Expanding the Scope of Electron-Deficient C–H Building Blocks: Direct Arylation of Pyromellitic Acid Diimide

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ABSTRACT: Direct C–H activation of pyromellitic diimide (PMDI) is reported for the first time. The method avoids cumbersome pathways involving bromination usually required for further cross-coupling. Good to excellent yields of monoand di-substituted PMDI derivatives can be obtained under optimized reaction conditions. The reaction scope was also explored, and the materials were characterized with respect to their thermal, optical, and electronic properties.

INTRODUCTION

The formation of Ar–Ar bonds is of major importance in all areas of organic chemistry. Traditional synthesis routes for sp2 C–C bond formation rely on Kumada, Neigishi, Stille, or Suzuki cross-coupling reactions, which require preparation of organomagnesium-, organozinc-, organotin-, or organoboron-functionalized monomers, respectively.1–4 This adds extra steps to the synthesis of the molecule under scrutiny. In the case of Stille cross-couplings, the use of toxic and environmentally harmful organotin reagents poses additional limitations. One possibility of alleviating these drawbacks is to form aryl–aryl bonds using C–H activation, also referred to as direct arylation (DA), which allows us to access compounds in fewer steps, in less time, in a more cost-efficient way, and with increased atom economy.5–8 Further benefits arise from the reduced toxicity compared to that of Stille reactions and increased functional group stability compared to that of, for example, Grignard compounds, which can be decisive in large-scale workup, separation, and storage of building blocks. Since the first reports on DA by Ames and Nakamura,9,10 C–H activation strategies have advanced to being one of the most researched topics, with ever increasing activity and importance. A large number of structures have been investigated with respect to aromatic C–H activation, including π-systems such as benzene, thiophene, indole, thiazole, tetracene, coronulene, or porphyrin.5–8,11,12 The diversity in C–H activation reactions is obvious, considering the ubiquitous nature of the C–H bonds. Although most of the π-systems investigated have been electron-rich structures, electron-deficient skeletons have been much less explored. Among them, tetrafluorobenzenes, thienopyrrolidones, and benzothiadiazoles have been reported.13–16 Among the class of perylene diimides, perylene diimides (PDIs) have been investigated with respect to C–H activation,17–22 and isolated reports dealing with the C–H activation of naphthalene diimides (NDIs) have been disclosed.23

Herein, we report the DA of N-alkyl-substituted pyromellitic diimide (PMDI). PMDI-based materials are less investigated compared with their larger analogues24,25 but are, due to their simplicity, of particular interest for molecular and electronic and for sensing applications. From a polymer design point of view, incorporation of aromatic diimides into conjugated polymers allows n-type materials with low-lying lowest unoccupied molecular orbital (LUMO) levels to be made, enabling efficient electron transport.26–28 However, compared to those on their NDI and PDI analogues, only a few reports on PMDI-based materials have been disclosed. PMDI compounds are commonly prefunctionalized via multistep syntheses involving cumbersome bromination (Scheme 1a).26,28–35

Thus, omitting bromination not only increases atom economy but also reduces the number of steps required to make PMDI-based materials. To the best of our knowledge, no direct functionalization of PMDI has been reported. Here, we present a method for C–H activation of PMDI and the reaction with aromatic halides (Scheme 1b).

RESULTS AND DISCUSSION

As a parameter set to start with, we selected symmetrically substituted N-ethylhexyl PMDI and an excess of 4-bromotoluene (Scheme 2).

The reaction was initially conducted in tetrahydrofuran with Pd2(dba)3, P(o-anisyl)3, PivOH, and Cs2CO3 as the typical reactants.36–38 Although the raw product showed the complete disappearance of PMDI, an intractable mixture of compounds was obtained, which could not be characterized sufficiently. We presumed that ring opening of the PMDI moiety occurred under the reaction conditions used, leading to

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the decomposition of PMDI. Fortunately, the use of mesitylene as the solvent led to fully soluble product mixtures containing 36% asymmetric 4-tolyl-substituted PMDI (monosubstituted compound 2) and 49% disubstituted target compound 3 (entry 1, Table 1). Mesitylene has already proven to be a good solvent for the DA of NDI derivatives, even though the functional groups are different.39,40 To further optimize the reaction conditions to the required level also for even polycondensation reactions, a detailed parameter screening was performed. Although temperature changes from 110 to 120 °C did not lead to remarkable changes in yield (entry 2, Table 1), the reaction proved to be extremely sensitive to subtle changes of other parameters. Specifically, the PMDI concentration turned out to be important, with concentrations of 0.2 M leading to the decomposition of PMDI even in mesitylene. Good yields of compound 3 (65%) were obtained, with a concentration of 0.05 M (entries 3 and 4, Table 1).

