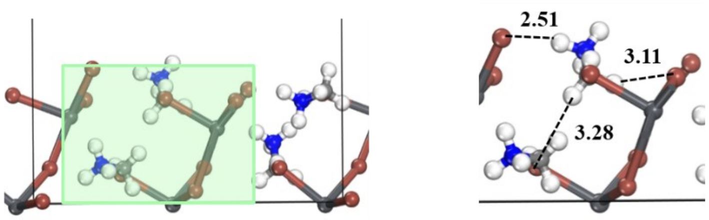
***m*-PDTP**

$E_{ads} = -0.96$ eV

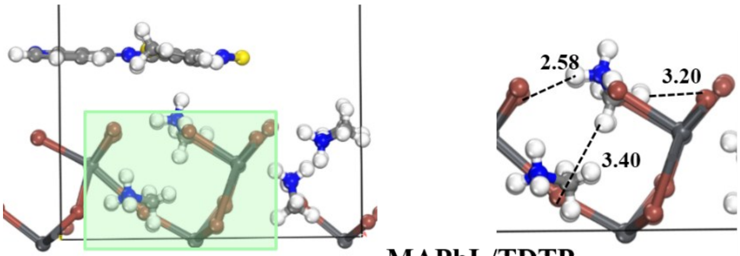
***p*-PDTP**

$E_{ads} = -0.55$ eV

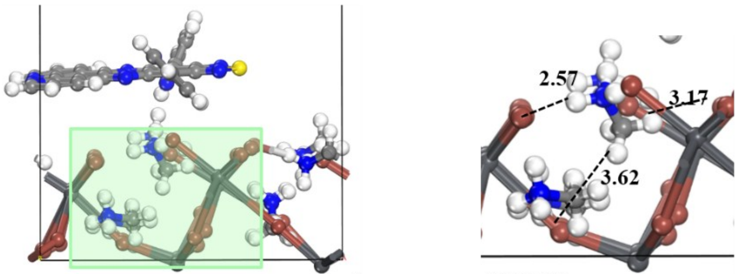
Fig. ESI4 Optimized structures and binding energies for ETMs on MA-terminated $MAPbI_3$ (110) surface. The dashed lines indicate the key S⋯H and N⋯H distances.



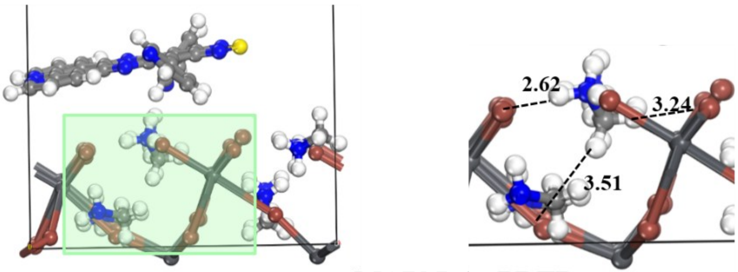
MAPbI$_3$



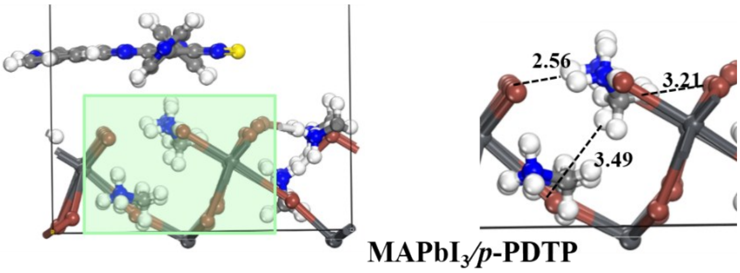
MAPbI$_3$/TDTP



MAPbI$_3$/*o*-PDTP



MAPbI$_3$/*m*-PDTP



MAPbI$_3$/*p*-PDTP

Fig. ESI5 The selected $H_{MA}\cdots I$ distances in MAPbI$_3$ with and without ETMs on the MA-terminated MAPbI$_3$ (110) surface.

