Mendeleev Communications

Mendeleev Commun., 2025, **35**, 386–389

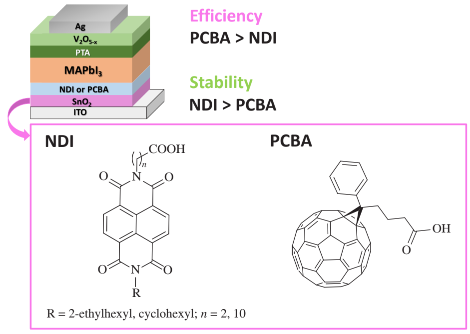
Naphthalenediimides with carboxyl anchoring groups as promising components of the electron transport layer in n-i-p perovskite solar cells

**Sergey L. Nikitenko,[a] Olga A. Kraevaya,[a] Alexandra A. Sokolova,[a,b] Nikita A. Slesarenko,[a]
Evgeniya P. Antoshkina,[c,d] Ekaterina A. Khakina,[c] Alexander S. Peregudov,[c]
Pavel A. Troshin*[e,a] and Sergey M. Aldoshin[a]**

[a] *Federal Research Center of Problems of Chemical Physics and Medicinal Chemistry, Russian Academy of Sciences, 142432 Chernogolovka, Moscow Region, Russian Federation. E-mail: troshin2003@inbox.ru*
[b] *Department of Fundamental Physical and Chemical Engineering, M. V. Lomonosov Moscow State University, 119991 Moscow, Russian Federation*
[c] *A. N. Nesmeyanov Institute of Organoelement Compounds, Russian Academy of Sciences, 119334 Moscow, Russian Federation*
[d] *Moscow Institute of Physics and Technology (National Research University), 141701 Dolgoprudny, Moscow Region, Russian Federation*
[e] *Zhengzhou Research Institute of HIT, 450003 Zhengzhou, China*

DOI: 10.71267/mencom.7683

A series of unsymmetrically substituted naphthalenediimide derivatives containing pendant carboxyl groups were used as a passivating coating of tin dioxide electron transport layer in n-i-p perovskite solar cells. Devices fabricated using naphthalenediimides showed competitive performances reaching 16.5% (compared to 17.6% provided by fullerene derivative PCBA) and, most importantly, demonstrated improved operational stability. These results indicate the potential for further exploration of naphthalenediimide derivatives as highly promising and cost-efficient electron transport layer materials for perovskite solar cells.



Keywords: naphthalenediimides, anchoring groups, electron transport materials, perovskite solar cells, passivation coatings.

Perovskite solar cells (PSCs) based on complex lead halides are a promising emerging photovoltaic technology that has the potential to become a lower-cost alternative to conventional silicon photovoltaic panels. The current efficiency record of PSCs is approaching 26.8%, which is very close to the best crystalline silicon solar cells (27.2%).[1] Among the challenges in translating perovskite photovoltaic technology from research laboratories to industry, the most important one is the problem of insufficient operational stability of PSCs.[2–4] In addition to the aging effects occurring in the perovskite absorber layer, there are also severe problems arising at the interfaces.[5] Both the efficiency and stability of PSCs are significantly affected by the charge transport layers located between the active perovskite layer and the metal electrodes.[6,7] The first-generation PSCs with negative-intrinsic-positive (n-i-p) device configuration used titanium dioxide as the electron transport layer (ETL) deposited on the bottom transparent electrode.[8] However, titanium dioxide is known for its photocatalytic properties, due to which the $TiO_2/APbI_3$ [A is a monovalent cation such as Cs^+, methylammonium (MA) or formamidinium (FA)] interface undergoes light-induced degradation, accompanied by partial reduction of Ti^{IV} and oxidation of I^-.[9] To mitigate this problem, TiO_2 was replaced with SnO_2 or other oxides in the second generation of n-i-p PSCs.

