

Naphthalimide-Fused Subphthalocyanines: Electron-Deficient Materials Prepared by Cascade Annulation

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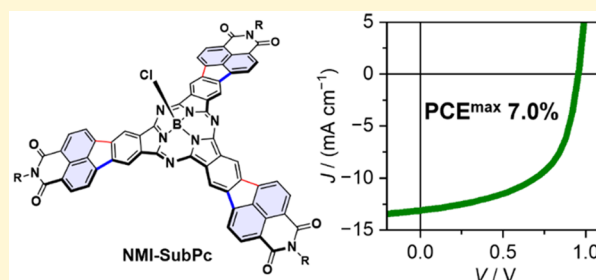


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Supporting Information

ABSTRACT: Imide-fused porphyrinoids are becoming key components in the area of molecular materials. Herein we report the synthesis of naphthalimide (NMI)-annulated subphthalocyanines (SubPcs) designed as an NIR-absorbing n-type organic semiconductor. Two different synthetic pathways could be applied for the preparation of NMI-fused SubPcs. The first consists of a [3 + 2] annulation between SubPc boronic ester and dibromo-NMI. This annulation, which involves the first CH activation reaction of a SubPc derivative reported so far, is totally regioselective to the β -position. Density functional theory (DFT) indicated that such position is favored both kinetically and thermodynamically. On the other hand, the second method relies on a cyclotrimerization of NMI-fused phthalonitrile. Electrochemical measurements and DFT calculations revealed that these NMI-fused SubPcs have low-lying LUMO energy levels suitable for electron charge transport. The *N*-alkyl substituted derivative (NMI-SubPc 2) was successfully applied as an nonfullerene acceptor (NFA) in combination with donor polymer PM6 in bulk-heterojunction (BHJ) organic solar cells (OSCs) with a highest power conversion efficiency (PCE) of 7.0%. This value is comparable to the record PCE of SubPc derivatives in BHJ-OSCs. Our results open a new vista in the preparation of π -extended contracted porphyrinoids and substantiate the potential of this new class of strong-absorbing electron-acceptor materials for applications in optoelectronic devices.



The installation of fused imide units at the periphery of aromatic compounds is recognized as an effective strategy for producing dyes and pigments with high tinctorial strength.¹ Such an imide functionalization leads furthermore to attractive characteristics including low-lying lowest unoccupied molecular orbitals (LUMOs), high photo/thermal stabilities, distinctive supramolecular properties, and good processability. Therefore, polycyclic aromatic imides have attracted considerable interest owing to their utility in organic electronics and photovoltaics as n-type semiconductors.² Motivated by these prospects, the synthesis and utilization of novel enlarged multiple imide-fused systems has recently gained momentum.³ Among them, imide-fused porphyrinoids are particularly exciting due to additional properties such as strong Vis–NIR absorption, tunable energy levels, and multiple reversible reductions.⁴ In this context, subphthalocyanines (SubPcs; Figure 1), which are cone-shape aromatic dyes composed of three aza-bridged diiminoisindole units and a central boron atom,⁵ have demonstrated an outstanding potential in bulk-heterojunction (BHJ) organic solar cells (OSCs).⁶ Hereby, Huang et al. reported a perylene bisimide-

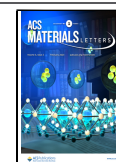
fused SubPc derivative that holds the power conversion efficiency (PCE) record of 7.5% for solution-processed SubPc-based OSCs in combination with donor polymer PM6.^{6c} However, while these examples show exciting performances, they often suffer from drawbacks such as tedious multistep syntheses or solubility issues. Thus, the exploration of other imide-functionalized SubPcs is highly desirable.

