

Diarylindenotetracenes via a Selective Cross-Coupling/C–H Functionalization: Electron Donors for Organic Photovoltaic Cells

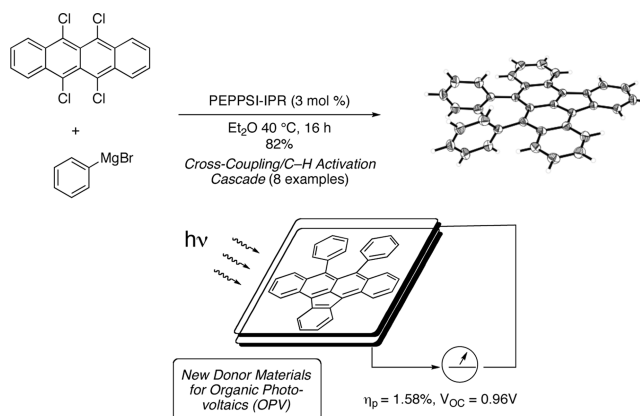
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Received January 14, 2012

ABSTRACT



A direct synthesis of new donor materials for organic photovoltaic cells is reported. Diarylindenotetracenes were synthesized utilizing a Kumada–Tamao–Corriu cross-coupling of *peri*-substituted tetrachlorotetracene with spontaneous indene annulation via C–H activation. Vacuum deposited planar heterojunction organic photovoltaic cells incorporating these molecules as electron donors exhibit power conversion efficiencies exceeding 1.5% with open-circuit voltages ranging from 0.7 to 1.1 V when coupled with C₆₀ as an electron acceptor.

Cross-coupling reactions of aryl nucleophiles with aryl electrophiles, such as the Kumada–Tamao–Corriu reaction,^{1,2} are now ubiquitous transformations in synthetic organic chemistry. Recently, Scott discovered that *peri*-substituted dihaloacenes can undergo an indene annulation reaction via a cross-coupling/C–H activation cascade reaction, albeit with high catalyst loadings (40 mol %

palladium).^{3–5} Given our interest in acene materials,^{6,7} we thought that 5,6,11,12-tetrachlorotetracene (**1a**)⁸ might undergo similar types of transformations. Hypothetically, reaction of phenyl magnesium bromide with **1a** could lead to rubrene (**1b**), 9,10-diphenylindeno[1,2,3-*fg*]tetracene (**2a**), or diindenotetracene (**3**) (Scheme 1). In some ways, **2a** might be more difficult to prepare from **1a**, since disparate reactivity between the two sets of *peri*-chlorides is required. Products **2a** and **3** are candidates for organic

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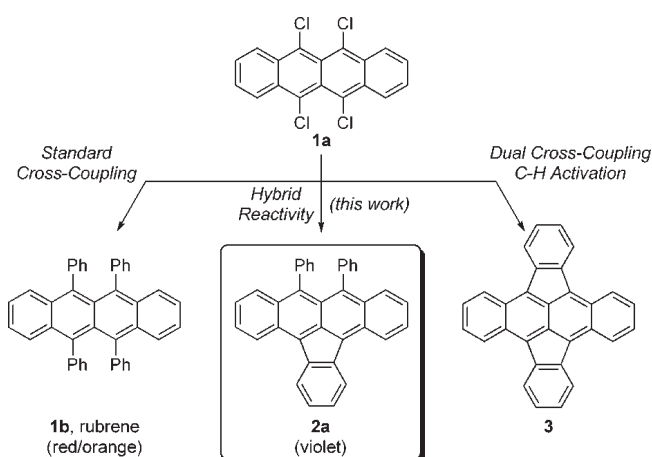
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(8) **1a** can be prepared in multigram quantities by a three-step, chromatography-free synthesis from 1,4-naphthalenediol and phthaloyl chloride. See ref 4b and Yagodkin, E.; McGarry, K. A.; Douglas, C. J. *Org. Prep. Proc. Int.* **2011**, *43*, 360.

Scheme 1. Potential Products upon Treatment of **1a** with a Phenyl Nucleophile and Pd Catalyst



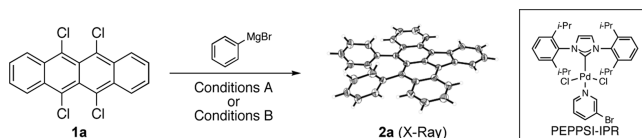
electronic devices, given their relationship to rubrene, a benchmark organic semiconductor.^{9–11} Although the syntheses of **2a**^{12–14} and **3**¹⁵ were reported decades ago, they require harsh reaction conditions and, in our hands, were low yielding.