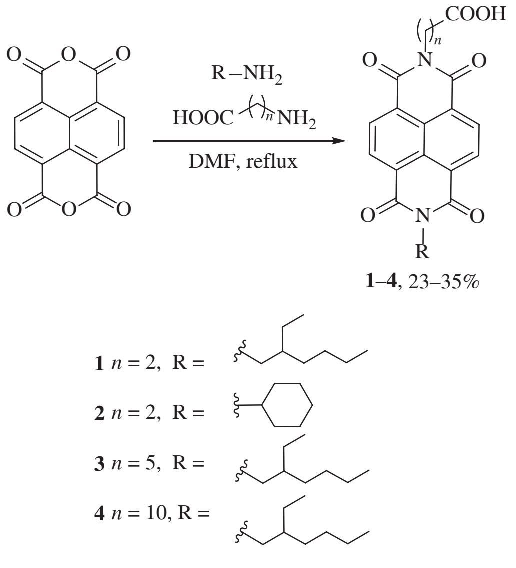
With lower photocatalytic activity compared to TiO_2, tin dioxide is considered as a very promising ETL material to achieve long-term stability of n-i-p as well as p-i-n PSCs.[10–12] Currently, the most efficient n-i-p PSCs use SnO_2 as the ETL material.[12,13] However, SnO_2 cannot be considered as a completely inert material toward complex lead halides because Sn^{IV} can oxidize I^- under light exposure. Previously, we introduced fullerene derivative PCBA (phenyl-C_{61}-butyric acid) as a passivation coating for SnO_2, which dramatically improved the photovoltaic performance and stability of n-i-p PSCs compared with bare oxide ETL devices.[14,15] However, it was shown that fullerene derivatives also tend to accelerate the light-induced degradation of complex lead halides at the perovskite absorber/ETL interface.[16] Therefore, this creates a strong motivation to replace PCBA with some non-fullerene passivation coatings, which could potentially improve the operational stability of PSCs.

In another context, the development of p-i-n PSCs has recently been streamlined by the introduction of hole-selective self-assembled monolayers (SAMs), mainly based on carbazole derivatives with pendant carboxyl or phosphonic anchoring groups, capable of directly attaching to the indium tin oxide (ITO) surface.[17,18] Following this approach, the ETL in n-i-p PSCs can also be potentially replaced by electron-selective SAMs, which would significantly reduce the series resistance of this layer and improve the power conversion efficiency (PCE) of the devices. The feasibility of this approach has been demonstrated very recently using SAMs of unsymmetrical naphthalenediimides (NDIs), which provided an impressive efficiency of up to 24%.[19] Thus, this result creates an impetus for further design and investigation of electron-selective monolayers based on electron-deficient organic molecules with carboxyl anchoring groups.

In this work, we synthesized and characterized a series of unsymmetrically substituted NDIs using a simple random condensation reaction of 1,4,5,8-naphthalenetetracarboxylic dianhydride with aliphatic amines (2-ethylhexylamine or cyclohexylamine) and 3-aminopropionic, 6-aminocaproic or 11-aminoundecanoic acids (Scheme 1). The target unsymmetrical NDIs were readily separated from symmetrical byproducts and isolated by column chromatography in acceptable yields of 23–35%. The resulting compounds were characterized by LDI ToF mass spectrometry and 1D and 2D NMR spectroscopy, which confidently confirmed the expected molecular structures (Figures S1–S24, see Online Supplementary Materials).

Unsymmetrically substituted NDIs **1**–**4** exhibit obvious amphiphilic properties and are well soluble in organic solvents of different polarity, such as chlorobenzene, tetrahydrofuran, dimethyl sulfoxide, DMF, *etc.* This enabled us to evaluate their performance as passivation coatings for the SnO_2 ETL in n-i-p PSCs. Basically, there are two most common approaches to deposit SAMs of compounds with anchoring groups. The first one is based on immersion of the SnO_2 sample into a solution of the SAM-forming compound, incubation for a certain time required for molecular adsorption, subsequent rinsing with pure solvent and drying. This approach, called 'soaking', provides enough time for the system to reach an equilibrium state, as a result of which a very dense SAM is usually formed. Alternatively, a very dilute (*e.g.*, 0.1 mg ml^{-1}) solution of the SAM-forming compound can be spin-coated onto the substrate, typically at a very high spin rate of 3000–6000 rpm. This process is very fast and therefore the SAM-forming compound is deposited at the most accessible (or reactive) defect sites, so the structure of the coating formed may be very different from a perfectly ordered monolayer.