This task, however, is far from being trivial due to the lack of proper synthetic methods for the aromatic ring fusion of SubPcs. Generally, π -extended SubPc derivatives are prepared by cyclotrimerization of phthalonitriles previously functionalized.⁵ Nevertheless, this method presents two major drawbacks: (i) there are few functional groups compatible

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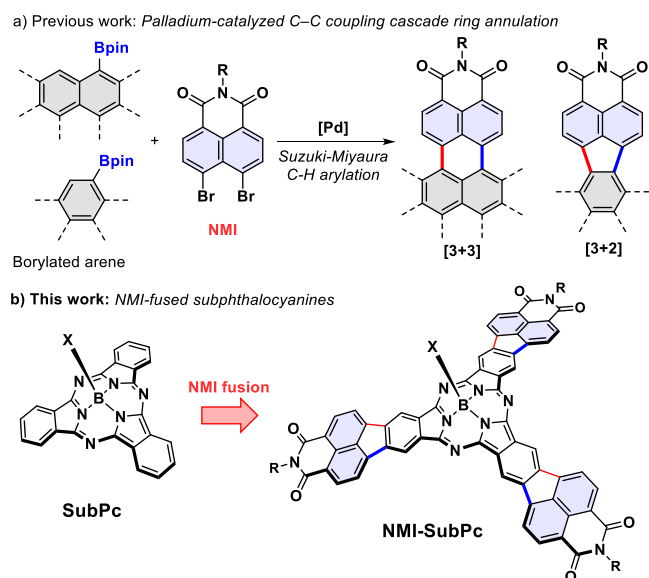


Figure 1. a) Reported cascade annulation reaction for the fusion of NMI to aromatic cores. b) Molecular structure of SubPcs and NMI-fused SubPcs reported in this work.

with the cyclotrimerization reaction conditions, and (ii) chlorinated byproducts that make the purification cumbersome are often obtained. This limitation led us to explore alternative reactivity pathways of SubPcs for the preparation of imide-fused derivatives.

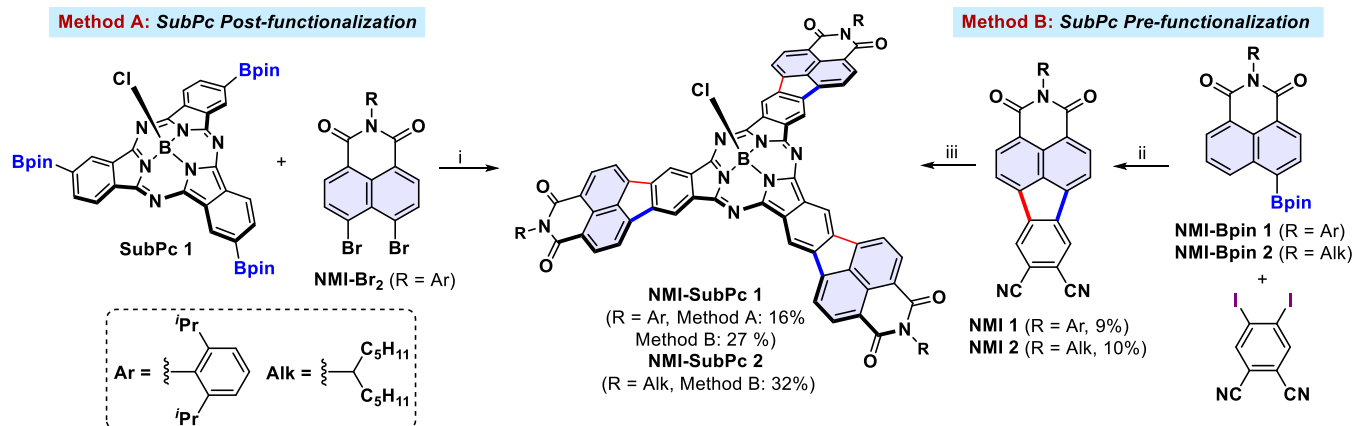
In recent years, palladium-catalyzed tandem arylation/annulation reactions have become a powerful tool for the construction of large π -scaffolds.⁷ In particular, Würthner and co-workers developed a practical procedure for the annulation of naphthalimide (NMI) to various aromatic compounds, such as corannulene, pyrene, or naphthalene.⁸ This annulation involves a Suzuki–Miyaura cross-coupling reaction followed by an intramolecular CH activation (Figure 1a). Inspired by these precedents, we thus turned our attention to the application of this reaction for the preparation of novel electron-deficient SubPcs (Figure 1b). Herein we report the synthesis of NMI-fused SubPcs employing a cascade annulation as the key step.

