Organic LETTERS

Letter

pubs.acs.org/OrgLett

Step-Economical Syntheses of Functional BODIPY-EDOT π-Conjugated Materials through Direct C−H Arylation

Hui Chong,[†] Hsing-An Lin,[†] Mo-Yuan Shen,[‡] Ching-Yuan Liu,[§] Haichao Zhao,[†] and Hsiao-hua Yu*[,†,‡]

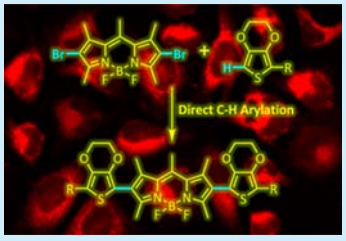
[†]Responsive Organic Materials Laboratory, 2-1 Hirosawa, Wako, Saitama 351-0198, Japan

[‡]Institute of Chemistry, Academia Sinica, 128 Academic Road, Sec. 2, Nankang, Taipei 11529, Taiwan

[§]Department of Chemical and Materials Engineering, National Central University, Jhongli District, Taoyuan 32001, Taiwan

Supporting Information

ABSTRACT: Palladium-catalyzed direct C−H arylations of 4,4-difluoro-4-bora-3a,4a-diaza-*s*-indacene (BODIPY) with 3,4-ethylenedioxythiophene (EDOT) derivatives at relatively low temperature (60 °C) provide moderate to good yields (47%−72%) of products having potential applications in fluorescent bioimaging and organic optoelectronics.

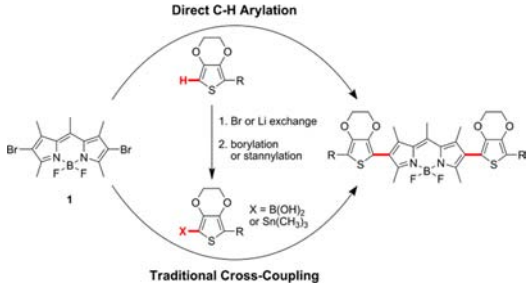


BODIPY (4,4-difluoro-4-bora-3a,4a-diaza-*s*-indacene), a luminescent dye first synthesized in 1968,[1] and its derivatives have attracted great interest over the past several decades because of their appealing chemical and photophysical properties, including high stability toward light and chemical agents, large molar extinction coefficients in the higher-wavelength visible region, high fluorescence quantum yields, narrow emission bandwidths, and relatively long fluorescence lifetimes.[2] Extending the conjugated π-system from the BODIPY core, through the introduction of aromatic substituents, can shift the absorption/emission maxima to even longer wavelengths and, thereby, finely tune the optoelectronic properties.[3] As a result, BODIPY-based π-conjugated molecules are being applied extensively as fluorescent imaging agents, switches, sensors, and organic optoelectronic materials.[4]

Considerable research activity has been focused recently on thiophene-conjugated BODIPY derivatives because of their applications in fluorescent labeling, light harvesting, dye-sensitized solar cells, and organic semiconducting materials.[5] Among the many available thiophene derivatives, 3,4-ethylenedioxythiophene (EDOT) has been the subject of the most detailed studies in recent years because of its high stability, commercial availability, and good biocompatibility. The appending of an EDOT moiety to a π-conjugated material results in a shorter intrinsic band gap,[6] enhanced π-donor ability,[7] and improved electrochromic properties.[8] Therefore, molecules bearing both EDOT and BODIPY units are attractive in materials science for use as both electronic materials and bioimaging probes. Indeed, several examples have been reported, with potential applications including broad-band light sensing and harvesting.[9]