We explored both approaches to modify the surface of SnO_2 films with NDIs **1**–**4**. The surface properties of the obtained coatings were analyzed using contact angle measurements with water and diiodomethane droplets. Films modified by the soaking approach generally showed higher water contact angles and lower surface energy values compared to the spin-coated samples (Table S1, see Online Supplementary Materials). The higher hydrophobicity of the samples prepared using the soaking approach indicates a complete surface modification, whereas for the spin-coated samples we could assume an island-type distribution of the deposited compounds. Still, both series of samples showed drastically different surface properties compared to bare SnO_2, indicating a rather strong surface modification.



Scheme 1

The samples modified with NDIs **1**–**4** also showed much higher total surface energy than the bare SnO_2 and SnO_2 coated with PCBA. Consequently, the wettability of the SnO_2/NDI films for the lead halide perovskite precursor solution in DMF was reduced, which significantly affected the uniformity of the grown $MAPbI_3$ films. Although we failed to obtain SnO_2/NDI **3**/$MAPbI_3$ films of sufficient quality for the fabrication of operational PSCs, the SnO_2 films coated with NDIs **1**, **2** and **4** were fully compatible with the PSC fabrication process, allowing us to evaluate their performance. The layout of the n-i-p PSC architecture used is schematically shown in Figure 1(*a*). Poly[bis(4-phenyl)(4-methylphenyl)amine], known as PTA,[20] was used as the hole transport layer material, while vanadium(V) oxide was evaporated to form the electron-blocking layer and the top metal electrode.[15]

It was observed that PSCs processed using soaking SnO_2 in the solutions of NDIs as well as PCBA showed significantly worse characteristics compared to similar cells fabricated by spin-coating of the corresponding passivation layers [Table S2 and Figure 1(*b*),(*c*)]. This is especially evident for the devices using SnO_2/NDI **2** as the ETL, which exhibited decent PCE of over 15% when NDI **2** was spin-coated, whereas the performance of PSCs fabricated by soaking approach was below 6%. This effect could be attributed to the unfavorable surface properties of ETL films modified by soaking SnO_2 in NDI solutions, which affects the uniformity of the coated perovskite absorber layer as discussed above. Therefore, partial surface modification of SnO_2 by spin-coating the modifying compounds represents a more promising technique to achieve reasonable solar cell performance.

The reference devices using bare SnO_2 showed very poor performance with huge hysteresis in the current–voltage characteristics [see Figure 1(*b*),(*c*)]. This indicates that the SnO_2 layer has many reactive OH groups and other defect sites on the surface, which lead to a suboptimal interface with the top-deposited $MAPbI_3$ perovskite absorber layer. In contrast, devices incorporating PCBA as a passivation coating showed the best performance with a PCE of over 17% regardless of its deposition method, be it soaking or spin-coating. PSCs using NDIs as passivation coatings demonstrated slightly reduced performance with PCEs of 15–16.5%. The main difference was in the open-circuit voltage (V_{OC}) values, which were 50–90 mV lower for cells assembled with NDIs compared to the PCBA-based reference cells. The voltage loss may be ascribed to an

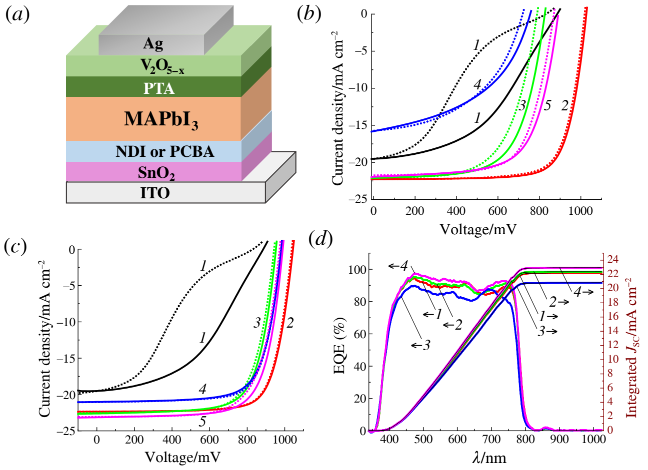


Figure 1 (*a*) Structure of n-i-p PSCs used in this work. (*b*),(*c*) Reverse (solid lines) and forward (dashed lines) scanned current–voltage characteristics of PSCs assembled using (*1*) bare SnO_2 or SnO_2 modified with (*2*) PCBA, (*3*) NDI **1**, (*4*) NDI **2** or (*5*) NDI **4** by (*b*) soaking or (*c*) spin-coating. (*d*) EQE spectra and integrated short-circuit current density spectra of PSCs fabricated using spin-coating of (*1*) PCBA, (*2*) NDI **1**, (*3*) NDI **2** or (*4*) NDI **4**.