The regioselectivity of this reaction was studied by density functional theory (DFT), and the optoelectronic properties of the resulting derivatives were examined experimentally and theoretically. Finally, we explored their photovoltaic performance by preparing BHJ OSCs from solution. Remarkably, these derivatives afforded impressive PCEs of up to 7.0% in combination with donor polymer **PM6**, which renders them highly valuable n-type semiconductor materials.

The synthesis of NMI-fused SubPcs was tackled following two strategies. Method A (Scheme 1, left) involved a palladium-catalyzed [3 + 2] annulation between the triborylated SubPc **1** and NMI-Br₂, which bears a bulky *N*-substituent to ensure solubility. It should be noted that this method involves a CH activation reaction in a SubPc derivative, which is unprecedented in SubPc chemistry. By contrast, method B consisted of the cyclotrimerization of NMI-fused phthalonitriles NMI **2**, **3**. We first examined the method A using monoborylated SubPc **2a** as a model substrate to screen reaction conditions (Figure 2a), which would result in the formation of SubPc **3a**. SubPc **2a** was synthesized by statistical cyclotrimerization followed by a standard palladium-catalyzed borylation reaction (see the Supporting Information). Then, various catalysts, solvents, ligands, and additives were screened for the annulation reaction between SubPc **2a** and NMI-Br₂. We found that [Pd₂(dba)₃].CHCl₃ as the catalyst, PCy₃.HBF₄ as the ligand, cesium carbonate as the base, and 1-chloronaphthalene as the solvent gave the highest yield of 64% upon microwave (MW) irradiation. Importantly, it was found that these conditions are compatible with SubPc axially functionalized with more labile groups, such as chlorine. Accordingly, SubPc **3b** could be prepared from SubPc **2b** in similar yields. With the optimal conditions in hand, we then examined the cascade annulation with SubPc **1**. In this case, higher amounts of catalyst and longer reaction times were needed for the total conversion of SubPc **1**. Thus, NMI-SubPc **1** was obtained in a 16% yield after 40 min in the MW reactor.

It is important to highlight that the annulation is totally regioselective to the β -position of the SubPc. To shed light into the origin of this finding, the CH activation step was explored by DFT calculations (Figure 2b; See SI for computational details), considering a concerted metalation–

Scheme 1. Synthetic Strategies toward NMI-fused SubPcs^a



^aReagents and conditions: (i) [Pd₂(dba)₃].CHCl₃ (15 mol %), PCy₃.HBF₄ (1.2 equiv), Cs₂CO₃ (9.0 equiv), 1-chloronaphthalene, MW, 160 °C, 1 h; (ii) [Pd₂(dba)₃].CHCl₃ (10 mol %), SPhos (40 mol %), Cs₂CO₃ (3.0 equiv), mesitylene, 120 °C, 2 d; (iii) BCl₃ (1 M *p*-xylene), *o*-dichlorobenzene, 150 °C, 2 h. dba: dibenzylideneacetone, pin: pinacolato, SPhos: 2-dicyclohexylphosphino-2',6'-dimethoxybiphenyl.

