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Imide-Fused Diazatetracenes: Synthesis, Characterization and Application in Perovskite Solar Cells

Kexiang Zhao⁺,^[a] Wenbo Liu⁺,^[a] Fei Yu,^[a] Guankui Long,^[b] Ahmed Ali Said,^[a] Zongrui Wang,^[a] Weibo Gao,^[b] and Qichun Zhang^{*[a]}

Abstract: A series of imide-fused diazatetracenes were synthesized via Buchwald-Hartwig C-N coupling with a highly active palladium source. The introduction of imide segment effectively lowers the LUMO levels compared with that of unsubstituted diazatetracene. By adjusting the alkyl chains of the diazatetracenes, different solid-state packings were achieved, resulting in distinct photoluminescent behaviors. Their electron transporting properties were demonstrated in the proof-of-concept Perovskite solar cells as electron transporting layers.

Azaacenes, which have a long-standing history, are promising n-type semiconductors in organic electronics.^[1] Since the first example of applying dihydro-azapentacene in thin-film transistor,^[2] great effort has been channeled into the syntheses of azaacene derivatives and the investigation on their performance in organic electronic devices.^[3] Organic field-effect transistors (OFETs) based on chlorinated azapentacene exhibited an astounding electron mobility of 27.8 cm²V⁻¹s⁻¹.^[3g] Despite the success in OFETs, the applications of azaacenes in other organic electronics are apparently lacking. Very recently, azaacenes have been firstly utilized in Perovskite solar cells (PSCs) as electron-transporting materials and showed good performance.^[4] Compared with the commonly used PC₆₁BM, the azaacenes displayed better electron mobilities, good morphological controllability and lower unit cost.^[5]

During the development of azaacenes, azapentacenes have been the focus of research attention owing to their eminent n-type mobility in the early reports.^[1b] In contrast to the azapentacene family, there are only a handful of reports on the azatetracene derivatives and their performance in organic electronics.^[6] The relatively shallower LUMO and less effective charge injection of azatetracenes make them less competitive in organic electronics compared to the azapentacene analogue.^[7] It is essential to lower the LUMO energy level of azatetracenes to achieve better n-type performance. From the synthetic perspective, the introduction of

electron-withdrawing units could evidently deepen the LUMO of azatetracenes.^[6a, 6e, 8] Mark et al. reported a series of anthracenedicarboximides, where two imide groups were linearly fused onto the backbone of anthracene unit.^[9] The attachment of imide groups successfully turned the anthracene into an air-stable n-type semiconductor. Moreover, other imide-based small molecules, such as NDIs and PDIs,^[10] also demonstrate their potential in various organic electronics, especially OFETs and organic solar cells.^[11] Thus, it is postulated that the incorporation of imide units to azatetracenes backbone should be able to lower their LUMO energy levels and improve their performance in organic electronics. Herein, we report the synthesis of a series of imide-fused diazatetracenes via Buchwald-Hartwig C-N coupling^[12] and their performance as electron-transporting materials in PSCs. Their optical and electronic properties are investigated and compared with unsubstituted diazatetracenes.^[6a] The electron-withdrawing imide segment effectively lowers the LUMO of the as-obtained diazatetracenes.

The synthetic route to imide-fused diazatetracenes is shown in Scheme 1. Starting from **1**, the Stille coupling in refluxing toluene gave the diamine precursor **2** in 89% yield. Further reduction of the thiadiazole unit furnished the thiophene-substituted naphthalene diamine **3a** quantitatively. Imide-fused diazatetracenes **5** - **8** were obtained through the Buchwald-Hartwig coupling of diamines **3a** - **b** and dihalides **4a** - **b**. It is noteworthy that **4a** - **b** are not active dihalides species especially when the halogen is chloride. However, the usage of highly active Pd source enabled the good coupling yields in range of 65 - 81 %.

Scheme 1. i) Pd BrettPhos G4, BrettPhos, Cs₂CO₃, dioxane, reflux, 1 d; ii) MnO₂, DCM, rt, 0.5 h. EH: 2-ethylhexyl.

- [a] K. Zhao, W. Liu, Dr. F. Yu, A. A. Said, Dr. Z. Wang, Prof. Q. Zhang
School of Materials Science and Engineering, Nanyang
Technological University
50 Nanyang Avenue, 639798, Singapore
E-mail: qc Zhang@ntu.edu.sg
- [b] Dr. G. Long, Prof. W. Gao
Division of Physics & Applied Physics, School of Physical and
Mathematics Science, Nanyang Technological University
639798 Singapore
- [*] These authors contributed equally to this work.