inappropriate energy level alignment at the perovskite/ETL interface, which is unlikely since NDI derivatives have electronic properties similar to fullerene derivatives (*e.g.*, PCBM or PCBA) and have been successfully used in p-i-n cells.[21,22] Alternatively, the V_{OC} losses could be associated with an increase in charge transfer resistance at the perovskite/ETL interface, probably caused by the relatively large alkyl side chains.

The results obtained in this work provide strong evidence that NDIs with anchoring groups can be used for surface passivation of the oxide-based ETLs. This approach seems to be economically very attractive since the cost of NDIs is 10–100 times lower compared to that of fullerene derivatives, while their performance is already comparable in this specific application. Some further material engineering focusing on the use of shorter and more polar substituents R in the core of unsymmetrically substituted NDIs may provide PSCs with higher PCE.

Another important aspect is the operational stability of the PSCs. We investigated the aging process of the fabricated PSCs with different ETLs under continuous white light illumination (100 mW cm^{-2}) at 40–50 °C. All cells were tested in the open-circuit mode, which is known to cause the most severe aging effects.[23] Figure 2 provides an overview of the initial performance of pristine and aged PSCs, respectively, before and after 300 h of continuous white light illumination. It can be seen that the efficiency of the reference cells with the PCBA passivation coating decreased significantly by 25–30%. Devices using NDIs as passivation coatings demonstrated drastically different behavior: their efficiency decay was much smaller, while some devices even showed increased performance after light exposure. In particular, devices using NDI **4** clearly outperformed PCBA-based cells after 300 h of aging. Thus, the obtained results demonstrate that NDI-based passivation coatings provide better operational stability of PSCs compared to fullerene derivatives such as PCBA. It is also worth noting that PSCs assembled using SnO_2 soaking in solutions of the corresponding passivation compounds demonstrated superior stability compared to solar cells produced using spin-coating of NDIs or PCBA. Thus, a more complete coverage of the oxide surface with SAM molecules is beneficial for the operational stability of the device, but creates some issues with the ETL surface wettability by the perovskite ink.

In summary, we designed, synthesized and characterized a series of unsymmetrically substituted NDI derivatives bearing carboxyl anchoring groups enabling these compounds to be adsorbed on metal oxide surfaces. The resulting NDIs **1**, **2** and **4** were investigated as passivation coatings for SnO_2 used as the ETL material in n-i-p PSCs. All NDIs were shown to significantly improve the photovoltaic performance of the cells compared to the reference devices based on bare unmodified SnO_2. Still, the best efficiency of ~16.5% achieved for the PSCs using NDIs as passivation coatings is noticeably lower compared to the performance provided by the fullerene derivative PCBA (17.6%), mainly due to the reduced open-circuit voltages. Therefore, further efforts are needed to optimize the NDI/perovskite absorber interface to reduce the voltage losses and thus boost the performance of n-i-p PSCs. The high positive effect of NDI-based passivation coatings on the operational stability of PSCs, combined with the low cost of these materials compared to fullerene derivatives, highlight the potential for their further exploration to develop an efficient, stable and commercially viable perovskite photovoltaic technology.

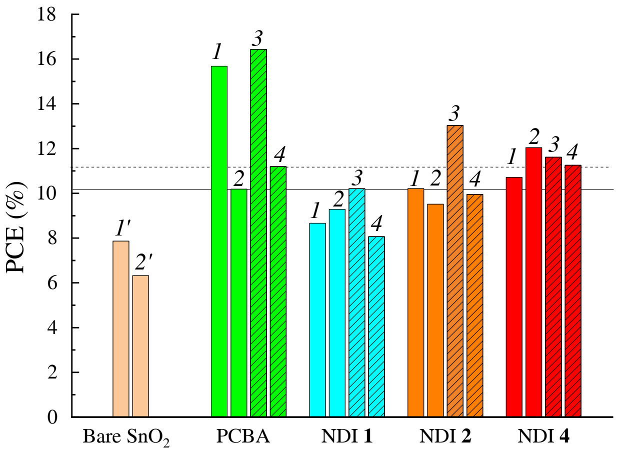


Figure 2 Effect of different ETL materials on the operational stability of (*1*),(*1′*),(*3*) pristine and (*2*),(*2′*),(*4*) aged PSCs, produced using (*1*),(*2*) soaking and (*3*),(*4*) spin-coating techniques or (*1′*),(*2′*) without them, (*1*),(*3*) before and (*2*),(*4*) after 300 h of continuous white light illumination under open circuit conditions.