One practical path toward EDOT/BODIPY-based compounds is chemical transformation of the BODIPY core. At present, derivatization of BODIPY can be achieved most efficiently through the use of functionalized pyrroles,[10] halogenated BODIPY derivatives,[11] or the Liebeskind−Srögl reaction,[12] but these approaches require tedious synthetic steps or environmentally unfriendly organometallic reagents. Transition-metal-catalyzed direct C−H arylation would be a step-economical and environment-friendly alternative.[13] Although several examples of direct C−H arylations of BODIPY have been reported,[14] the conditions, which have not been optimized, require long reaction times. Herein, we report a comprehensive synthetic investigation of Pd-catalyzed direct C−H arylation between BODIPY and EDOT derivatives, in which we have screened various ligands, bases, and solvents. The reactions of BODIPY with EDOT derivatives under the optimized conditions provided their products in acceptable yields. Thus, the direct C−H arylations of BODIPY can be more efficient and atom-economical than traditional syntheses of functional BODIPY-based π-conjugated functional materials, potentially facilitating their use as fluorescent bioimaging agents and optoelectronic materials (Scheme 1).

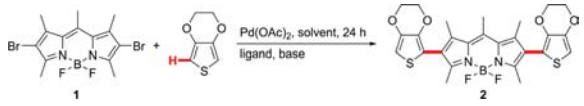
Scheme 1. Syntheses of Functional BODIPY/EDOT π-Conjugated Derivatives



Received: March 24, 2015
Published: June 22, 2015

DOI: 10.1021/acs.orglett.5b00875
Org. Lett. 2015, 17, 3198−3201

Table 1. Reaction Conditions Optimization for the Synthesis of 2[a]



entry	ligand	base	solvent	temp (°C)	yield (%)[b]
1	none	K_2CO_3	dioxane	80	trace
2	PPh_3	K_2CO_3	dioxane	80	28
3	dppf	K_2CO_3	dioxane	80	4
4	P(*m*-Tol)$_3$	K_2CO_3	dioxane	80	18
5	P(furyl)$_3$	K_2CO_3	dioxane	80	trace
6	PCy_3·HBF_4	K_2CO_3	dioxane	80	11
7	P(*t*-Bu)$_3$	K_2CO_3	dioxane	80	trace
8	Phenanthroline	K_2CO_3	dioxane	80	trace
9	P(*o*-Anisyl)$_3$	K_2CO_3	dioxane	80	60
10	P(*o*-Anisyl)$_3$	K_2CO_3	toluene	80	53
11	P(*o*-Anisyl)$_3$	K_2CO_3	*o*-xylene	80	54
12	P(*o*-Anisyl)$_3$	K_2CO_3	*p*-xylene	80	20
13	P(*o*-Anisyl)$_3$	K_2CO_3	*m*-xylene	80	58
14	P(*o*-Anisyl)$_3$	K_2CO_3	*m*-xylene	130	45
15	P(*o*-Anisyl)$_3$	K_2CO_3	DMAc	80	trace
16	P(*o*-Anisyl)$_3$	K_2CO_3	DMF	80	20
17	P(*o*-Anisyl)$_3$	Na_2CO_3	dioxane	80	3
18	P(*o*-Anisyl)$_3$	Cs_2CO_3	dioxane	80	11
19	P(*o*-Anisyl)$_3$	Ag_2CO_3	dioxane	80	9
20	P(*o*-Anisyl)$_3$	KOAc	dioxane	80	10
21	P(*o*-Anisyl)$_3$	K_2CO_3	dioxane	70	55
22	P(*o*-Anisyl)$_3$	K_2CO_3	dioxane	60	60
23	P(*o*-Anisyl)$_3$	K_2CO_3	dioxane	50	20
24	P(*o*-Anisyl)$_3$	K_2CO_3	dioxane	40	15

[a]The reaction between **1** (1 equiv) and EDOT (10 equiv) was performed for 24 h in the presence of $Pd(OAc)_2$ (5 mol %), a ligand (10 mol %), and a base (2.4 equiv) in 1 mL of solvent. [b]Isolated yield.