The influence of the base was investigated next (entries 15–25, Table 1). Cs2CO3 is required to achieve good yields; other carbonates yielded drastically lower yields of PMDI (entries 15–16, Table 1). Drastically lower yields also resulted when using pivalate instead of pivalic acid in combination with Cs2CO3 (entries 17–18, Table 1). We also found the amount of PivOH to be important for the outcome of the reaction (entries 23–24, Table 1). No reaction was observed in the absence of pivalic acid, with only Cs2CO3 as the base (entry 25, Table 1). Finally, the catalyst loading was varied to enable quantitative conversion of PMDI (entries 26–29, Table 1), revealing a strong dependence on the yield of 3. The best result, with satisfying yields of 95% of 3 and 5% of 2 was obtained with 4 mol % PdG3 (entry 28, Table 1).

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The effect of the position of the methyl group is interesting, as it causes torsion between the phenyl ring and the PMDI core. Considering different bromotoluenes, 4-bromotoluene gave the highest yield (entries 1–3, Table 2). However, similar conversions were obtained even for 2- and 3-bromotoluene, indicating a weak effect of the steric parameters of the substrate. This can be ascribed to the use of P(o-anisyl)3, which is known to be suitable for cross-coupling of o-bromides.35 The reaction with bromobenzene also exhibited good catalytic activity (entry 4, Table 2). The less reactive chlorobenzene, 8, was also tested as a substrate (entry 5, Table 2) without any loss of activity compared to that of bromobenzene, indicating good reactivity. Moreover, the electronic effects of the substituent on the aryl halide were tested. Compared to that of the model reaction with 4-bromotoluene, the modification of the para-substituent led to a strongly different outcome. Although the use of 4-methoxybromobenzene (9) and 4-trifluoromethyl-bromobenzene (11) gave the disubstituted compound in 24 and 71%
yields, respectively, the reaction did not proceed with 4-cyanobromobenzene \( \text{10} \) (entries 6–8, Table 2). Also, increased reaction times of up to 16 days did not lead to measurable conversion of PMDI. Interestingly, this behavior cannot be explained by simply classifying substituents as electron rich or electron poor, as good conversion is seen with \( \text{11} \) (entry 8, Table 2) but no reaction occurred with \( \text{10} \) (entry 7, Table 2).

Finally, the coupling of PMDI with halides exhibiting stronger electronic modification was investigated. The use of bromopentafluorobenzene \( \text{12} \) only afforded a mixture of starting materials together with insoluble products that could not be characterized (entry 9, Table 2). The synthetic protocol was not efficient with heterocycles such as 2-bromopyrimidine (entry 10, Table 2), with the raw mixture again containing PMDI together with an intractable mixture of compounds.

Optical absorption of the disubstituted PMDI derivatives in solution is characterized by a weak donor−acceptor system, whereby both the torsional angle between PMDI and the phenyl ring and the electron rich or deficient nature of the halide are the main parameters governing donor strength. The most red-shifted charge-transfer band is found for the disubstituted PMDI with the least torsion and coupled to the most electron-rich substrate, \( \text{9} \) (see Supporting Information). This trend is also confirmed by cyclic voltammetry (CV) measurements, wherein a stronger donor increases the LUMO energy level from \(-3.52 \text{ eV}\) for substrate \( \text{11} \) to \(-3.36 \text{ eV}\) for substrate \( \text{9} \) (see Supporting Information). Differential scanning calorimetry (DSC) measurements of some of the crystalline