This work was supported by the Ministry of Science and Higher Education of the Russian Federation (grant no. 075-15-2022-1216). The contribution of Center for molecule composition studies of INEOS RAS is gratefully acknowledged.

Online Supplementary Materials

Supplementary data associated with this article can be found in the online version at doi: 10.71267/mencom.7683.

References

1 M. A. Green, E. D. Dunlop, M. Yoshita, N. Kopidakis, K. Bothe, G. Siefer, D. Hinken, M. Rauer, J. Hohl-Ebinger and X. Hao, *Prog. Photovoltaics*, 2024, **32**, 425; https://doi.org/10.1002/pip.3831.

2 T. A. Chowdhury, Md. A. Bin Zafar, Md. Sajjad-Ul Islam, M. Shahinuzzaman, M. A. Islam and M. U. Khandaker, *RSC Adv.*, 2023, **13**, 1787; https://doi.org/10.1039/D2RA05903G.

3 H. Zhu, S. Teale, M. N. Lintangpradipto, S. Mahesh, B. Chen, M. D. McGehee, E. H. Sargent and O. M. Bakr, *Nat. Rev. Mater.*, 2023, **8**, 569; https://doi.org/10.1038/s41578-023-00582-w.

4 N. A. Emelianov, V. V. Ozerova, A. A. Bizyaeva, M. S. Leshchev and P. A. Troshin, *Mendeleev Commun.*, 2024, **34**, 844; https://doi.org/10.1016/j.mencom.2024.10.024.

5 Y. Xiao, X. Yang, R. Zhu and H. J. Snaith, *Science*, 2024, **384**, 846; https://doi.org/10.1126/science.adh8086.

6 S. A. Kuklin, S. V. Safronov, A. S. Peregudov, E. A. Khakina, M. M. Babaskina, M. G. Ezernitskaya, O. Yu. Fedorovskii, E. S. Kobeleva, L. V. Kulik, L. A. Frolova, P. A. Troshin and A. R. Khokhlov, *Mendeleev Commun.*, 2024, **34**, 316; https://doi.org/10.1016/j.mencom.2024.04.003.

7 E. A. Komissarova, S. A. Kuklin, A. F. Latypova, S. L. Nikitenko, V. V. Ozerova, M. N. Kevreva, N. A. Emelianov, L. A. Frolova and P. A. Troshin, *Mendeleev Commun.*, 2024, **34**, 656; https://doi.org/10.1016/j.mencom.2024.09.010.

8 Q. Fatima, A. A. Haidry, H. Zhang, A. El Jery and M. Aldrdery, *Materials Today Sustainability*, 2024, **27**, 100857; https://doi.org/10.1016/j.mtsust.2024.100857.

9 S. Ahmmed, Y. He, Md. E. Kayesh, Md. A. Karim, K. Matsuishi and A. Islam, *ACS Appl. Mater. Interfaces*, 2024, **16**, 32282; https://doi.org/10.1021/acsami.4c05180.

10 D. Gao, B. Li, Q. Liu, C. Zhang, Z. Yu, S. Li, J. Gong, L. Qian, F. Vanin, K. Schutt, M. A. Davis, A. F. Palmstrom, S. P. Harvey, N. J. Long, J. M. Luther, X. C. Zeng and Z. Zhu, *Science*, 2024, **386**, 187; https://doi.org/10.1126/science.adq8385.

11 N. Ren, L. Tan, M. Li, J. Zhou, Y. Ye, B. Jiao, L. Ding and C. Yi, *iEnergy*, 2024, **3**, 39; https://doi.org/10.23919/IEN.2024.0001.

