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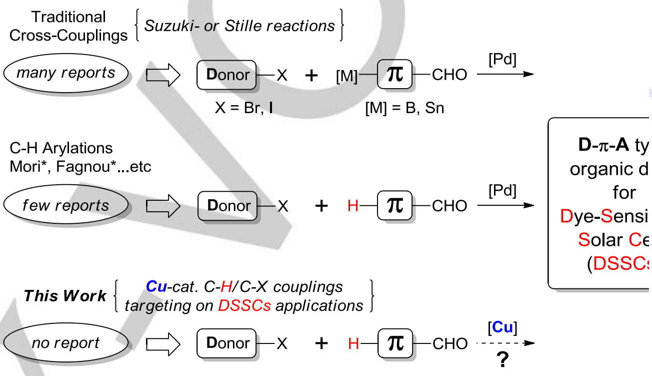
Greener Synthesis of D-π-A Organic Sensitizers via Cu-Catalyzed Direct Arylations: Development of Sn- & Pd-Free Process for Dye-Sensitized Solar Cells

Jiung-Huai Huang,[a] Po-Han Lin,[a] Wei-Ming Li,[a] Kun-Mu Lee,[b] and Ching-Yuan Liu*[a]

Abstract: A variety of D–π–A type functional organic dyes have been facilely synthesized via direct C-H arylations using inexpensive copper salts as catalyst. Under well-optimized reaction conditions, a broad substrate scope with good functional group compatibility was achieved. Based on this synthetic strategy, we designed and prepared three new dye sensitizers (**CYL-5~7**) that were fabricated as dye-sensitized solar cells (DSSCs). Photovoltaic characterizations showed that these devices gave a V_{oc} of 0.65~0.75 V, a J_{sc} of 5.90~12.60 mA/cm^2, and a *FF* of 65.6~76.9%, corresponding to the power conversion efficiency (PCE) of 2.95~6.20%**.** This work represents the first example using Cu-catalyzed C-H arylations as step-saving and Sn-free synthesis of various precursor dyes for DSSCs applications.

Introduction

Donor–π–acceptor (D–π–A) type metal-free organic dyes constitute a prominent part in modern research of dye-sensitized solar cells (DSSCs) because of their lower cost, flexible molecular design, and efficient intramolecular charge transfer (ICT).[1-5] Over the last decade, pioneers in this field have disclosed promising power conversion efficiencies (over 10.0%) based on a variety of organic sensitizers.[6-8] In general, these D–π–A or D–A–π–A' type organic dyes were synthesized via palladium-catalyzed cross couplings such as Stille- or Suzuki reactions, which requires tedious synthetic transformations including the pre-generation of organometallic reagents. Up to date, only a few reports described the step-economical direct arylation synthesis of DSSCs-oriented D–π–A type molecules[9-14] (Scheme 1). More importantly, we noticed that either by traditional cross-coupling techniques or through above mentioned C-H activation/arylation strategies,[9-14],[15-21] preparation of these organic dyes must involve the use of palladium-based catalysts for the key carbon-carbon bond formations. Hence, we anticipate that developing an equally efficient while Pd- & Sn-free greener catalytic system for the dye synthesis would be highly desirable. Accordingly, we demonstrate herein a step-saving new synthesis of the D–π–A type sensitizers using inexpensive copper salts as catalyst (Scheme 1). To the best of our knowledge, this work represents the first example applying Cu-catalyzed direct C-H arylations in the facile preparation of DSSCs-oriented small molecules.



Scheme 1. Different synthetic routes and catalytic systems to access D–π–A type organic sensitizers.