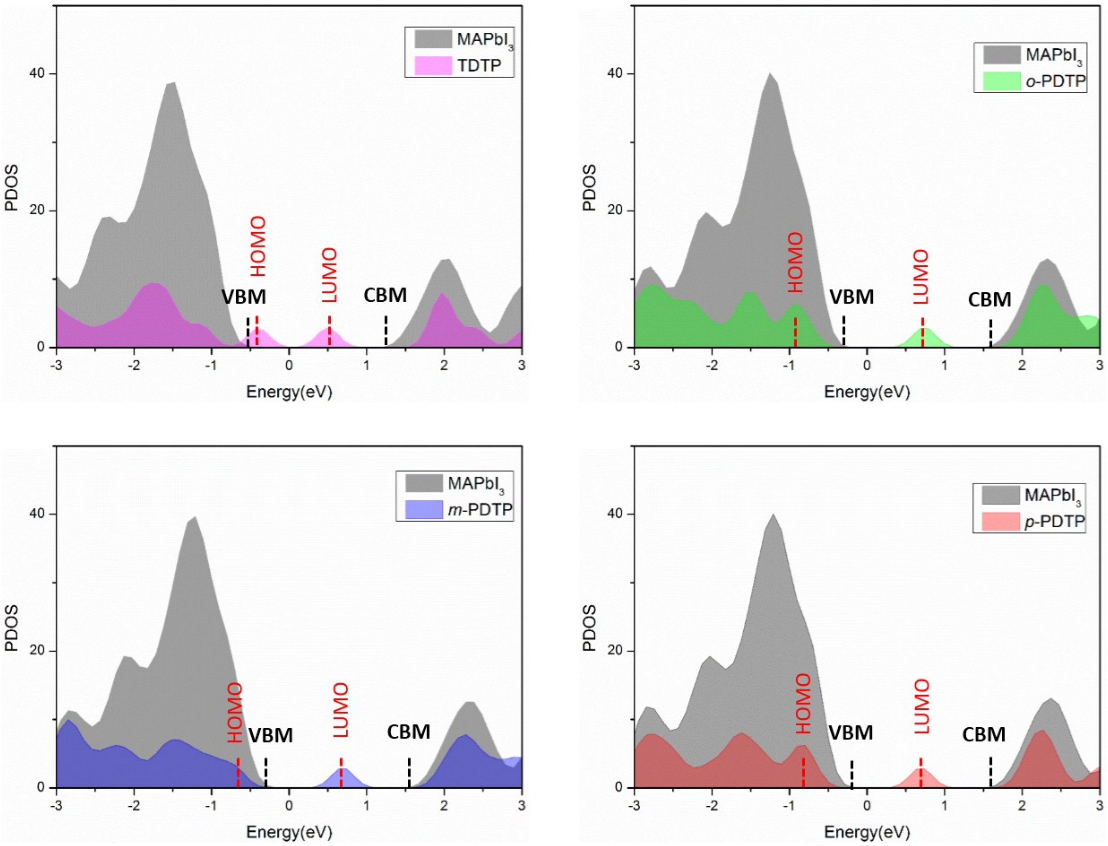


Fig. ESI6 Partial density of states (PDOS) with summed contributions from ETMs and MAPbI$_3$ for the MA-terminated MAPbI$_3$ (110)/ETMs interface. The HOMO and LUMO energy levels of ETMs and the VBM and CBM of MAPbI$_3$ are also shown.