To develop a general and efficient synthetic approach for Pd-catalyzed direct C−H diarylations of the BODIPY derivative **1**, we tested commercially available EDOT as its initial coupling partner (Table 1). Because of its two C−H bonds, which could result in polymerization upon coupling with **1**, we added an excess of EDOT (10 equiv) to the reaction medium. We selected $Pd(OAc)_2$ as the palladium source because, in previous studies,[15a,b] it provided an excellent coupling yield for the diarylation of EDOT; in addition, it has also been applied in the direct C−H arylation of BODIPY.[14c] The reaction performed in the presence of $Pd(OAc)_2$ (5%) and K_2CO_3 (2.4 equiv) in dioxane at 80 °C for 24 h resulted in no isolated product (Table 1, entry 1). Accordingly, we screened for potentially useful ligands. Tricyclohexylphosphine tetrafluoroborate (PCy_3·HBF_4), tri(*m*-tolyl)phosphine [P(*m*-Tol)$_3$], and tris(*o*-methoxyphenyl)-phosphine [P(*o*-Anisyl)$_3$] have all been reported as ligands for efficient Pd-catalyzed direct C−H arylations of either BODIPY or thiophene.[14c,15f] Considering the similarity of these transformations to ours, we screened these (and some additional) phosphine ligands to determine the most appropriate reaction conditions. We conducted each reaction under the same conditions, but using the different ligands (Table 1, entries 2−9). Several ligands facilitated the formation of the coupling product. The presence of triphenylphosphine (PPh_3) led to the coupling product in a yield of 28% (Table 1, entry 2). The combination of P(*m*-Tol)$_3$ and $Pd(OAc)_2$, reported previously to effectively catalyze direct C−H coupling between EDOT and aryl bromides, did not result in an acceptable yield of our product (18%, Table 1, entry 4). Similarly, the combination of PCy_3·HBF_4 and $Pd(OAc)_2$, reported previously to catalyze direct C−H couplings between BODIPY and aryl bromides and between EDOT and aryl bromides, was not helpful (11%, Table 1, entry 6). In addition, reactions performed in the presence of some other popular phosphine ligands were all inefficient (Table 1, entries 3, 5, 7, and 8). To our delight, however, the yield reached 60% when using P(*o*-Anisyl)$_3$ as the ligand (Table 1, entry 9). We did not observe any unreacted **1** in the reaction mixture, but some high-polarity residues—possibly oligomeric/polymeric BODIPY-EDOTs or products from the decomposition of the BODIPY—were evident when we purified the product.

This preliminary screening encouraged us to search for the optimal solvent. The yield did not improve, however, when using other solvents, either nonpolar (toluene, xylenes) or polar (DMAc, DMF) (Table 1, entries 10−16), but we did obtain an isolated yield of 58% when we performed the reaction in *m*-xylene (Table 1, entry 13). Notably, the reaction yield decreased dramatically when we used *p*-xylene as the solvent, possibly because it has the lowest polarity among the aromatic hydrocarbons that we tested as solvents. When we performed the reaction in *m*-xylene at elevated temperature (Table 1, entry 14, 130 °C), the isolated yield decreased to 45%, possibly because of polymerization or decomposition of the product under such conditions. Accordingly, we concluded that dioxane was the optimal solvent. Next, we examined the effect of the base (Table 1, entries 17−20). Although Na_2CO_3, Cs_2CO_3, Ag_2CO_3, and KOAc have all been used commonly as bases in direct C−H arylations, their application in our transformation led to dramatic decreases in the isolated yield (to 3−10%). Hence, we suspected that K_2CO_3 was the optimal base for this reaction.