Results and Discussion

In order to access the targeted D–π–A type dye molecule via copper-catalyzed C-H arylations, 4-iodotriphenylamine **1a** (as Donor) and 2-thiophenecarboxaldehyde **2a** (as π–Acceptor) were selected as starting materials and the optimization of their reaction conditions was summarized in Table 1. Initially, the C-H arylation was tested under an optimal reaction condition disclosed previously by our group[22] [$CuCl_2$, mono-dentate phosphine ligand (PPh_3 or PCy_3), and Cs_2CO_3 in DMPU/*m*-xylene], giving the desired product **3a** in 40-52% yields (entries 1 2). Using bidentate ligands (dppe, dppb) afforded **3a** in relatively lower yields (18-39%, entries 3-4). Xantphos and DPEphos, the bidentate ligands with wide bite angles, showed better results and **3a** was produced in 60-72% yields (entries 5-6). C-H arylation with *N*, *N*-bidentate ligands generally gave poor yields (16-40%, entries 7, 9, 11, 12), except for phenanthroline (85%, entry 8) and bathophenanthroline (66%, entry 10). In the absence of ligand, **3a** was obtained in only 31% yield (entry 13). Based on above preliminary results, phenanthroline was used as the optimal ligand for following base and (co)solvent screenings. In contrast to Cs_2CO_3, less basic K_2CO_3 and Na_2CO_3 were shown to be inefficient in C-H arylations (24%, trace; entries 14, 15). When the base was switched to the more basic K_3PO_4, the arylation proceeded smoothly and **3a** was isolated in moderate yield (60%, entry 16). Without the addition of base, C-H arylation

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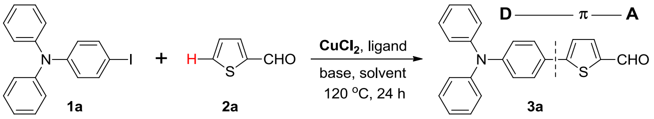
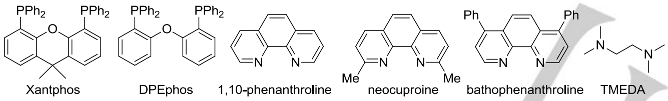
Table 1. Synthesis of the D-π-A type dye molecule **3a** via Cu-catalyzed direct C-H arylation: Optimization of the reaction parameters.[a]



Entry	Ligand	Base	Solvent	Yield (%)[c]
1	PPh_3	Cs_2CO_3	DMPU/*m*-xylene	40
2	PCy_3	Cs_2CO_3	DMPU/*m*-xylene	52
3	dppe	Cs_2CO_3	DMPU/*m*-xylene	18
4	dppb	Cs_2CO_3	DMPU/*m*-xylene	39
5	Xantphos	Cs_2CO_3	DMPU/*m*-xylene	60
6	DPEphos	Cs_2CO_3	DMPU/*m*-xylene	72
7	2,2'-bipyridyl	Cs_2CO_3	DMPU/*m*-xylene	36
8	1,10-phenanthroline	Cs_2CO_3	DMPU/*m*-xylene	85
9	neocuproine	Cs_2CO_3	DMPU/*m*-xylene	40
10	bathophenanthroline	Cs_2CO_3	DMPU/*m*-xylene	66
11	ethylenediamine	Cs_2CO_3	DMPU/*m*-xylene	16
12	TMEDA	Cs_2CO_3	DMPU/*m*-xylene	33
13	---	Cs_2CO_3	DMPU/*m*-xylene	31
14	1,10-phenanthroline	K_2CO_3	DMPU/*m*-xylene	24
15	1,10-phenanthroline	Na_2CO_3	DMPU/*m*-xylene	trace
16	1,10-phenanthroline	K_3PO_4	DMPU/*m*-xylene	60
17	1,10-phenanthroline	---	DMPU/*m*-xylene	0
18	1,10-phenanthroline	Cs_2CO_3	diglyme/*m*-xylene	74
19	1,10-phenanthroline	Cs_2CO_3	DMAc/*m*-xylene	66
20	1,10-phenanthroline	Cs_2CO_3	DMSO/*m*-xylene	13
21	1,10-phenanthroline	Cs_2CO_3	NMP/*m*-xylene	25
22	1,10-phenanthroline	Cs_2CO_3	DMPU	70
23	1,10-phenanthroline	Cs_2CO_3	*m*-xylene	45
24[b]	1,10-phenanthroline	Cs_2CO_3	DMPU/*m*-xylene	25