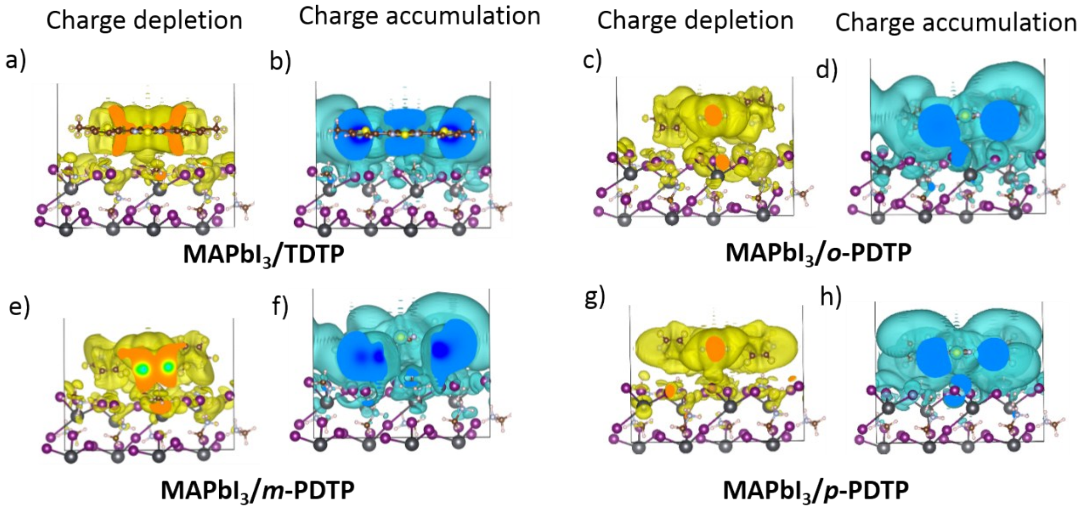


Fig. ESI7 Electron charge density difference for TDTP-based ETMs on MA-terminated $MAPbI_3$ (110) surface with an isovalue of 1×10^{-4} e/$Å^3$.

Cartesian coordinates of the studied compounds optimized by B3LYP/6-31g (d, p) in dichloromethane

TDTP

C	0.73512700	-3.02940000	-0.12941300
C	1.50290300	-1.82476700	-0.12064700
C	0.73095000	-0.63266000	-0.10017500
C	-0.72933200	-0.63442200	-0.10046200
C	-1.49855800	-1.82831100	-0.11984600
C	-0.72801100	-3.03113500	-0.12880400
C	-0.72409000	1.68766700	-0.09858900
C	0.72002900	1.68946200	-0.09667500
C	1.44259100	2.96316100	-0.10446900
C	0.73486700	4.18924600	-0.09105000
C	-0.74546500	4.18732800	-0.09476500
C	-1.44993100	2.95942400	-0.11023800
C	-2.71253200	5.38725400	-0.11228000
C	-3.49889300	4.22573700	-0.13834300
C	-2.85536300	2.99914100	-0.13857600
H	-3.18425300	6.36763800	-0.10963500
H	-4.58123500	4.29565800	-0.15931600
H	-3.41081700	2.06917400	-0.16017800
C	2.84802000	3.00661400	-0.12648200
C	3.48833100	4.23489000	-0.12191100
C	2.69884300	5.39433000	-0.09779800
H	3.40602100	2.07814900	-0.14660700
H	4.57057100	4.30764500	-0.13792000
H	3.16799300	6.37592800	-0.09149500
S	0.00625900	-5.32084800	-0.07547500
C	-5.43430000	-1.47769700	0.27599900
C	-5.15775200	-2.67312200	-0.34569100
C	-3.77204900	-2.89835300	-0.55556100
C	-2.95546800	-1.86721800	-0.11434300
S	-3.96418400	-0.58743100	0.56944000
H	-5.93004300	-3.37461900	-0.64327200
H	-3.37817900	-3.79359100	-1.01471300
C	5.43843200	-1.46581600	0.27052700
C	5.16365500	-2.66137700	-0.35165800
C	3.77815500	-2.88949500	-0.55975600
C	2.95991600	-1.86050600	-0.11660800
S	3.96674300	-0.57902800	0.56671500
H	5.93707200	-3.36092500	-0.65090000
H	3.38562700	-3.78521900	-1.01910900
C	6.77530800	-0.90130400	0.64925200
H	6.96748700	0.05686500	0.15325000
H	6.85280400	-0.73143500	1.72920300
H	7.56572500	-1.59840800	0.35806500
C	-6.77188400	-0.91589700	0.65627400
H	-6.84819900	-0.74555100	1.73623500
H	-6.96688700	0.04155300	0.15998500
H	-7.56118500	-1.61490700	0.36664000
N	-1.38056700	5.37655700	-0.09352100
N	1.36683600	5.38016100	-0.08524500
N	-1.39232500	0.55326400	-0.09963700
N	1.39106700	0.55668200	-0.09738400
N	-1.24298800	-4.27677700	-0.09789600
N	1.25303500	-4.27384200	-0.09897500