Herein, we report a new synthesis of 9,10-diarylindeno[1,2,3-*fg*]tetracenes via a chemoselective Kumada–Tamao–Corriu coupling/C–H activation cascade reaction. In our cascade, one pair of *peri*-chlorides undergoes standard Kumada–Tamao–Corriu coupling while the other pair undergoes the C–H activation cascade. We reduced the catalyst loading for the C–H activation by an order of magnitude. Our route is easily scaled and allows for late-stage diversification. To the best of our knowledge, these diarylindeno[1,2,3-*fg*]tetracenes constitute a new class of acene materials for organic photovoltaic cells (OPVs).^{16–18}

Our success in the cross-coupling reaction of **1a** with MeMgBr as a nucleophile⁶ using the PEPPSI-IPR^{19,20} catalyst encouraged us to explore the reaction of PhMgBr with **1a**. We did not isolate any rubrene (**1b**) or di-indene (**3**) from this attempt. Rather, we isolated 9,10-diphenylindeno[1,2,3-*fg*]tetracene (**2a**) in 84% yield as the

major product (Scheme 2).²¹ Additional optimization of the reaction conditions allowed us to lower the catalyst loading (from 12 to 3 mol %) and reaction temperature (from 80 to 40 °C) with a negligible decrease in yield (82%). These lower catalyst loadings, when compared to prior work,³ are valuable in the preparation of pure materials for device studies. Prior work with **2a** was reported before modern structural characterization methods were available.¹² Our data for **2a** are in agreement with the previous reports, and we were able to confirm the structure by X-ray crystallography.

Scheme 2. Synthesis of 9,10-Diphenylindeno[1,2,3-*fg*]tetracene **2a**^a



^a Conditions A: PhMgBr (12 equiv), PEPPSI-IPR (10 mol %), dioxane, 80 °C, 24 h (84%). Conditions B: PhMgBr (10 equiv), PEPPSI-IPR (3 mol %), Et₂O, 40 °C, 16 h (82%). Yields are of recrystallized material.

We explored the reaction scope by incorporating groups that might alter optoelectronic properties. The reaction tolerated both electron-donating and -releasing substituents at the *para* position of the Grignard reagents (entries 2–6, Table 1). An aryl Grignard reagent bearing 3, 5-dimethoxy groups reacted with **1a** to provide **2g** in good yield (73%, entry 7). Albeit in diminished yields, an aryl Grignard reagent with even more substituents was tolerated under the reaction conditions (entry 8). The lower yields of **2h** and **2f** are partially attributed to difficulties in the purification (entries 6 and 8). Grignard reagents bearing *ortho*-alkyl groups (entries 9 and 10) were not effective, likely because additional steric hindrance slows the cross-coupling step. We were unable to isolate any of the corresponding diarylindeno[1,2,3-*fg*]tetracene in an attempted reaction of **1a** with 4-trifluoromethylphenyl magnesium bromide (not shown).

To probe whether indene formation precedes or follows the standard cross-coupling events, we prepared two potential intermediates **4** and **5** (Scheme 3), which were separately subjected to our above reaction conditions. Indene **2a** was formed in both experiments, indicating that either **4** or **5** is a potential intermediate. Compound **4** proceeded cleanly to **2a** (44%). By contrast, the conversion of **5** to **2a** was very low yielding (< 5%), likely because of the poor solubility of **5**. If **5** is a viable intermediate in the conversion of **1a** to **2a**, it must not build up in sufficient amounts to precipitate from solution.

Thin film absorption spectra can indicate the degree of conjugation of the various functional groups (Figure 1). Figure 1a compares the thin film absorption spectra of indenenes with R = H, R = F, and R = OMe. Figure 1b compares changes in the thin film absorption for indenenes containing either three, six, or nine OMe groups. Increased conjugation of the oxygen lone pairs (R = OMe) may

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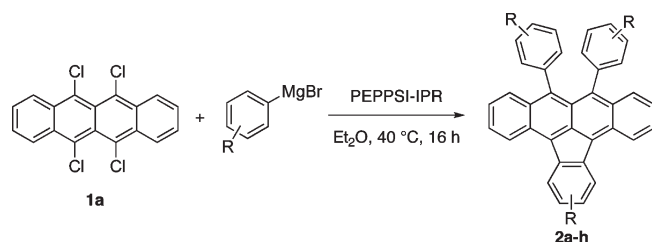
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(21) A sample of **2a** was bench stable for up to 6 months in a N₂-flushed, clear glass scintillation vial, as determined by ¹H NMR.