### Table 1. Summary of Reaction Conditions of the DA of PMDI

| entry | additive/equiv | base/equiv | catalyst/mol % | ligand/mol % | T/h | [PMDI]/mol L−1 | temp/°C | PMDI/% | 2/%b | 3/%b |
|-------|----------------|------------|----------------|--------------|-----|----------------|---------|---------|------|------|
| 1     | PivOH/1        | Cs2CO3/3   | Pd(dba)3/3     | P(o-anisyl)3/6 | 16  | 0.1            | 110     | 15      | 36   | 49   |
| 2     | PivOH/1        | Cs2CO3/3   | Pd(dba)3/3     | P(o-anisyl)3/6 | 16  | 0.1            | 120     | 12      | 35   | 53   |
| 3     | PivOH/1        | Cs2CO3/3   | Pd(dba)3/3     | P(o-anisyl)3/6 | 16  | 0.05           | 110     | 7       | 27   | 65   |
| 4     | PivOH/1        | Cs2CO3/3   | Pd(dba)3/3     | P(o-anisyl)3/6 | 16  | 0.2            | 110     | insoluble products |
| 5     | PivOH/1        | Cs2CO3/3   | Pd(dba)3/3     | PCy3/6       | 16  | 0.05           | 110     | 45      | 43   | 12   |
| 6     | PivOH/1        | Cs2CO3/3   | Pd(dba)3/3     | P(o-anisyl)3/6 | 40  | 0.05           | 110     | 3       | 21   | 76   |
| 7     | PivOH/1        | Cs2CO3/3   | Pd(dba)3/3     | P(o Tol)/6   | 40  | 0.05           | 110     | 100     |      |      |
| 8     | PivOH/1        | Cs2CO3/3   | Pd(dba)3/3     | DMPP/6       | 40  | 0.05           | 110     | 100     |      |      |
| 9     | PivOH/1        | Cs2CO3/3   | Pd(dba)3/3     | P(o-anisyl)3/12 | 40 | 0.05           | 110     | 4       | 21   | 76   |
| 10    | PivOH/1        | Cs2CO3/3   | PdG3/3         | P(o-anisyl)3/6 | 40  | 0.05           | 110     | 12      | 88   |      |
| 11    | PivOH/1        | Cs2CO3/3   | Pd(OAc)2/3     | P(o-anisyl)3/6 | 40  | 0.05           | 110     | 2       | 19   | 79   |
| 12    | PivOH/1        | Cs2CO3/3   | Pd(dba-OMe)2/3 | P(o-anisyl)3/6 | 40  | 0.05           | 110     | 3       | 21   | 76   |
| 13    | PivOH/1        | Cs2CO3/3   | Pd(dba-CF3)2/3 | P(o-anisyl)3/6 | 40  | 0.05           | 110     | 20      | 43   | 37   |
| 14    | PivOH/1        | Cs2CO3/3   | Pd(OPiv)2/3    | P(o-anisyl)3/6 | 40  | 0.05           | 110     | 5       | 27   | 68   |
| 15    | PivOH/1        | Cs2CO3/3   | K3CO3/3        | P(o-anisyl)3/6 | 40  | 0.05           | 110     | 29      | 47   | 24   |
| 16    | PivOH/1        | Li2CO3/3   | PdG3/3         | P(o-anisyl)3/6 | 40  | 0.05           | 110     | 100     |      |      |
| 17    | PivOCs/1       | PdG3/3     | P(o-anisyl)3/6 | 40  | 0.05           | 110     | 94      | 5     | 1    |
| 18    | PivOK/1        | PdG3/3     | P(o-anisyl)3/6 | 40  | 0.05           | 110     | 87      | 13    |      |
| 19    | PivOH/1        | Cs2CO3/1   | PdG3/3         | P(o-anisyl)3/6 | 40  | 0.05           | 110     | 30      | 43   | 28   |
| 20    | PivOH/1        | Cs2CO3/2   | PdG3/3         | P(o-anisyl)3/6 | 40  | 0.05           | 110     | 12      | 40   | 47   |
| 21    | PivOH/1        | Cs2CO3/4   | PdG3/3         | P(o-anisyl)3/6 | 40  | 0.05           | 110     | 13      | 42   | 45   |
| 22    | PivOH/1        | Cs2CO3/5   | PdG3/3         | P(o-anisyl)3/6 | 40  | 0.05           | 110     | 5       | 37   | 58   |
| 23    | PivOH/2        | Cs2CO3/3   | PdG3/3         | P(o-anisyl)3/6 | 40  | 0.05           | 110     | 12      | 39   | 48   |
| 24    | PivOH/0.5      | Cs2CO3/3   | PdG3/3         | P(o-anisyl)3/6 | 40  | 0.05           | 110     | 10      | 13   | 87   |
| 25    | Cs2CO3/3       | PdG3/3     | P(o-anisyl)3/6 | 40  | 0.05           | 110     | 100     |      |      |
| 26    | PivOH/1        | Cs2CO3/3   | PdG3/2         | P(o-anisyl)3/4 | 40  | 0.05           | 110     | 3       | 24   | 73   |
| 27    | PivOH/1        | Cs2CO3/3   | PdG3/1         | P(o-anisyl)3/2 | 40  | 0.05           | 110     | 37      | 44   | 19   |
| 28    | PivOH/1        | Cs2CO3/3   | PdG3/4         | P(o-anisyl)3/8 | 40  | 0.05           | 110     | 5       | 5    | 95   |
| 29    | PivOH/1        | Cs2CO3/3   | PdG3/5         | P(o-anisyl)3/10 | 40 | 0.05           | 110     | 11      | 87   |      |

All reactions were performed in mesitylene. The NMR ratio between the starting material and products, calculated by \(^1\)H NMR. PivOH: pivalic acid, DMPP: tris(2,6-dimethoxyphenyl)phosphine. Structures of the catalysts are given in Scheme 3.