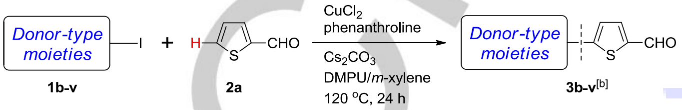
[a] Unless specified, the C-H arylation was conducted with 4-iodotriphenylamine **1a** (2.00 mmol) and 2-thiophenecarboxaldehyde **2a** (1.00 mmol) under N_2 in the presence of $CuCl_2$ (30 mol%, ultra-dry, 99.995% metals basis), ligand (30 mol%), and base (2.00 mmol) in 2 mL solvent (v/v = 1:1 if a cosolvent system is used) at 120 °C for 24 h. [b] 4-Bromotriphenylamine was used instead of **1a**. [c] Isolated yield.

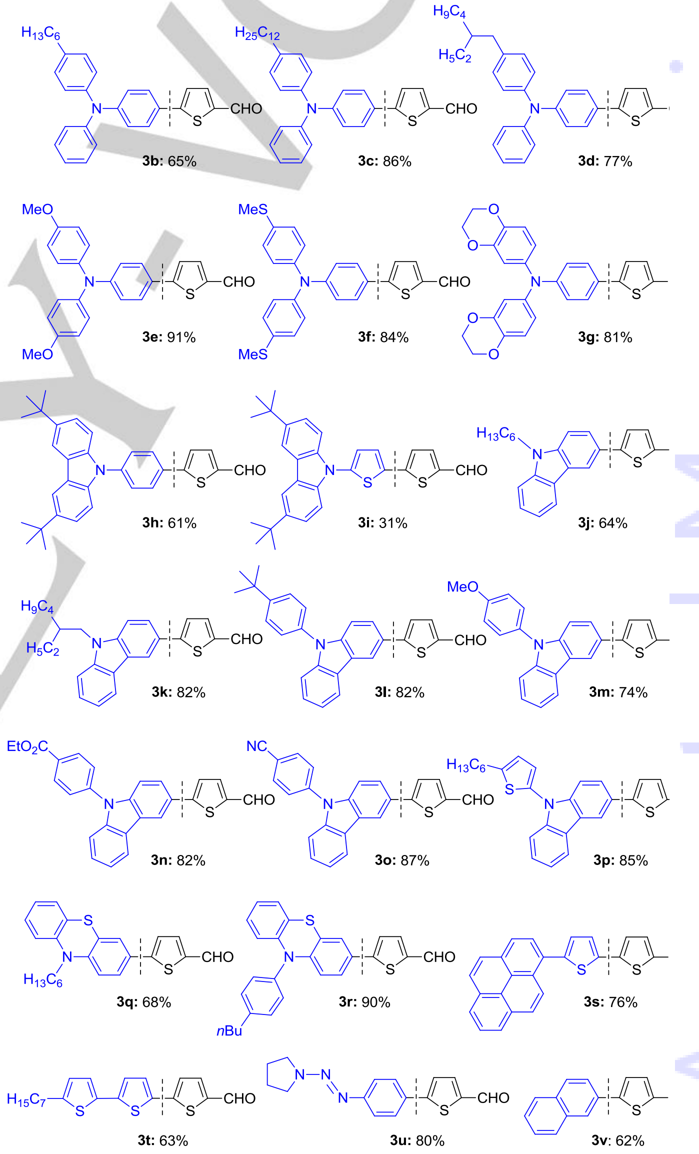
did not occur and both starting substrates (**1a**, **2a**) could be recovered (entry 17).

Next on, the (co)solvent system was examined. Combining *m*-xylene with diglyme or DMAc gave **3a** in moderate yields (74%, 66%; entries 18, 19). Reaction in other cosolvents such as DMSO/*m*-xylene or NMP/*m*-xylene appeared to be much less effective (13%, 25%; entries 20, 21). Importantly, using either DMPU or *m*-xylene as sole reaction solvent led to lower yields of **3a** (70%, 45%; entries 22, 23) when compared with the result of entry 8 (85%), indicating DMPU/*m*-xylene as cosolvent was essential to high conversion of the C-H arylation. Finally, under optimum reaction conditions ($CuCl_2$, phenanthroline, Cs_2CO_3, DMPU/*m*-xylene, 120 °C, 24 h), we tested the C-H arylation with 4-bromotriphenylamine, however, it was found that product **3a** was generated in only 25% yield (entry 24).