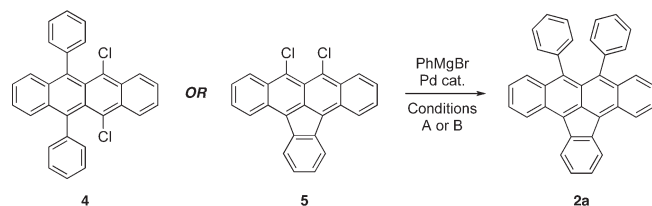
Table 1. Reaction Scope^a

entry	R	product	% yield ^b
1	H	2a	82
2	4-F	2b	32
3	4-Me	2c	73 ^c
4	4- <i>n</i> Bu	2d	76 ^c
5	4- <i>t</i> Bu	2e	40 ^d
6	4-OMe	2f	31
7	3,5-di-OMe	2g	73
8	3,4,5-tri-OMe	2h	31
9	2-Me	2i	— ^e
10	2,6-di-Me	2j	— ^e

^a Conditions: **1a**, PEPPSI-IPR (3 mol %), ArMgBr (10 equiv), Et₂O (0.05 M of **1a**), sealed vessel, 40 °C, 16 h. ^b Yields after purification by alumina chromatography and recrystallization. ^c Purification by alumina chromatography only. ^d PEPPSI-IPR (12 mol %), ArMgBr (12 equiv), dioxane, sealed vessel, 80 °C, 24 h. Purification by silica gel chromatography. ^e **2i** or **2j** was not observed in the mixture of products.

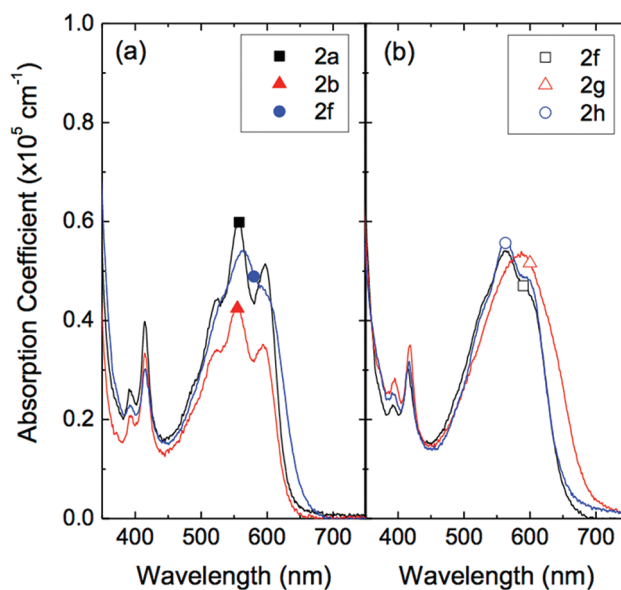
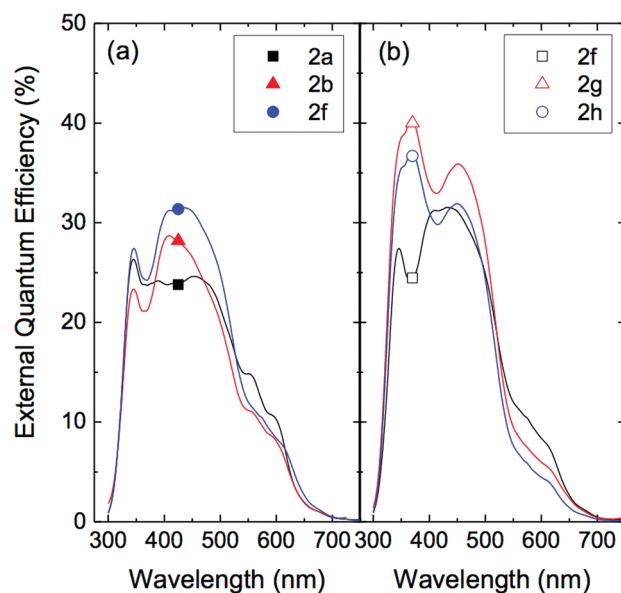
cause a red shift observed in the spectra of compounds **2f–h** compared to **2a** (R = H). Compound **2h** (R = 3,4,5-tri-OMe) is blue-shifted relative to **2g** (R = 3,5-di-OMe) even though **2h** has additional methoxy groups. The all-*ortho* substitution pattern likely prevents the oxygen lone pairs from donating effectively to the π -system of **2h**.