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Table 1. Experimental and calculated optical and electronic properties of compounds **5** – **9**.

Compound	$\lambda_{\text{max, abs}}$ [nm]	$\lambda_{\text{onset, abs}}$ [nm]	$\lambda_{\text{max, ems.}}$ [nm]	LUMO [eV] meas ^[a] /calcd ^[b]	HOMO [eV] meas ^[c] /calcd ^[b]	gap [eV] meas ^[d] /calcd ^[b]	Φ (Solution)	Φ (Solid)
5	604	731	---	-3.66/-3.12	-5.36/-5.34	1.70/2.23	---	---
6	604	730	---	-3.65/-3.09	-5.34/-5.32	1.70/2.23	---	---
7	613	656	664	-3.71/-3.37	-5.60/-5.53	1.89/2.16	0.41	---
8	612	655	665	-3.71/-3.35	-5.60/-5.51	1.89/2.16	0.43	0.09
9	571	630	610	-3.46/-3.29 ^[e]	-5.67/-5.58 ^[e]	2.06/2.29 ^[e]	---	---

[a] First reduction potentials measured by cyclic voltammetry (CV) in DCM using Bu₄NPF₆ as electrolyte. LUMO_{meas} = - (E_{red(onset)} + 4.8) (eV); [b] DFT calculations (B3LYP/6-31G*) using Gaussian 09; [c] E_{HOMO} = E_{LUMO(CV)} - E_{gap(opt)} (eV); [d] gap_{meas} was calculated from 1240 nm/λ_{onset}; [e] Calculated data for **9** was taken from Ref[6a]

Because of the structural similarity, **5** and **6** (or **7** and **8**) have almost identical electronic and optical properties. Hence, only **6** and **8** will be mentioned in this paragraph instead of **5** – **8**. The normalized absorption spectra of **6**, **8** and “pristine” diazatetracene **9** (without imide segment) in DCM are shown in Figure 1. λ_{onset} of TIPS substituted tetracene imide **8** shows a significant redshift compared with that of **9**, which results in a narrower optical band gap of **8**. The difference between **6** and **9** in λ_{onset} is even larger (reaching 130 nm). Both **6** and **8** possess considerably redshifted λ_{max} compared to **9**, which indicates size-dependent redshift in the absorption. The minute difference in λ_{max} of **6** and **8**, on the other hand, is in good agreement with their identical conjugated backbone. However, despite the structural resemblance of **6** and **8**, their photoluminescence properties are drastically different. **8** has strong red emission in solution, whereas **6** is non-emissive. The quenched fluorescence of **6** is caused by the intramolecular charge transfer from the thiophene unit to the pyrazine unit.^[13] The optical and electronic properties of **5** – **9** are summarized in Table 1. As expected, the incorporation of imide segment to the diazatetracene backbone leads to a deeper LUMO (0.25 eV decrease for **8** and 0.19 eV decrease for **6**). The LUMO of **6** is slightly shallower than that of **8** (0.06 eV), which is probably due to the attachment of electron-donating thiophene side chains to **6**. The calculated HOMO levels show good congruence with the experimental values with a maximum difference of 0.09 eV, whereas larger discrepancies (0.54 eV for **5**, 0.56 eV for **6**, 0.34 eV for **7** and 0.36 eV for **8**) are observed between the calculated and measured LUMOs. It needs to be pointed out that global hybrid functionals like B3LYP do not predict the energies of virtual orbitals as accurately as those of the occupied orbitals, thus gives rise to the apparent discrepancy.

Figure 1. Normalized absorption spectra of **6**, **8** and **9** in DCM (10⁻⁶ M). **Figure 2.** Photographs of compound **5** – **8** in solid state (left) and in solution (right) under daylight (top) and under 365 nm UV light (bottom).

The crystals suitable for single-crystal X-ray analysis were grown by slow diffusion of isopropanol into the chlorobenzene solutions of **5** – **8** (CCDC numbers for **6** – **8** are 1967660-1967662, respectively). Unfortunately, a satisfactory crystal structure cannot be established for **5** since it crystallized as very thin sheets.

Figure 3. Crystal structures of a) **6**, b) **7** and c) **8**.