Subsequently, reaction scope with respect to the donor moiety of the D-π-A dye molecule was investigated under the reaction conditions obtained in entry 8 of Table 1. Initially, as shown in Table 2, reaction of **2a** with various triphenylamine (TPA)-based aryl iodides (**1b**-**g**) bearing linear-/branched alkyl groups, methoxyl, thiomethyl, or ethylenedioxy substituents led to the

Table 2. Substrate scope exploration concerned with donor moieties.[a]





[a] Unless specified, the C-H arylation was conducted with (hetero)aryl iodides **1b-v** (2.00 mmol) and 2-thiophenecarboxaldehyde **2a** (1.00 mmol) under N_2 in the presence of $CuCl_2$ (30 mol%, ultra-dry, 99.995% metals basis), 1,10-phenanthroline (30 mol%), and Cs_2CO_3 (2.00 mmol) in DMPU/*m*-xylene (2 mL, v/v = 1:1) at 120 °C for 24 h. [b] Isolated yields.

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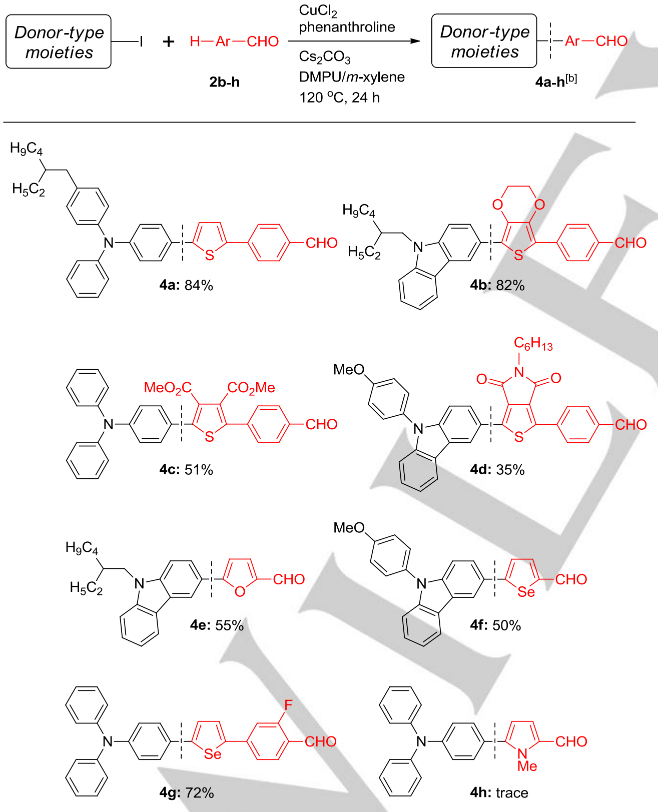
formation of desired D-π-A type products in moderate to good isolated yields (65-91%, **3b**-**3g**). When the donor moiety was changed to carbazole-based derivatives, we obtained relatively lower yields of pure **3h** and **3i** (61%, 31%), due to the inefficient separation of product **3h** or **3i** from the unreacted (4-iodophenyl)- or (5-iodothienyl)carbazoles (**1h**-**i**). In addition, we examined a series of 9-substituted-3-iodocarbazoles (**1j**-**p**) as another important class of hole-transporting/donor-type molecules. Under optimum reaction conditions, products **3j**-**3p** were isolated in 64-87% yields and we found ester (**3n**) and nitrile (**3o**) groups were well tolerated. Further, aryl iodides (**1q**-**r**) containing electron-rich phenothiazines were also tested, affording products **3q**, **3r** in 68%, 90% yields, respectively. Donor substrates involving pyrene (**1s**) or alkyl bithiophene (**1t**) proceeded to give the corresponding products in moderate yields (76%, 63%; **3s**, **3t**). Interestingly, 4-iodophenyltriazene (**1u**) underwent C-H arylation smoothly with 2-thiophenecarboxaldehyde and **3u** was obtained in good yield (80%). Organic-electronically important naphthyl group (from 2-iodonaphthalene, **1v**) was also efficiently introdcued to D-π-A system to furnish product **3v** in 62%.