***o*-PDTP**

C	-3.03283800	-0.72450900	-0.00067300
C	-1.83075900	-1.46706800	0.01345100
C	-0.63441900	-0.72853100	0.02223800
C	-0.63127800	0.73090100	0.01545100
C	-1.82451900	1.47144500	0.01702000
C	-3.02815100	0.73390300	0.00131300
C	1.67857100	0.72387800	-0.03146700
C	1.67667400	-0.72895900	-0.00523900
C	2.95175400	-1.45178900	-0.00836400
C	4.17861000	-0.74776100	-0.04375300
C	4.18060000	0.73334300	-0.08502000
C	2.95582900	1.44175100	-0.07795600
C	5.38439800	2.69608700	-0.16409300
C	4.22541400	3.48653200	-0.15788100
C	2.99775700	2.84645100	-0.11406400
H	6.36567100	3.16449700	-0.19930300
H	4.29813900	4.56842000	-0.18685900
H	2.06784800	3.40306300	-0.10671700
C	2.98971500	-2.85669200	0.02665400
C	4.21579200	-3.50130800	0.02674400
C	5.37713600	-2.71507300	-0.00788500
H	2.05816300	-3.41005800	0.05392600
H	4.28559600	-4.58345900	0.05315400
H	6.35733000	-3.18705100	-0.00773900
S	-5.31370600	0.01310700	0.03149200
N	5.37086200	1.36411500	-0.12846900
N	5.36721300	-1.38305100	-0.04230100
N	0.55647300	1.40583600	-0.02457000
N	0.55219400	-1.40715000	0.01047800
N	-4.27193200	1.26608300	0.01841900
N	-4.28043600	-1.24567800	0.02170300
C	-1.84151600	2.96310800	0.04993300
C	-2.30545800	3.69233200	-1.05326400
C	-2.31510600	5.08526000	-0.98429600
H	-2.64442400	3.17469600	-1.94428600
C	-1.43781800	4.89240800	1.23711900
H	-2.66302500	5.67445000	-1.82729000
H	-1.09221800	5.33709400	2.16767900
C	-1.85010300	-2.95787000	0.01600200
C	-1.34319200	-3.68275900	1.10392300
C	-2.44018100	-4.89428200	-1.08059500
C	-1.40706800	-5.07503500	1.07380500
H	-0.91477700	-3.16094300	1.95235700
H	-2.87844300	-5.34327500	-1.96904500
H	-1.02723700	-5.66009000	1.90589000
C	-1.87170900	5.70298100	0.18563100
C	-1.96620900	-5.69905600	-0.04248300
N	-1.41623100	3.55273700	1.18251400
N	-2.39340100	-3.55413900	-1.06131800
H	-1.86264300	6.78317100	0.28745900
H	-2.03543300	-6.77964800	-0.11180800
C	-0.63127800	0.73090100	-0.00067300