The space group for **6**, **7** and **8** is $P\bar{1}$, $P2_1/c$ and $P2_1/c$, respectively. In the crystal of **7**, molecules form pairs through π – π stacking with a distance of 3.51 Å. The pairs are further held together by carbonyl– π interaction with a shorter distance of 3.38 Å, which gives rise to a brick-wall motif. By changing the methyl group into cyclohexyl group, the crystal of **8** takes on a different packing motif. Due to the bulkiness of both TIPS group and cyclohexyl group, **8** is more twisted in the solid state and no π – π stacking is observed. The degree of planarity is quantified by the dihedral angle between the imide segment and the farthest benzene ring from the imide segment. For **6** and **8** where cyclohexyl group is present, their dihedral angles (9.64° for **6** and 9.28° for **8**) are larger than that of **7** (3.62°). Instead of π – π interaction the carbonyl– π interaction and CH– π interaction dominate the crystal of **8** with distances of 3.42 Å and 2.76 Å, respectively. In order to overcome the steric hindrance, **8** shows a slipped one-dimensional packing. This arrangement is so much offset that no

brick-wall motif could form. For **6**, one-dimensional stacking is observed with antiparallel cofacial π – π stacking distances of 3.43 Å and 3.44 Å. The dihedral angle between the thiophene moieties and azatetracene backbone are 61.73° and 65.41° . Because of the less steric hindrance imposed by the thiophene side chains, there is a decrease in π – π stacking distance compared to **7**. From the crystal structures of **6**–**8**, it could be concluded that imide-fused diazatetracenes have strong tendency to form pairs in solid state and adopt an antiparallel packing mode. However, in the case of **8**, the steric hindrance is so prominent that the antiparallel packing is interrupted. This also explains why **8** has solid-state fluorescence while **7** does not, since the strong π – π stacking of **7** in the solid-state would quench the fluorescence.

To explore the application of imide-fused diazatetracenes in organic electronics, PSCs with **5**–**8** as ETLs were fabricated. The inverted planar PSCs architecture and the energy level diagram are shown in Figure 4a and 4b. The statistical photovoltaic

performances are shown in Figure 4, Table 2 and Figure S22. It is found out that the open circuit voltage (V_{oc}) and short circuit current density (J_{sc}) of the methyl substituted compounds (**5** and **7**) are higher than those of cyclohexyl substituted compounds (**6** and **8**). The possible reason could be the better contact between methyl group and the perovskite surface, which further results in better electron extraction. However, better contact with the perovskite layer does not mean better PCE performance. Even though the V_{oc} of **5**-based PSCs is larger than that of **6**-based PSCs, the PCE of **5** is lower than that of **6**, which is caused by higher fill factor (FF) of **6**-based PSCs (average FF = 66.4 %). The reason could be lower series resistance and better aggregation of compound **6** as ETL. While PSCs based on **5** – **7** show reasonable similarities in device performance, the average PCE for **8** is 5.15 %, which is 3 % lower than devices based on **5** – **7**. This result might be unexpected at first glance, since the electronic properties of **5** – **8** are quite similar. However, in solid state, **8** exhibits rather weak π – π interaction, which is supported by its crystal structure and the unquenched solid-state fluorescence compared with **7**. Thus, we propose that the weak π – π interaction of **8** in solid state may result in less efficient electron transport in PSCs, which then leads to a lower PCE.

Figure 4. a) Device architecture of PSC used in this work; b) Corresponding energy level diagrams; c) J-V curves of the PSCs with **5** and **6** as ETLs; d) J-V curves of the PSCs with **7** and **8** as ETLs.

Table 2. Device parameters of PSCs compounds **5** – **8**.

ETL	J_{sc} (mA/cm ²)	V_{oc} (mV)	FF (%)	PCE (%)	Highest PCE (%)
5	19.66 ± 1.50	842.2 ± 29.4	49.6 ± 5.3	8.17 ± 0.40	8.7
	16.84 ± 0.91	786.7 ± 6.7	66.4 ± 3.4	8.79 ± 0.27	
6	20.17 ± 2.82	803.2 ± 11.8	55.4 ± 5.9	8.86 ± 0.30	9.4
	16.84 ± 3.72	628.9 ± 55.0	50.9 ± 12.6	5.15 ± 0.76	

We also notice that the energy levels between Perovskite and imide-fused diazatetracenes are not well matched, which is the major cause of low V_{oc} and fill factor. The performance of PSCs

could be further enhanced by tuning the LUMOs of imide-fused diazatetracenes to deeper positions by adding fluorinated alkyl chains to the imide moiety.^[14]