Table 3. Substrate scope exploration concerned with π-acceptor moieties.[a]



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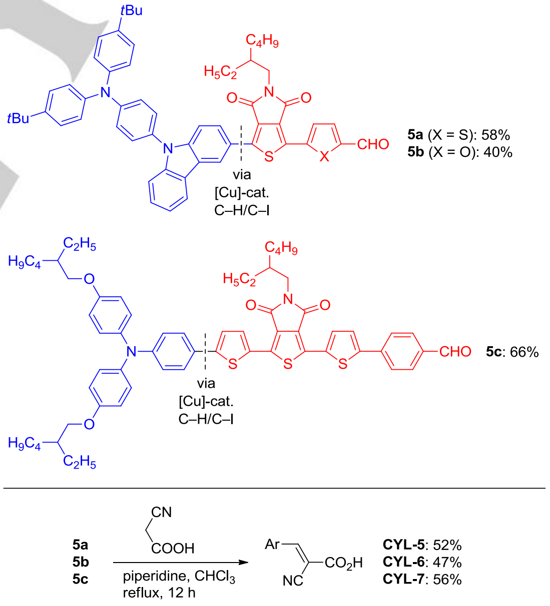
[a] Unless specified, the C-H arylation was conducted with aryl iodides (2.00 mmol) and various aldehydes **2b**-**h** (1.00 mmol) under N_2 in the presence of $CuCl_2$ (30 mol%, ultra-dry, 99.995% metals basis), 1,10-phenanthroline (30 mol%), and Cs_2CO_3 (2.00 mmol) in DMPU/*m*-xylene (2 mL, v/v = 1:1) at 120 °C for 24 h. [b] Isolated yields.

The reaction scope was further explored using various (hetero)-aryl aldehydes (Table 3). C-H arylation of aldehydes **2b** or **2c** with different donor-type iodoarenes under optimum reaction conditions generated dye molecules **4a**, **4b** in good isolated yields (84%, 82%). Electron-deficient aldehydes bearing diester-group (**2d**) or thieno[3,4-*c*]pyrrole-4,6-dione (TPD, **2e**) underwent arylation to provide products **4c** and **4d** in relatively lower yields (51%, 35%), presumably owing to the steric effect resulted from the ester or TPD moiety of **2d** or **2e**. Additionally, we also investigated other heteroaryls including furan, selenophene, and pyrrole, affording the corresponding products in 50-72% yields (**4e**, **4f**, **4g**). Notably, desired molecule **4h** was isolated in trace amount, due to the poor reactivity of *N*-methyl-2-formylpyrrole under present reaction conditions (starting materials mostly recovered).

In order to apply current synthetic methodology in modern dye-sensitized solar cells (DSSCs), three D-π-A type organic dyes (**5a**, **5b**, and **5c**) were facilely prepared using Cu-catalyzed C-H arylation as key step. As shown in Scheme 2, under our optimum reaction conditions employed in Table 2-3, **5a**-**c** were isolated in moderate yields (40-66%). Conversion of the aldehyde group of **5a**-**c** into cyanoacetic acid (as anchoring groups for TiO_2 attachment) by Knövenagel condensation afforded desired dye-sensitizers **CYL-5** ~ **CYL-7**.



Scheme 2. [Cu]-catalyzed C-H arylations as key-step to synthesize new sensitizers **CYL-5**, **CYL-6**, and **CYL-7**.