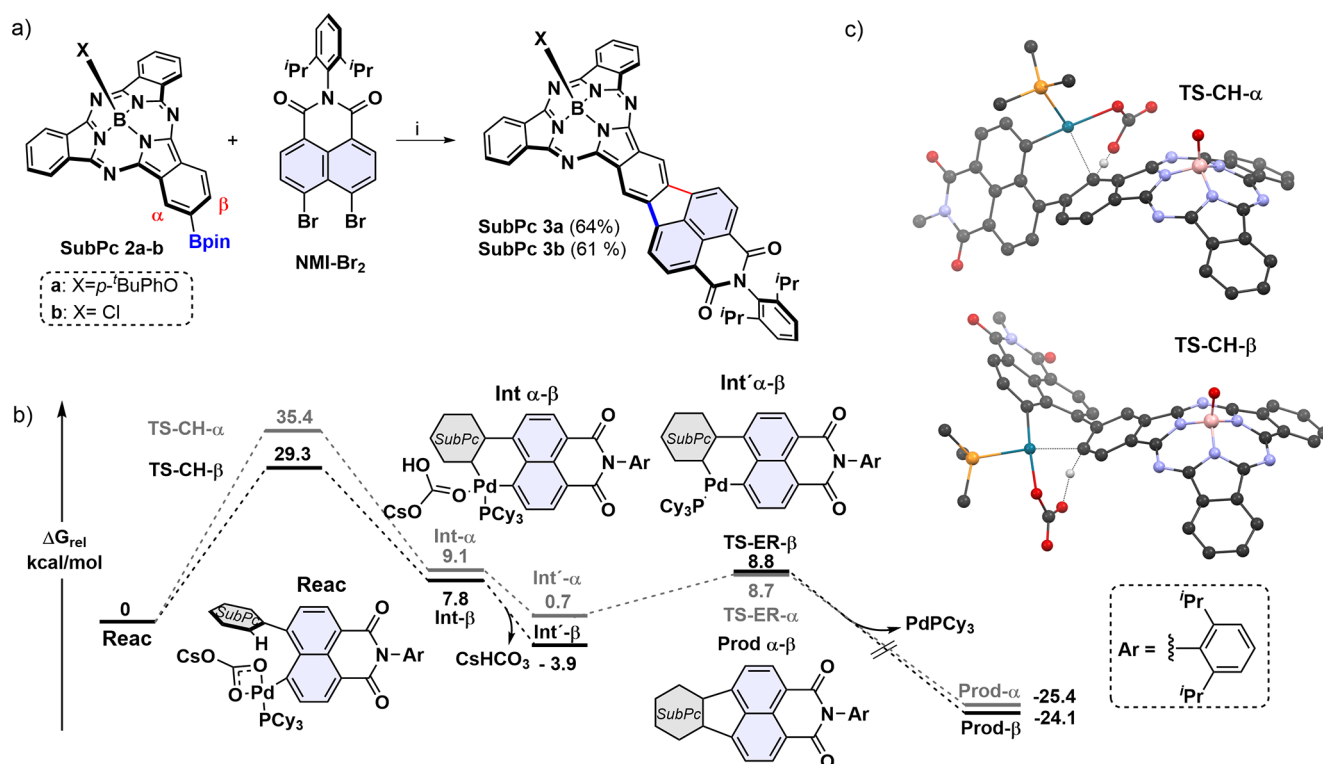


Figure 2. a) Synthetic route to NMI-fused SubPcs 3a–b. b) Free energy profile (kcal mol^{−1}) for the DFT calculated annulation of NMI-Br₂ to SubPc 2a. The black and gray lines represent the calculated profiles for the β- and α-paths, respectively. c) Optimized transition states for the α- (top) and β- (bottom) CH activation step (PCy₃, bulky *N*-substituent and SubPc axial substituent have been simplified for clarity). Reagents and conditions: (i) a) [Pd₂(dba)₃]·CHCl₃ (5 mol %), PCy₃·HBF₄ (40 mol %), Cs₂CO₃ (3.0 equiv), 1-chloronaphthalene, MW, 160 °C, 15 min dba: dibenzylideneacetone.