### Scheme 3. Pd Catalyst and Ligands Used

![Scheme 3](image)

### Scheme 4. Halide Substrates Used

![Scheme 4](image)
disubstituted PMDIs showed unconventional behavior, which is strongly dependent on the position and nature of the substituent on the phenyl ring. Most surprisingly, disubstituted PMDI made from 1 melted at 111 °C and subsequently recrystallized at 239 °C during the first heating cycle, indicating the formation of a different polymorph. Further heating to the maximum applicable temperature of 300 °C (for thermogravimetric measurements, see Supporting Information) did not lead to subsequent melting of the recrystallized material. Accordingly, the cooling trace was entirely featureless. Moving the methyl group from the para to the meta and ortho positions weakened this behavior with respect to the ability to recrystallize during heating. By contrast, the thermal behavior of the disubstituted PMDIs derived from 7, 9, and 11, included simple melting and crystallization events during heating and crystallization, respectively (see Supporting Information).

**CONCLUSIONS**

In conclusion, we have presented a straightforward and thoroughly optimized protocol enabling difunctionalization of electron-deficient \( N,N \)-dialkylated PMDI via DA, with excellent yield. The synthetic methodology makes commonly used bromination of PMDI precursors redundant and thus shortens the synthetic pathways to a variety of arylated PMDI derivatives. The near-quantitative formation of disubstituted PMDI derivatives is a necessary condition for further elaboration of this protocol toward the quantitative yield required for polycondensation with dihalides, which might lead to highly simplified two-step protocols toward efficient n-type copolymers for use in organic electronics. The initial results regarding copolymerization of PMDI and 1,4-dibromobenzene indicate that this is possible and also that optimization is required to increase the molecular weight to an acceptable level (see Supporting Information).

**EXPERIMENTAL SECTION**

**Materials.** All chemicals were obtained from Sigma Aldrich and used without further treatment unless otherwise stated. PMDI was synthesized according to a previously reported method. \(^3\) \( \text{Pd}_2(\text{dba-R})_3 \) complexes were synthesized according to the literature.\(^4\)

**General Procedure for the Model Reaction of PMDI and 4-Bromotoluene.** PMDI (20.00 mg, 0.04539 mmol, 1 equiv), 4-bromotoluene (77.64 mg, 0.4539 mmol, 10 equiv), \( \text{Cs}_2\text{CO}_3 \) (136.18 mg, 44.371 mmol, 3 equiv), \( \text{PivOH} \) (4.64 mg, 45.4 mmol, 1 equiv), \( \text{PdG}_3 \) (1.34 mg, 1.82 mmol, 4 mol %), and tris(o-methoxyphenyl)phosphine (1.28 mg, 3.63 mmol, 8 mol %) were charged in a dried vial containing a stirring bar. The contents of the vial were degased for 30 min. Then, 0.09 mL of degased mesitylene was added under a N\(_2\) atmosphere. The vial was sealed, placed in a preheated oil bath, and stirred for 40 h at 110 °C. After cooling to RT, the mixture was filtered through a short silica plug to remove any trace of mesitylene and then extracted with pure dichloromethane (DCM). After evaporation of the solvent, the residual material was characterized by \(^1\)H NMR spectroscopy to calculate the mole percentage of products 2 and 3 in the reaction mixture. The products could be purified via column chromatography using a mixture of DCM and i-hexane (3:1).

**General Procedure for Screening of the Reaction Scope.** The same procedure that is described above was used, with an increase in the reaction time to 3 days and with a PMDI loading of 200 mg instead of 20 mg.

**ASSOCIATED CONTENT**

\(^5\) Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acsomega.7b00420.

Analytical data, copies of the \(^1\)H and \(^1^3\)C NMR spectra for all new products thermogravimetric analysis and DSC curves, UV–vis spectra, and data from CV in solution (PDF)

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**Author Contributions**

The manuscript was written through contributions of all authors. All authors have given approval to the final version of the manuscript.

**Notes**

The authors declare no competing financial interest.

**Table 2. Reaction Scope**

| entry | substrate | PMDI/% | monosubstituted product/% | bis-substituted product/% |
|-------|-----------|--------|--------------------------|--------------------------|
| 1     | 4         |        | 12                       | 88                       |
| 2     | 5         |        | 19                       | 75                       |
| 3     | 6         |        | 18                       | 80                       |
| 4     | 7         |        | 17                       | 78                       |
| 5     | 8         |        | 18                       | 79                       |
| 6     | 9         |        | 50                       | 24                       |
| 7     | 10        |        | 17                       | 71                       |
| 8     | 11        |        | 12                       | insoluble products       |
| 9     | 12        |        | insoluble products       |                          |

\(^6\) All reactions were performed in mesitylene ([PMDI] = 0.05 M) at 110 °C, additive = 1 equiv PivOH, base = 3 equiv \( \text{Cs}_2\text{CO}_3 \), reaction time = 3 days. \(^4\) Conversion was calculated by \(^1\)H NMR. The structures of the substrates are given in Scheme 3.
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