In summary, a highly active palladium catalyst was selected to synthesize a series of novel imide-fused diazatetracenes in the yields ranging from 65 % to 81%. Their optical and electronic properties were then investigated. The introduction of imide moiety successfully lowered the LUMO level by 0.25 eV when compared with the reference diazatetracene **9**. Obviously redshifted absorption also indicates the extension of π -backbone. The effect of alkyl chains on solid state structures were also discussed. Besides π – π interactions, due to the presence of imide groups, carbonyl– π interactions were also observed in the crystal structure. PSCs with imide-fused diazatetracenes as ETLs gave the highest PCE of 9.4 %. The preliminary results show that the imide-fused diazatetracenes holds the potential as promising ETL candidates.

Experimental Section

Compound **1**^[15], **3b**^[16], **4a**^[17] and **4b**^[18] were synthesized according to literature procedures.

Device Fabrication

The ITO-coated glass substrates were cleaned successively with Decon 90 (detergent) diluted solution, deionized water, acetone, isopropanol and ethanol in an ultrasonic bath for 20 min, respectively, and dried with nitrogen gas purge. The ITO-coated glasses are then air-plasma treated for 20 min prior to the deposition of other layers. A hole transport layer of PEDOT:PSS was spin coated onto cleaned ITO transparent glass substrates at 6000 rpm for 60 s in ambient condition and annealed at 130 °C for 20 min. The perovskite films were deposited using single-step deposition method from the precursor solution containing FAI (0.26 M), PbI₂ (1.26 M), MAI (1.08 M) and PbCl₂ (0.14 M) in DMSO/GBL (3:7 (v:v)). The precursor solution was spin-coated onto the PEDOT: PSS substrates in a two-step method at 1200 and 4300 rpm for 18 and 60 s, respectively. During the second step, 550 μ l of toluene was dropped on the spinning substrate for 30 s prior to the end of the spin coating. After spin coating of the precursor solution, the substrates were transferred to hot plate and heated at 105 °C for 30 min. ETL solution was spun at 2000 rpm for 60 s and immediately heat-treated at 100 °C for 10 min. Finally, about 100nm silver was deposited on the ETL by high temperature vacuum evaporation. The perovskite and ETL deposition were carried out in a glove box filled with nitrogen. The current density–voltage (J–V) characteristic curves were measured under simulated solar irradiation (AM 1.5, 100 mW cm^{−2}) for the PSCs. The measurements are proceeded under the ambient condition (temperature: 25 °C, humidity: 66%). The dependence of device performance on ETL thickness was explored by varying concentrations of **5** – **8** in 1,2-dichlorobenzene spun onto active layers with the same rotate speed (2000 rpm). For each ETL with a specific concentration, the data are achieved from 10 devices. Finally, 4 mg/ml is found to be the proper concentration to fully exhibit the electron transport character of those ETL materials.

4,9-Bis(5-(2-ethylhexyl)thiophen-2-yl)naphtho[2,3-c][1,2,5]thiadiazole (2)

In a heatgun-dried Schlenk flask, **1** (344 mg, 1 mmol) and tin reagent (1.08 g, 3 mmol) were dissolved in 10 ml dry toluene. After the solution was purged with argon for 15 min, Pd(dba)₂ (28.8 mg, 5 mol%) and P(o-tol)₃ (15.2 mg, 5 mol%) were added. The mixture was purged for additional 5 min and then heated to reflux for 1 d. After cooling to room temperature, solvent was removed *in vacuo*. The residue was purified by column chromatography on silica gel using a Hexane/DCM (v/v, 4:1) solvent mixture. The product was obtained as a dark purple highly viscous liquid (515 mg, 89.5 %). ¹H NMR (300 MHz, CDCl₃) δ 8.41 – 8.33 (m, 2H), 7.45 – 7.37 (m, 2H), 7.29 (d, J = 3.5 Hz, 2H), 6.98 (d, J = 3.5 Hz, 2H), 2.91 (d, J = 6.7 Hz, 4H), 1.77 – 1.67 (m, 2H), 1.54 – 1.27 (m, 18H), 0.99 – 0.89 (m, 12H). ¹³C {¹H} NMR (75 MHz, CDCl₃) δ 151.6, 147.5, 134.0, 132.8, 130.2, 127.2, 126.7, 125.3, 123.7, 41.4, 34.3, 32.6, 29.0, 25.8, 23.0, 14.2, 10.9. HRMS (ES), m/z: [M+H]⁺ calcd for C₃₄H₄₃N₂S₃: 575.2588; found: 575.2581.