deprotonation (CMD) mechanism.⁹ As can be seen from Figure 2b, the CH activation step is rate-determining and highly exergonic; therefore, this step is likely to be irreversible. The transition state of this transformation is ca. 6 kcal mol^{−1} more stable for the β-position (TS-CH-β) than that of the α-position (TS-CH-α), which is in good agreement with the experimental regioselectivity. Given the similar Mulliken charge of the α- and β-H atoms (0.15 and 0.13, respectively), we hypothesized that this regioselectivity mainly arises from the more distorted square-planar geometry of the palladium(II) complex in TS-CH-α due to steric congestion. The CH activation reaction leads to palladacycles Int α-β, which after a ligand dissociation and a reductive elimination gives rise to annulated NMI-fused SubPcs (Prod α-β). It should be noted that these two steps do not depend much on the path considered.

Next, we explored method B as an alternative route for NMI-fused SubPcs (Scheme 1, right). Our synthetic route started with 4,5-diiodophthalonitrile, which underwent a cascade annulation reaction with NMI-Bpin **1** to afford NMI **1** in 9% yield. Alternatively, NMI **1** could also be prepared *via* a two-step annulation (See SI). NMI **1** was then subjected to a cyclotrimerization reaction employing BCl₃ (1 M *p*-xylene) in *o*-dichlorobenzene at 150 °C, to give NMI-SubPc **1** in 27% yield. Importantly, the scalability of this method is higher than that of method A. Accordingly, we employed the method B to prepare NMI-SubPc **2** (Scheme 1), which bears more suitable substituents for photovoltaic applications (i.e., alkyl chains at the NMI nitrogen atom).⁶ Thus, NMI-SubPc **2** was synthesized in 32% yield *via* a cyclotrimerization reaction of NMI **2**.

To assess the potential of NMI-SubPc **2** as an acceptor material for organic photovoltaics, we then studied its electronic properties by UV–vis–NIR absorption and fluorescence spectroscopy as well as voltammetry in THF solution (Figure 3). As shown in Figure 3a, NMI-SubPc **2** exhibits split Soret bands in the range of 350–430 nm, and an intense Q-band at 668 nm which is remarkably red-shifted compared to the nonsubstituted SubPc (578 nm), thus indicating an effective π -conjugation with the NMI units. Furthermore, the Q-band had a high molar extinction coefficient (63 000 M^{−1} cm^{−1}),¹⁰ which may be attributed to the increased transition dipole moment, which, in the case of SubPcs, is polarized along the longer molecular axis. On the other hand, the absorption is similar in shape to that of typical SubPcs, suggesting negligible electronic perturbation upon NMI insertion. As observed by time-dependent DFT calculations (TD-DFT; See SI for further details), the Q-band is mainly derived from degenerated HOMO → LUMO and HOMO → LUMO+1 transitions (f = 1.0233 and 1.0525, respectively). With regard to the emission properties, NMI-SubPc **2** exhibits a fluorescence maximum at 690 nm with a quantum yield of 32%.

On the other hand, cyclic and differential pulse voltammetry of NMI-SubPc **2** (Figure 3b) revealed an interesting redox behavior as it undergoes five reversible one-electron reduction processes between −1.12 and −1.88 V (vs Fc⁺/Fc). Moreover, one irreversible oxidation event at ca. 0.70 V is observed. Therefore, an electrochemical energy gap of 1.82 eV is calculated. From these results, the LUMO level is estimated to be −4.03 eV, which is comparable to other high performing SubPc acceptors (−4.25 eV)⁶ or PC₆₁BM (−4.26 V).¹¹