12 Q. Wali, M. Aamir, M. Ejaz Khan, R. Jose, W. Fan and S. Yang, *Sol. Energy*, 2024, **270**, 112382; https://doi.org/10.1016/j.solener.2024.112382.

13 S. Y. Park and K. Zhu, *Adv. Mater.*, 2022, **34**, 2110438; https://doi.org/10.1002/adma.202110438.

14 S. Tsarev, T. S. Dubinina, S. Yu. Luchkin, I. S. Zhidkov, E. Z. Kurmaev, K. J. Stevenson and P. A. Troshin, *J. Phys. Chem. C*, 2020, **124**, 1872; https://doi.org/10.1021/acs.jpcc.9b10709.

15 M. M. Tepliakova, A. N. Mikheeva, L. A. Frolova, A. G. Boldyreva, A. Elakshar, A. V. Novikov, S. A. Tsarev, M. I. Ustinova, O. R. Yamilova, A. G. Nasibulin, S. M. Aldoshin, K. J. Stevenson and P. A. Troshin, *J. Phys. Chem. Lett.*, 2020, **11**, 5563; https://doi.org/10.1021/acs.jpclett.0c01600.

16 A. F. Akbulatov, L. A. Frolova, M. P. Griffin, I. R. Gearba, A. Dolocan, D. A. Vanden Bout, S. Tsarev, E. A. Katz, A. F. Shestakov, K. J. Stevenson and P. A. Troshin, *Adv. Energy Mater.*, 2017, **7**, 1700476; https://doi.org/10.1002/aenm.201700476.

17 S. Zhang, F. Ye, X. Wang, R. Chen, H. Zhang, L. Zhan, X. Jiang, Y. Li, X. Ji, S. Liu, M. Yu, F. Yu, Y. Zhang, R. Wu, Z. Liu, Z. Ning, D. Neher, L. Han, Y. Lin, H. Tian, W. Chen, M. Stolterfoht, L. Zhang, W.-H. Zhu and Y. Wu, *Science*, 2023, **380**, 404; https://doi.org/10.1126/science.adg3755.

18 X. Zheng, Z. Li, Y. Zhang, M. Chen, T. Liu, C. Xiao, D. Gao, J. B. Patel, D. Kuciauskas, A. Magomedov, R. A. Scheidt, X. Wang, S. P. Harvey, Z. Dai, C. Zhang, D. Morales, H. Pruett, B. M. Wieliczka, A. R. Kirmani, N. P. Padture, K. R. Graham, Y. Yan, M. K. Nazeeruddin, M. D. McGehee, Z. Zhu and J. M. Luther, *Nat. Energy*, 2023, **8**, 462; https://doi.org/10.1038/s41560-023-01227-6.

19 W. Wang, X. Li, P. Huang, L. Yang, L. Gao, Y. Jiang, J. Hu, Y. Gao, Y. Che, J. Deng, J. Zhang and W. Tang, *Adv. Mater.*, 2024, **36**, 2407349; https://doi.org/10.1002/adma.202407349.

20 S. Tsarev, I. K. Yakushchenko, S. Yu. Luchkin, P. M. Kuznetsov, R. S. Timerbulatov, N. N. Dremova, L. A. Frolova, K. J. Stevenson and P. A. Troshin, *Sustainable Energy Fuels*, 2019, **3**, 2627; https://doi.org/10.1039/C9SE00448C.

21 S.-K. Jung, J. H. Heo, D. W. Lee, S.-C. Lee, S.-H. Lee, W. Yoon, H. Yun, S. H. Im, J. H. Kim and O-P. Kwon, *Adv. Funct. Mater.*, 2018, **28**, 1800346; https://doi.org/10.1002/adfm.201800346.

22 S.-K. Jung, J. H. Heo, D. W. Lee, S.-H. Lee, S.-C. Lee, W. Yoon, H. Yun, D. Kim, J. H. Kim, S. H. Im and O-P. Kwon, *ChemSusChem*, 2019, **12**, 224; https://doi.org/10.1002/cssc.201802234.

23 K. Domanski, E. A. Alharbi, A. Hagfeldt, M. Grätzel and W. Tress, *Nat. Energy*, 2018, **3**, 61; https://doi.org/10.1038/s41560-017-0060-5.

Received: 15th November 2024; Com. 24/7683