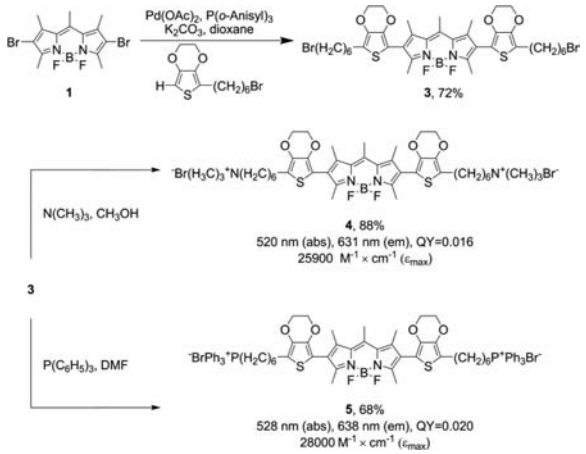
Next, we investigated the effect of the temperature on our reaction. The yield did not improve when we performed the reaction at higher temperatures. Interestingly, when we performed the reaction at lower temperatures (70 and 60 °C, Table 1, entries 21 and 22), we isolated the product in acceptable yields (55% and 60%, respectively). Nevertheless, when we decreased the reaction temperature further, to 50 and 40 °C (Table 1, entries 23 and 24), the yields dropped dramatically, to 20% and 15%, respectively. Accordingly, we concluded that the conditions in entry 22 were optimal, with its lower temperature decreasing the energy consumption relative to that in entry 9.

The UV−vis absorption maximum for compound **2** in $CHCl_3$ appeared at 526 nm, with the signal covering the range from 450 to 600 nm. The fluorescence emission appeared in the range from 550 to 700 nm, with the emission maximum at 592 nm (Figure S1). Compared with the signals of BODIPY (its absorption and emission maxima centered at 505 and 515 nm, respectively),[16] the red-shifted absorption and emission ranges of **2** moved beyond the spectral regions where severe damage to an organism would occur and where most autofluorescence occurs.[17] Thus, the spectroscopic properties of **2** meet the requirements of a good fluorescent bioimaging agent. Thus, we examined whether it would be possible to synthesize water-soluble BODIPY-based fluorescent imaging agents using this facile direct C−H arylation approach in conjunction with water-soluble EDOT derivatives as coupling partners.

As displayed in Scheme 2, we used our established protocol to synthesize two BODIPY-based π-conjugated molecules for

DOI: 10.1021/acs.orglett.5b00875
Org. Lett. 2015, 17, 3198−3201

Scheme 2. Syntheses of the Bio-Imaging Probes 4 and 5



fluorescent cell imaging. We employed the bromohexyl-bearing EDOT derivative as a coupling partner so that we could subsequently introduce a positive charge to the BODIPY-based π-conjugated product in a facile manner, thereby imparting water solubility to the molecule. Furthermore, the presence of the bromohexyl chain on EDOT eliminated the possibility of polymerization, further improving the coupling yield.

We prepared the bromohexyl-bearing EDOT in a yield of 54% through deprotonation of EDOT with *n*-butyllithium (*n*-BuLi) and subsequent reaction with 1,6-dibromohexane. Coupling of **1** and the bromohexyl-bearing EDOT derivative (2.1 equiv) afforded its desired product **3** in 72% yield. We introduced positive charges through reactions of **3** with trimethylamine and triphenylphosphine, obtaining the corresponding water-soluble compounds **4** (88%) and **5** (68%), respectively.

We examined the spectroscopic characteristics of **4** and **5** in aqueous media. Compound **4** exhibited an absorption maximum at 520 nm, corresponding to its $\pi-\pi^*$ transition, and a fluorescence emission maximum at 631 nm. Similarly, **5** exhibited an absorption maximum at 528 nm and a fluorescence emission maximum at 638 nm. Figure S1 displays the normalized UV−vis and fluorescence spectra. The molar excitation coefficient and fluorescence quantum yield for **4** were 2.59×10^4 M^{-1} cm^{-1} and 1.62%, respectively; for **5**, they were 2.80×10^4 M^{-1} cm^{-1} and 2.02%, respectively. We attribute the different photophysical properties for compounds **4** and **5** to their different hydrophobicities. The more hydrophobic environment provided by the triphenylphosphonium groups in **5** would presumably promote aggregation of the BODIPY-EDOT chromophore. As a result, we observed absorption of light at longer wavelengths and stronger aggregation-induced emission for **5**.[18]