The UV-Vis absorption and electrochemical properties of sensitizers **CYL-5~7** were studied and the results were collected in Table 4. Although **CYL-5** and **CYL-6** are structurally similar, in absorption spectra they exhibited fairly different λ_{max} and ε in THF solutions. Particularly, the furan-containing sensitizer (**CYL-6**) showed much higher molar extinction coefficient in the intramolecular charge transfer (ICT) band (ε = 22703 $M^{-1}cm^{-1}$ for **CYL-5**; ε = 49278 $M^{-1}cm^{-1}$ for **CYL-6**). On the other hand, **CYL-7** was found to exhibit more red-shifted absorption band and narrower optical band gap (E_g^{opt} = 1.07~1.09 eV for **CYL-5** & **CYL-6**; E_g^{opt} = 0.89 eV for **CYL-7**), indicating the electron-donating ability of the alkoxyl-substituted triphenylamine (TPA) is stronger than the TPA-Cbz-hybrid donor moieties of **CYL-5** & **CYL-6** and a more efficient ICT effect in **CYL-7**. In addition, cyclic voltammetry measurements were conducted in THF solutions containing $(n\text{-}C_4H_9)_4NPF_6$ as supporting electrolyte. Compared with **CYL-5~6**, the uplifted E_{HOMO} of **CYL-7** (E_{HOMO} = -5.58 eV) was also attributable to the stronger electron-donating ability of its TPA unit.

Table 4. UV-Vis absorption and electrochemical properties of sensitizers **CYL-5**, **CYL-6**, and **CYL-7**.

Dyes	λ_{max} [nm][a]	ε [$M^{-1}cm^{-1}$][a]	λ_{max} on TiO_2 [nm][a]	E_g^{opt} [eV][b]	$E_{1/2}$ [V][c]	E_{HOMO}/E_{LUMO} [eV][d]
CYL-5	427	22703	438	2.08	1.07	-5.77/-3.69
CYL-6	402	49278	449	2.06	1.09	-5.79/-3.72
CYL-7	481	20645	442	1.71	0.89	-5.58/-3.88

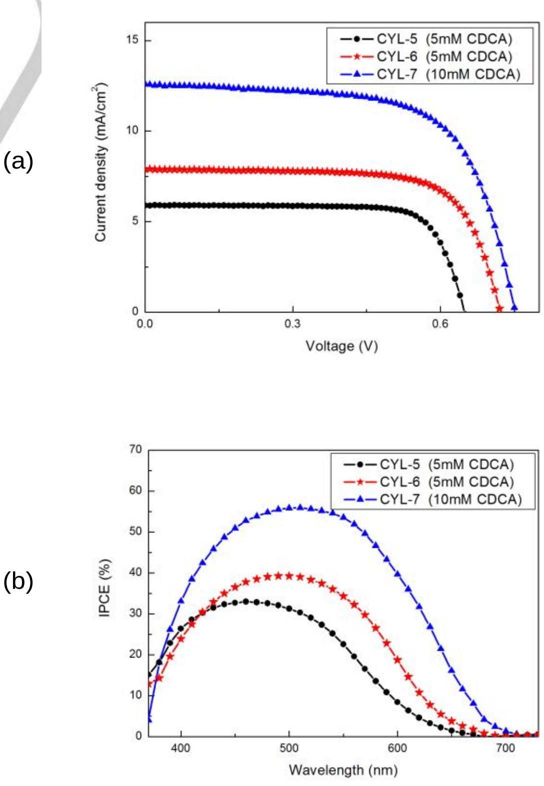
[a] Measured in THF solutions (~10^{-5} M); ε: extinction coefficient. [b] The optical band gap, E_g^{opt}, was calculated by $1240/\lambda^{onset}$ (dyes on TiO_2 films). [c] The half-wave potential, $E_{1/2}$, was calculated by $(E_{pa}+E_{pc})/2$, where E_{pa} and E_{pc} are the potential energy of anodic and cathodic peaks, respectively; The measurements are conducted in THF solutions (~10^{-4} M) containing $(n\text{-}C_4H_9)_4NPF_6$ as a supporting electrolyte under a scan rate of 100 mVs^{-1}. [d] The HOMO energy level, E_{HOMO}, was calculated by $-[(E_{1/2} + 0.197)_{vs.NHE} + 4.500]$ eV; $E_{LUMO} = E_{HOMO} + E_g^{opt}$.