1,4-Bis(5-(2-ethylhexyl)thiophen-2-yl)naphthalene-2,3-diamine (3a)

In a heatgun-dried round bottom flask, **2** (500 mg, 0.87 mmol) was dissolved in 10 ml dry THF under argon. After the solution was cooled to 0 °C, 2M LiAlH₄ solution in THF (3.5 ml, 7 mmol, 8 eq) was added dropwise. Then the solution was warmed to room temperature and stirred for 12 h. The mixture was cooled again to 0 °C and carefully quenched with saturated NH₄Cl(aq). Afterwards, the mixture was extracted with diethyl ether (20 ml × 3), and the organic phase was combined and dried over sodium sulphate. Flash column chromatography on silica gel using hexane/ethyl acetate (v/v, 10/1) as eluent yielded the product as a slightly yellow viscous oil (470 mg, quantitative). ¹H NMR (300 MHz, Acetone-d₆) δ 7.41 – 7.33 (m, 2H), 7.12 – 7.04 (m, 2H), 7.00 (d, J = 3.3 Hz, 2H), 6.90 (d, J = 3.3 Hz, 2H), 4.41 (s, 4H), 2.94 – 2.85 (m, 4H), 1.74 – 1.64 (m, 2H), 1.51 – 1.30 (m, 18H), 0.99 – 0.88 (m, 12H). ¹³C {¹H} NMR (75 MHz, CDCl₃) δ 146.4, 135.2, 134.9, 129.5, 128.6, 125.7, 124.5, 123.4, 115.0, 41.5, 34.5, 32.6, 29.0, 25.9, 23.1, 14.2, 11.0. HRMS (ES), m/z: [M+H]⁺ calcd for C₃₄H₄₇N₂S₂: 547.3181; found: 547.3174.

General procedure (GP) for the coupling reaction

In a heatgun-dried Schlenk flask, ortho-diamine (0.2 mmol), ortho-dichloride (0.24 mmol) and Cs₂CO₃ (163 mg, 0.5 mmol) were suspended in 5 ml dry toluene and 1 ml dry tert-butanol. The mixture was purged with argon for 15 min followed by the addition of BrettPhos Pd G4 (9.2 mg, 5 mol%) and BrettPhos (5.4 mg, 5 mol%). After stirring at 100 °C for 1 d, the mixture was cooled to room temperature, and the solvent was removed *in vacuo*. The residue was purified by column chromatography on silica gel using a hexane/DCM solvent mixture. The as-obtained N,N'-dihydroazatetracene was quickly dissolved in 10 ml DCM and treated with MnO₂ (20 eq) due to the instability at ambient condition. After stirring at room temperature for 30 min, the mixture was filtered through Celite, and the solvent was removed *in vacuo*. The crude product was purified by flash column chromatography on silica gel using a hexane/DCM solvent mixture.

6,11-Bis(5-(2-ethylhexyl)thiophen-2-yl)-2-methyl-1H-benzo[b]pyrrolo[3,4-i]phenazine-1,3(2H)-dione (5)

The GP was applied to **3a** (109 mg) and **4a** (55 mg). Column chromatography (hexane/DCM= 2:1 – 1:1) yielded **5** (113 mg, 81%) as dark blue solid. ¹H NMR (300 MHz, CDCl₃) δ 8.66 (s, 2H), 8.46 – 8.36 (m, 2H), 7.59 – 7.49 (m, 2H), 7.24 (d, J = 3.5 Hz, 2H), 7.02 (d, J = 3.5 Hz, 2H), 3.31 (s, 3H), 2.97 (d, J = 6.8 Hz, 4H), 1.82 – 1.72 (m, 2H), 1.55 – 1.34 (m, 16H), 1.01 (t, J = 7.4 Hz, 6H), 0.95 (t, J = 7.2 Hz, 6H). ¹³C {¹H} NMR (75 MHz, CDCl₃) δ 166.7, 148.1, 144.2, 138.7, 134.8, 133.8, 132.3, 130.8, 130.8, 127.8, 127.7, 127.6, 124.9, 41.6, 34.4, 32.6, 29.0, 25.9, 24.7, 23.1, 14.2, 11.0. HRMS (ES), m/z: [M+H]⁺ calcd for C₄₃H₄₈N₃O₂S₂: 702.3188; found: 702.3189.