Next, we examined the utility of **4** and **5** in fluorescent cell imaging. First, we added an aqueous solution of **4** or **5** to human cervical cancer (HeLa) cells and then incubated the mixture for 30 min in the dark prior to recording images. While the incorporation of **4** clearly led to the penetration of the imaging probe across the membrane and lighting up of the cytoplasm (Figure S2), we observed more interesting phenomena with **5**. The triphenylphosphonium group, which was part of compound **5**, is well documented to facilitate the entrance of molecular probes into mitochondria, as a result of its lipophilicity and electrostatic forces.[18]

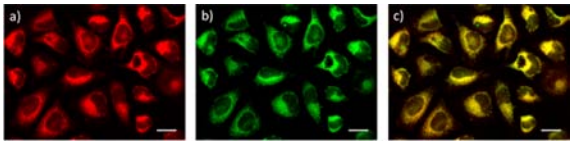


Figure 1. (a, b) Fluorescence images of HeLa cells stained with (a) the bioimaging probe **5** and (b) MitoTracker Green FM (MT). (c) Merged view of the images in (a) and (b). Scale bars: 20 μm.

Hence, we tested the fluorescence imaging capability of the triphenylphosphonium-bearing compound **5** in living cells. To confirm whether **5** could achieve mitochondrial imaging specifically, we added solutions of **5** and MitoTracker Green FM (MT), a commercially available mitochondrial imaging agent, to HeLa cells, followed by incubation of the mixture in the dark for 30 min prior to recording images. Figure 1a and b display the fluorescence images obtained using **5** and MT, respectively. The bright green spots in Figure 1b indicate the distribution of the mitochondria in the HeLa cells. The bright yellow fluorescence in Figure 1c, a merging of the images in Figure 1a and b, suggests that compound **5** was localized in the mitochondria of the living HeLa cells. Furthermore, using ImageJ software, we calculated a quantitative overlap ratio of 98.6% from the fluorescence signals of the two dyes collected from two independent channels. Thus, we conclude that **5** can be used specifically for mitochondrial imaging. The mitochondria is an organelle existing in almost all eukaryotic cells; it plays a vital role in the life and death of cells.[19] Moreover, the morphology of the mitochondria is controlled by a series of proteins, mutations of which are involved in severe diseases, including Parkinson's and Alzheimer's diseases.[20] Therefore, new means of mitochondrial imaging in living cells are always welcome.

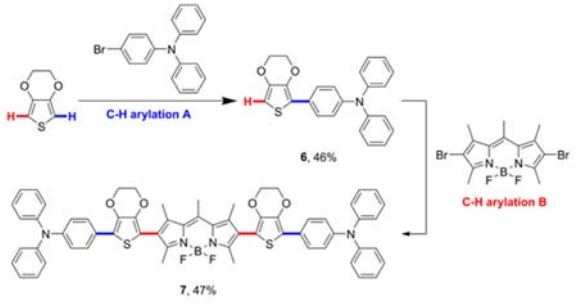
In addition to the syntheses of fluorescent bioimaging agents, we also applied this approach to the efficient synthesis of functional π-conjugated BODIPY derivatives having potential applications in organic optoelectronic devices. Triphenylamine (TPA)-containing molecules have been employed extensively as electron-donating entities in the hole injection/transport layers of organic optoelectronic devices.[21] The Lin group[22] used traditional Stille coupling to synthesize donor/acceptor/donor-type functional π-conjugated molecules comprising TPA, thiophene, and BODIPY moieties, obtaining a device exhibiting a power conversion efficiency (PCE) of 3.22%. Using our new synthetic protocol, we suspected that replacing the thiophene unit with an EDOT moiety would further increase the electron-donating capability of TPA, thereby enhancing the PCE of the corresponding device. Thus, we investigated whether we could apply our established conditions to introduce a TPA moiety into the BODIPY-EDOT structure.