CYL-5~7 were employed as sensitizers to fabricate dye-sensitized solar cells and the photovoltaic performance/parameters were summarized in Table 5 and Figure 1 (detailed procedures for solar cells fabrication and characterization were recorded in *Supporting Information*). Dye sensitizer with a furan moiety (**CYL-6**) showed higher open-circuit voltage (V_{oc}) and short-circuit current (J_{sc}) than its thiophene congener (**CYL-5**), thus leading to an enhanced PCE of 4.06%. **CYL-7** has the longest conjugation extension[23] among three sensitizers, making it exhibit much higher J_{sc} (12.60 mA/cm^2). This may also result from the superior electron-donating ability of alkoxyl-substituted triphenylamine of **CYL-7** thereby generating an efficient intramolecular charge transfer (ICT). This result was in agreement with the outcome obtained from the incident photon-to-current conversion efficiency (IPCE, Figure 1b), showing that **CYL-7** had the largest integral area of IPCE curve. In addition, three dyes were also investigated by electrochemical impedance spectroscopy (EIS). Figure 1c demonstrated Nyquist plots concerned with DSSCs based on **CYL-5~7** in dark with a bias of 0.65~0.75 V. Under dark conditions, **CYL-7** exhibited the largest charge transfer impedance between TiO_2-electrolyte interface, thus leading to a higher V_{oc} while irradiated under AM 1.5G solar simulator. Among three new sensitizers, **CYL-7** achieved a V_{oc} of 0.75 V, a J_{sc} of 12.60 mA/cm^2, and a fill factor (*FF*) of 65.6%, corresponding to the highest power conversion efficiency (PCE) of 6.20 %. In terms of the photovoltaic performance and the molecular structure of the dyes (**CYL-5~7**), we may conclude that longer conjugation length could lead to a higher J_{sc} thus giving a better PCE in the case of **CYL-7**. Besides, to further enhance PCE, selection of an appropriate hole-transporting unit (electron donors) would be of high importance. In three sensitizers, we assumed that the electron-donating ability of alkoxyl-substituted triphenylamine (in **CYL-7**) is greater than that of triphenylamine-carbazole-hybrid type donors (in **CYL-5~6**), which was consistent with the UV-Vis absorption data obtained in Table 4.

Table 5. Photovoltaic performance of dye-sensitized solar cells fabricated using **CYL-5**, **CYL-6**, and **CYL-7**.[a], [b]

DSSCs	V_{oc} [V]	J_{sc} [mA/cm^2]	*FF* [%]	*PCE* [%]
CYL-5	0.65	5.90	76.9	2.95
CYL-6	0.72	7.90	71.3	4.06
CYL-7	0.75	12.60	65.6	6.20
Z907	0.69	14.75	69.5	7.07

[a] Irradiation light source: AM 1.5G solar simulator (100 mW/cm^2); Photo-electrode (working electrode): TiO_2 film was composed of 16 μm thick mesoporous anatase-TiO_2 nanoparticles with a diameter of 20 nm and has an active area of 0.160 cm^2; Electrolyte solution: a mixture of 0.6 M 1-butyl-3-methylimidazolium iodide ([bmim][I]), 0.1 M LiI, 0.05 M I_2, 0.1 M guanidinium thiocyanate (GuNCS) and 0.5 M 4-*t*-butylpyridine (TBP) in acetonitrile. [b] Chenodeoxycholic acid (CDCA) was added as co-adsorbent (5 mM for **CYL-5**; 5 mM for **CYL-6**; 10 mM for **CYL-7**). Optimization of the different amount of CDCA addition has been summarized in Table S1 in Supporting Information.



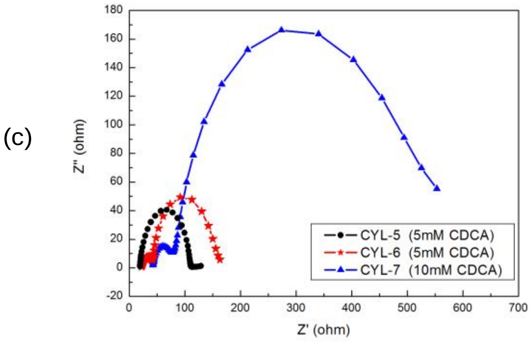


Figure 1. Photovoltaic characteristics of **CYL-5**, **CYL-6**, and **CYL-7**: (a) photocurrent density vs. photovoltage; (b) Incident photon-to-current conversion efficiency (IPCE); (c) electrochemical impedance spectroscopy (EIS).