The photovoltaic performance of **2a**, **2b**, **2f**, **2g**, and **2h** as electron donors was evaluated by fabricating devices on indium–tin oxide (ITO) coated glass substrates. A layer of poly(3,4-ethylenedioxythiophene) poly(styrenesulfonate) (PEDOT:PSS) was spun-cast on the substrate at a speed of 7000 rpm for 45 s.²² The organic semiconductor materials were deposited by high vacuum thermal sublimation (< 10^{−7} Torr) at a rate of 0.2 nm s^{−1}. Optimum device

Scheme 3. Possible Intermediates in the Formation of **2a**^a

^a Conditions A: PhMgBr (12 equiv), PEPPSI-IPR (10 mol %), dioxane, 80 °C, 24 h. Conditions B: PhMgBr (10 equiv), PEPPSI-IPR (3 mol %), Et₂O, 40 °C, 16 h.

efficiencies were found for structures containing a 10–15-nm-thick donor layer and a 40-nm-thick acceptor layer of C₆₀. All structures were capped with a 10-nm-thick exciton blocking layer of 2,9-dimethyl-4,7-diphenyl-1,10-phenanthroline (BCP),²³ and a 70-nm-thick Al cathode defining an active area that is 1 mm in diameter.

**Figure 1.** Thin film absorption spectra for compounds (a) **2a**, **2b**, **2f** and (b) **2f**, **2g**, **2h**.**Figure 2.** External quantum efficiency (η_{EQE}) spectra for devices containing donor material compounds (a) **2a**, **2b**, **2f** and (b) **2f**, **2g**, **2h**.

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Device performance was characterized by measuring current density–voltage characteristics under AM 1.5G solar simulated illumination. All of the donor (D) materials exhibited a large open-circuit voltage (V_{OC}) when used with a C_{60} acceptor (A) due to their low dark current characteristics, with the largest V_{OC} of > 1 V obtained for the fluorinated compound (**2b**, Table 2). This is significant as it is comparable to the highest V_{OC} values reported for single junction OPVs.^{24,25} Peak values of the fill factor (FF) and power conversion efficiency (η_P) exceed 0.5 and 1.5%, respectively. This performance is comparable to that previously reported for planar heterojunction OPVs based on the D–A pairing of rubrene- C_{60} .¹⁰

Table 2. Device Performance under AM 1.5G Solar Simulated Illumination (44 mW/cm²)

donor	J_{SC} (mA/cm ²) ^a	V_{OC} (V)	FF	η_P (%)
2a (10 nm)	1.295	0.955	0.563	1.58
2b (15 nm)	1.259	1.120	0.437	1.40
2f (15 nm)	1.341	0.810	0.381	0.94
2g (10 nm)	1.314	0.702	0.536	1.12
2h (10 nm)	1.177	0.834	0.408	0.91

^a Short-circuit current density.

A clear response from each donor is observed in the range of 500–700 nm (Figure 2). Slight variations in the external quantum efficiency (η_{EQE}) corresponding to the activity of C_{60} ($\lambda = 350$ –400 nm) are attributed to changes

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in the optical field in the device depending on the optimized donor layer thickness.^{26,27}

In conclusion, a direct and selective catalytic synthesis of new donor materials for organic photovoltaic cells was reported. The synthesis uses readily available **1a** and aryl Grignard reagents in a Kumada–Tamao–Corriu cross-coupling/C–H functionalization cascade. A variety of intermediates can account for the formation of the products. These materials show high V_{OC} and power conversion efficiencies approaching 1.6% as donors in bilayer OPVs. Further improvements in efficiency could be expected in a mixed D–A–heterojunction OPV architecture.

Acknowledgment. This work was supported by the National Science Foundation (NSF) DMR-0819885 and DMR-1006566, University of Minnesota: Initiative for Renewable Energy and the Environment (IREE), DuPont, and 3M. We thank Dr. J. Dalluge, Dr. S. Francis, and Mr. S. Murray (UMN) for assistance with mass spectrometry and Prof. G. Georg (UMN) for translating ref 15.

Supporting Information Available. Complete experimental details and spectral data for all compounds described (including FID files), crystallographic data (.cif file) for **2a**, and current density–voltage characteristics for devices containing donor material compounds **2a**, **2b**, **2f**, **2g**, and **2h**. This material is available free of charge via the Internet at <http://pubs.acs.org>.

(27) Preliminary experiments indicate that 9,10-diphenylindeno-[1,2,3-*fg*]tetracene (**2a**) reacts slowly with C_{60} in an NMR tube experiment. The structure of the product of this reaction, and the implications of this experiment with regard to devices fabricated from **2a** and C_{60} , is currently under investigation. We thank a reviewer for suggesting this course of investigation.

The authors declare no competing financial interest.