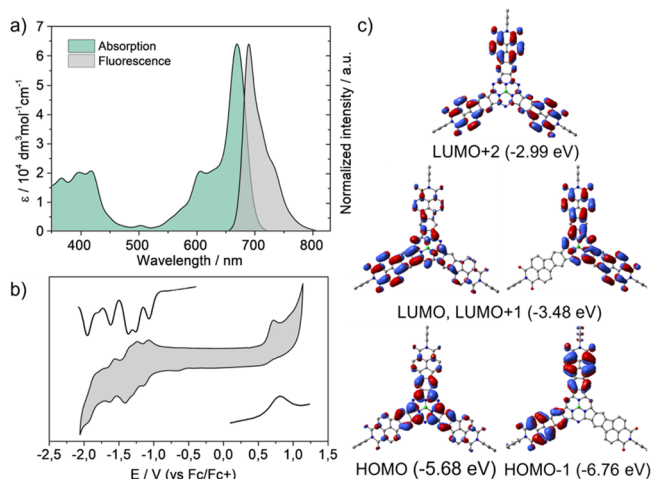


Figure 3. Optical and electrochemical properties of NMI-SubPc 2. a) UV-vis-NIR and fluorescence ($\lambda_{\text{ex}} = 600$ nm) spectra of NMI-SubPc 2 in THF at room temperature. (2.0×10^{-5} M for UV-vis-NIR and 1.0×10^{-6} M for fluorescence). b) Cyclic and differential-pulse voltammograms of NMI-SubPc 2 in THF at room temperature using Bu_4NPF_6 as the electrolyte. A platinum rod was used as working electrode, platinum wire served as counter electrode and Ag/AgCl as reference electrode. c) Selected molecular orbitals of NMI-SubPc 2 and their energy levels calculated by DFT at the CAM-B3LYP/6-31G+(d,p) level of theory. Hydrogen atoms and side chains are omitted for clarity.

Further insight into these redox properties was obtained by inspection of the DFT calculated frontier molecular orbitals. As shown in Figure 3c, the HOMO of NMI-SubPc 2 is mainly localized at the SubPc macrocycle, while the LUMO and LUMO+1 are extended over the fused NMIs. Therefore, it can be assumed that the oxidation removes electron mainly from the SubPc core and the reductions take place over the whole π -system. Importantly, LUMO and LUMO+1 are degenerated and close in energy to LUMO+2, which is consistent with the five reductions experimentally observed.

Prompted by the promising optical and redox properties of NMI-SubPc 2 next to its high solubility, we tested its performance as a nonfullerene acceptor (NFA) in OSCs. A simple inverted BHJ device architecture (Figure 4a) with a 1:1 (mass ratio) blend of NMI-SubPc 2 and the donor polymer PM6 in chlorobenzene was chosen, as these two materials show both complementary thin-film absorption as well as energetic (frontier orbital) properties (Figure S6.1), and their mixture afforded homogeneous and smooth thin films (root-

mean-square surface roughness of 1 nm, Figure S6.2). The resulting OSCs according to their current density–voltage (J – V) characteristics (Figure 4b) show a short-circuit current density (J_{sc}) of -12.5 ± 0.3 and a good diode-like behavior ($J_{-1\text{ V}} J_{\text{sc}}^{-1} = 1.09$) along with an appreciably high open-circuit voltage (V_{oc}) and fill factor (FF) of 0.94 ± 0.02 V and $54 \pm 1\%$, respectively. The external quantum efficiency (EQE) spectrum of the OSC mirrors the Vis–NIR absorption spectrum of the corresponding active layer with an EQE of $>50\%$ in the range of 560–680 nm. Most important, a significant photocurrent contribution of NMI-SubPc 2 around its thin-film absorption maximum at ~ 670 nm is observed (Figure 4c). Finally, these devices show a PCE of $6.4 \pm 0.3\%$, even reaching a PCE^{max} value of 7.0% (Table S6.1) that is among the best so far accomplished for single-heterojunction SubPc-based OSCs in literature.¹² These results nicely demonstrate the potential of our approach of NMI-fused SubPcs as novel NFA materials for organic photovoltaics.