Conclusions

Unlike the traditional synthetic approaches for organic electronics, we demonstrate herein a step-economical, Pd and Sn-free new synthetic pathway to access various D–π–A type dye molecules employing inexpensive $CuCl_2$ as catalyst. We find that, after reaction condition optimizations, most desired products targeting on dye-sensitized solar cells (DSSCs) applications can be isolated in good to excellent yields (total 32 examples). Based on this Cu-catalyzed C-H arylation methodology, new sensitizers (**CYL-5**~**7**) are facilely obtained and fabricated as DSSCs devices. One of them (**CYL-7**) can reach the power conversion efficiency (PCE) of 6.20%. We expect this relatively greener synthetic protocol would turn into a viable alternative for the efficient preparation of small-molecule π-functional materials.

Experimental Section

Representative procedure for the Cu-catalyzed C-H arylation of 2-thiophenecarboxaldehyde (2a) with 4-iodo-*N*,*N*-bis(4-methoxyphenyl)aniline (1e) — Synthesis and characterization of product 3e: To a solution of $CuCl_2$ (40 mg, 0.30 mmol), phenanthroline (54 mg, 0.30 mmol), Cs_2CO_3 (652 mg, 2.00 mmol) in the co-solvent of *N*,*N'*-dimethylpropylene urea (DMPU) and *m*-xylene (total 2 mL, v/v = 1:1) in a flame-dried Schlenk tube were added 4-iodo-*N*,*N*-bis(4-methoxyphenyl)aniline (**1e**) (862 mg, 2.00 mmol) and 2-thiophenecarboxaldehyde (**2a**) (112 mg, 1.00 mmol) under N_2. The reaction mixture was then heated at 120 °C under N_2 for 24 h. After the reaction mixture had cooled to room temperature, water (10 mL) was added. The mixture was extracted with ethyl acetate (2 × 30 mL), and the combined organic layers were washed with brine (50 mL), dried (Na_2SO_4) and concentrated in *vacuo*. Purification by flash chromatography (ethyl acetate : hexanes = 20 : 80) yielded the pure product **3e** (378 mg, 91 %). Red viscous liquid. ^1H NMR ($CDCl_3$, 300 MHz, ppm): δ 9.82 (s, 1 H), 7.67 (d, J = 4.0 Hz, 1 H), 7.46 (d, J = 8.8 Hz, 2 H), 7.25 (d, J = 4.0 Hz, 1 H), 7.05-7.15 (comp, 4 H), 6.80-6.97 (comp, 6 H), 3.81 (s, 6 H); ^{13}C NMR ($CDCl_3$, 75 MHz, ppm): δ 182.4, 156.5, 155.1, 150.0, 140.8, 139.9, 137.7, 127.2, 127.1, 124.2, 122.3, 119.3, 114.9, 55.5.

Acknowledgements

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Keywords: Copper • Direct C-H Arylations • Dye-Sensitized Solar Cells (DSSCs) • Sn- & Pd-Free Process

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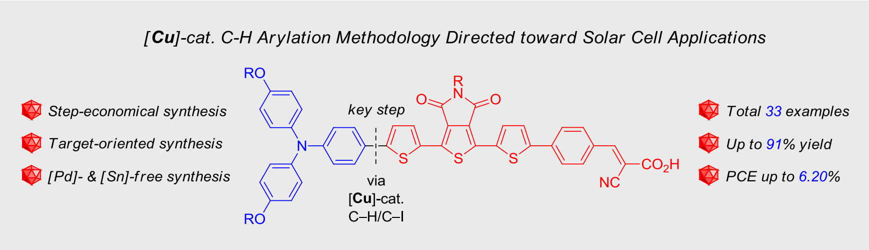

Cu-catalyzed direct C-H arylation is, for the first time, used as key step to synthesize various D-π-A type organic dyes for efficient dye-sensitized solar cells (DSSCs).

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Greener Synthesis of D-π-A Organic Sensitizers via Cu-Catalyzed Direct Arylations: Development of Sn- & Pd-Free Process for Dye-Sensitized Solar Cells