2-Cyclohexyl-6,11-bis(5-(2-ethylhexyl)thiophen-2-yl)-1H-benzo[b]pyrrolo[3,4-i]phenazine-1,3(2H)-dione (6)

The GP was applied to **3a** (109 mg) and **4b** (72 mg). Column chromatography (hexane/DCM= 2:1 – 1:1) yielded **6** (100 mg, 65%) as dark blue solid. ¹H NMR (300 MHz, CDCl₃) δ 8.61 (s, 2H), 8.44 – 8.37 (m, 2H), 7.57 – 7.49 (m, 2H), 7.24 (d, J = 3.5 Hz, 2H), 7.02 (d, J = 3.5 Hz, 2H), 4.26 (tt, J = 12.3, 3.7 Hz, 1H), 2.97 (d, J = 6.7 Hz, 4H), 2.39 – 2.23 (m, 2H), 1.96 – 1.70 (m, 7H), 1.55 – 1.33 (m, 19H), 1.06 – 0.89 (m, 12H). ¹³C {¹H} NMR (75 MHz, CDCl₃) δ 166.7, 148.0, 144.3, 138.7, 134.7, 133.8, 132.3, 130.8, 130.8, 127.7, 127.6, 127.3, 124.9, 51.8, 41.6, 34.4, 32.6, 29.6, 29.0, 26.0, 25.9, 25.1, 23.1, 14.2, 11.0. HRMS (ES), m/z: [M+H]⁺ calcd for C₄₈H₅₆N₃O₂S₂: 770.3814; found: 770.3809.

2-Methyl-6,11-bis((triisopropylsilyl)ethynyl)-1H-benzo[b]pyrrolo[3,4-i]phenazine-1,3(2H)-dione (7)

The GP was applied to **3b** (104 mg) and **4a** (55 mg). Column chromatography (hexane/DCM= 2:1 – 1:1) yielded **7** (101 mg, 75%) as dark blue solid. ¹H NMR (300 MHz, CDCl₃) δ 8.80 – 8.73 (m, 2H), 8.69 (s, 2H), 7.77 – 7.67 (m, 2H), 3.36 (s, 3H), 1.33 (d, J = 3.5 Hz, 42H). ¹³C {¹H} NMR (75 MHz, CDCl₃) δ 166.6, 145.3, 141.5, 136.3, 131.4, 129.0, 127.8, 127.6, 121.5, 109.9, 102.1, 24.9, 18.9, 11.6. HRMS (ES), m/z: [M+H]⁺ calcd for C₄₁H₅₂N₃O₂Si₂: 674.3598; found: 674.3591.

2-Cyclohexyl-6,11-bis((triisopropylsilyl)ethynyl)-1H-benzo[b]pyrrolo[3,4-i]phenazine-1,3(2H)-dione (8)

The GP was applied to **3b** (104 mg) and **4b** (72 mg). Column chromatography (hexane/DCM= 2:1 – 1:1) yielded **8** (115 mg, 77%) as dark blue solid. ¹H NMR (300 MHz, CDCl₃) δ 8.81 – 8.72 (m, 2H), 8.65 (s, 2H), 7.76 – 7.67 (m, 2H), 4.30 (tt, J = 12.3, 3.6 Hz, 1H), 2.42 – 2.26 (m, 2H), 1.98 – 1.72 (m, 5H), 1.49 – 1.38 (m, 3H), 1.36 – 1.28 (m, 42H). ¹³C {¹H} NMR (75 MHz, CDCl₃) δ 166.6, 145.4, 141.5, 136.2, 131.4, 128.9, 127.8, 127.2, 121.4, 109.8, 102.2, 51.9, 29.6, 26.0, 25.2, 18.9, 11.6. HRMS (ES), m/z: [M+H]⁺ calcd for C₄₁H₅₂N₃O₂Si₂: 742.4224; found: 742.4225.

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COMMUNICATION

Add the imide: A series of imide-fused diazatetracenes were synthesized via Buchwald-Hartwig C-N coupling. Their optical and electronic properties as well as solid state structures were investigated. Further application in Perovskite solar cells also illustrated the electron transporting properties of our imide-fused diazatetracenes.

*Kexiang Zhao, Wenbo Liu, Dr. Fei Yu, Dr. Guankui Long, Ahmed Ali Said, Dr. Zongrui Wang, Prof. Weibo Gao, Prof. Qichun Zhang**

Page No. – Page No.

Imide-Fused Diazatetracenes: Synthesis, Characterization and Application in Perovskite Solar Cells