In summary, we have accomplished the synthesis of subphthalocyanines bearing laterally annulated naphthalimide moieties and demonstrated their application as nonfullerene acceptor materials in OSCs. 3-fold [3 + 2] annulation of dibromonaphthalimide and the tris(boronic ester) of subphthalocyanine successfully yielded the desired product NMI-SubPc 1 with excellent regioselectivity. Computational investigations indicated that the stabilization of the *ortho,ortho*-transition state (TS-CH- β) over *ortho,meta*-transition state (TS-CH- α) by the CMD mechanism is responsible for this high selectivity. The introduction of three naphthalimide moieties resulted in a low LUMO energy level of NMI-SubPc 1, which is below that of pristine SubPc or a benchmark fullerene acceptor PC₆₁BM. The BHJ OSC using *N*-alkyl substituted NMI-SubPc 2 as the acceptor and PM6 as the donor showed efficient photocurrent generation with good diode character with a PCE^{max} of 7.0%. This value is comparable to the record PCE reported for SubPc-based fullerene-free BHJ-OSCs.

Given the highly regioselectivity of the annulation reaction herein reported, together with the excellent photovoltaic performance of NMI-fused SubPcs, we strongly believe that this work paves the way for the preparation of novel imide-annulated porphyrinoids. Current efforts toward larger systems with different geometries are ongoing in our laboratories.

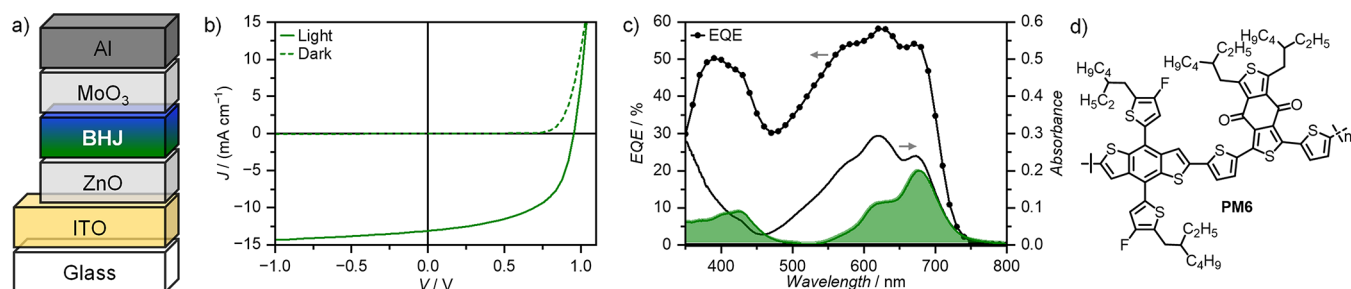


Figure 4. a) Schematic device architecture of the fabricated inverted BHJ OSCs. b) Representative current density vs voltage (J – V) curves measured under inert conditions in dark (dotted) and under AM1.5G illumination (bold) of OSCs with an ITO/ZnO/PM6: NMI-SubPc2/MoO₃/Al architecture and c) the respective EQE (black symbols) as well as UV-vis-NIR (black solid) spectra of a OSC compared with the UV-vis-NIR absorption spectrum of the neat NMI-SubPc2 layer (green) on quartz. d) Chemical structure of PM6.

■ ASSOCIATED CONTENT

■ Supporting Information

The Supporting Information is available free of charge at <https://pubs.acs.org/doi/10.1021/acsmaterialslett.2c01132>.

Cartesian coordinates (PDF)

Instrumentation and materials, synthetic procedures and compound data (PDF)

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Notes

The authors declare no competing financial interest.

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(9) Heck-type or nucleophilic aromatic substitution mechanisms were discarded because these involve the formation of sterically hindered seven-membered palladacycle. In addition, the SubPc benzene rings do not have double bond character and are not prone to undergo electrophilic attacks.

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