_m_-PDTP

C	-3.03660800	-0.72898300	-0.01121300
C	-1.83383100	-1.47780600	-0.01929500
C	-0.63850800	-0.73000800	0.00109600
C	-0.63850500	0.73001000	-0.00111000
C	-1.83382400	1.47781400	0.01928800
C	-3.03660500	0.72899600	0.01121100
C	1.67492200	0.72438700	-0.04022400
C	1.67491900	-0.72439400	0.04021600
C	2.94957500	-1.44349800	0.10624600
C	4.17577500	-0.73859800	0.05911700
C	4.17577800	0.73858000	-0.05911900
C	2.94958100	1.44348600	-0.10625100
C	5.37613400	2.69859100	-0.21895700
C	4.21557500	3.48524500	-0.26976600
C	2.98865200	2.84486000	-0.21217300
H	6.35681500	3.16739500	-0.26368700
H	4.28662600	4.56446000	-0.35233600
H	2.05750800	3.39855600	-0.24737100
C	2.98864000	-2.84487300	0.21216900
C	4.21556000	-3.48526300	0.26976400
C	5.37612200	-2.69861300	0.21895900
H	2.05749300	-3.39856500	0.24736500
H	4.28660600	-4.56447800	0.35233500
H	6.35680100	-3.16742100	0.26369100
S	-5.32236900	0.00001200	-0.00001900
N	5.36502200	1.37000900	-0.11625100
N	5.36501600	-1.37003200	0.11625200
N	0.54966100	1.40181100	-0.04971800
N	0.54965500	-1.40181300	0.04970900
N	-4.28213700	1.25357800	0.02959800
N	-4.28214300	-1.25356000	-0.02957700
C	-1.85440700	2.95743100	0.04503200
C	-2.62760000	3.70004900	-0.85999200
C	-2.61602400	5.09180600	-0.78519300
H	-3.21744600	3.19511000	-1.61720700
H	-3.19536700	5.69279100	-1.47843100
C	-1.85442200	-2.95742300	-0.04502900
C	-2.62761400	-3.70003100	0.86000400
C	-2.61604700	-5.09178800	0.78521400
H	-3.21745300	-3.19508300	1.61721900
H	-3.19539000	-5.69276500	1.47846000
C	-1.83915500	5.70386500	0.19917300
C	-1.83918800	-5.70385800	-0.19915300
H	-1.80548500	6.78744000	0.28330400
H	-1.80552600	-6.78743400	-0.28327700
N	-1.10307400	5.01426900	1.08657000
N	-1.10310900	-5.01427300	-1.08655900
C	-1.11592700	-3.67886500	-1.00135800
C	-1.11590100	3.67886100	1.00136000
H	-0.52095900	-3.14522300	-1.73661800
H	-0.52093000	3.14521100	1.73661200

_p_-PDTP

C	-3.02963600	0.72913300	0.01154700
C	-1.82653000	1.47533300	0.02365100
C	-0.63082000	0.72975900	0.00328900
C	-0.63085000	-0.72973400	-0.00337700
C	-1.82659200	-1.47525000	-0.02372500
C	-3.02966400	-0.72900300	-0.01164400
C	1.68173500	-0.72500700	0.03486000
C	1.68176400	0.72492600	-0.03489000
C	2.95635800	1.44419700	-0.09681800
C	4.18242100	0.73887700	-0.05459500
C	4.18239300	-0.73905200	0.05453900
C	2.95630300	-1.44432300	0.09679000
C	5.38252100	-2.69988300	0.20365100
C	4.22199100	-3.48688300	0.25013800
C	2.99507400	-2.84622500	0.19567800
H	6.36317500	-3.16888800	0.24612700
H	4.29319200	-4.56645000	0.32764600
H	2.06373800	-3.39982300	0.22881100
C	2.99517600	2.84609900	-0.19566600
C	4.22211700	3.48671400	-0.25010300
C	5.38261900	2.69967000	-0.20363600
H	2.06385900	3.39972900	-0.22877400
H	4.29335900	4.56628100	-0.32757200
H	6.36328800	3.16864300	-0.24610500
S	-5.31437000	0.00010000	-0.00001400
N	5.37151000	-1.37068500	0.10848800
N	5.37156200	1.37046900	-0.10850900
N	0.55681200	-1.40270300	0.03930700
N	0.55687200	1.40267000	-0.03936700
N	-4.27541800	-1.25353700	-0.03082100
N	-4.27537500	1.25370500	0.03071700
C	-1.84732700	-2.95785600	-0.05369700
C	-2.60072600	-3.69181900	0.87498800
C	-1.13628000	-3.68613300	-1.01988500
C	-2.60021400	-5.08503400	0.80349900
H	-3.17196600	-3.19137800	1.64845900
C	-1.20957200	-5.07861700	-1.01262200
H	-0.54289300	-3.17973300	-1.77203100
N	-1.92275300	-5.78471900	-0.12023300
H	-3.17330000	-5.66495500	1.52318000
H	-0.66821400	-5.65376800	-1.76018900
C	-1.84717600	2.95793400	0.05368600
C	-1.13609700	3.68611200	1.01993000
C	-2.60051300	3.69200600	-0.87496300
C	-1.20929100	5.07859900	1.01274600
H	-0.54276900	3.17963500	1.77207000
C	-2.59991500	5.08521700	-0.80338700
H	-3.17178200	3.19166000	-1.64847200
N	-1.92242200	5.78480300	0.12039400
H	-0.66792700	5.65366600	1.76037400
H	-3.17296600	5.66521200	-1.52303600

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