As displayed in Scheme 3, we obtained the desired product **7** through a two-step successive direct C−H arylation strategy. First, we applied our C−H arylation conditions to synthesize the mono TPA-EDOT adduct **6**, which we have reported previously.[15a] We attributed the moderate yield (46%) to the tendency to form doubly TPA-bearing EDOT as a byproduct, even in the presence of excess EDOT (10 equiv). Subsequently, we used the established conditions to conduct a second direct C−H arylation to afford **7** in a yield of 46.5%. This straightforward strategy proceeded without the need for repeated halogenation or the introduction of activation groups.

Figure S3 presents the electrochemical and spectroscopic properties of **7**. The half-wave potentials were 0.75, 0.98, and 1.24 V (vs Ag/Ag^+). Because of the elongated π-conjugation, the UV−vis absorption maximum appeared at 552 nm, with a molar extinction coefficient of 2.54×10^4 M^{-1} cm^{-1} in $CHCl_3$.

DOI: 10.1021/acs.orglett.5b00875
Org. Lett. 2015, 17, 3198−3201

Scheme 3. Synthesis of the Extended EDOT-BODIPY Derivative 7 through Sequential C−H Arylations



	[Pd]	ligand	base	solvent	temp
C-H arylation A	$Pd(OAc)_2$	P(*m*-Tol)$_3$	Cs_2CO_3	toluene	110 °C
C-H arylation B	$Pd(OAc)_2$	P(*o*-Anisyl)$_3$	K_2CO_3	dioxane	60 °C

In summary, we demonstrated an atom-economical Pd-catalyzed direct C−H arylation approach for the efficient syntheses of BODIPY-based π-conjugated functional molecules. This method avoids traditional Suzuki or Stille couplings, which require additional activation steps and the use of toxic or environmentally harmful reagents, yet achieves products of similar structure in acceptable yields from reactions performed at relatively low temperature. The coupling products have potential applications in fluorescence bioimaging and organic electronics. Our ongoing research is focused on expanding the substrate scope of the established procedure and further improving its yields.

■ ASSOCIATED CONTENT

Supporting Information

Synthetic details; fluorescence imaging details; compound characterization (^{1}H and ^{13}C NMR spectra; UV−vis spectra; electrochemical data). The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.orglett.5b00875.

■ AUTHOR INFORMATION

Corresponding Author

*E-mail: bruceyu@gate.sinica.edu.tw.

Notes

The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

This work was supported by RIKEN and Grant-in-Aid for Young Scientist (No. 22681016) from JSPS/MEXT, Japan. This study was also supported by Academia Sinica, Taiwan, Academia Sinica Research Project on Nano Science and Technology, and Academia Sinica Thematic Research Program. We thank the Research Resources Center, RIKEN Brain Science Institute, for recording the high-resolution mass spectra; Dr. Kyoji Hagiwara, Professor Yoshihiro Ito (RIKEN Center for Emergent Matter Science) and Dr. Chiung-Wen Kuo (Academia Sinica, Taiwan) for their kind help and discussions regarding the fluorescence images; and Professor Hiroyuki Koshino (RIKEN Molecular Characterization Team) for kindly helping with recording of ^{13}C NMR spectra.

■ REFERENCES

(1) Treibs, A.; Kreuzer, F. H. *Liebigs. Ann. Chem.* **1968**, *718*, 208.
(2) (a) Loudet, A.; Burgess, K. *Chem. Rev.* **2007**, *107*, 4891. (b) Ziessel, R.; Ulrich, G.; Harriman, A. *New J. Chem.* **2007**, *31*, 496.
(3) Umezawa, K.; Matsui, A.; Nakamura, Y.; Citterio, D.; Suzuki, K. *Chem.—Eur. J.* **2009**, *15*, 1096.
(4) (a) Ulrich, G.; Ziessel, R.; Harriman, A. *Angew. Chem., Int. Ed.* **2008**, *47*, 1184. (b) Nepomnyashchii, A. B.; Bard, A. J. *Acc. Chem. Res.* **2012**, *45*, 1844. (c) Boens, N.; Leen, V.; Dehaen, W. *Chem. Soc. Rev.* **2012**, *41*, 1130. (d) Yang, S.; Shi, X.; Park, S.; Ha, T.; Zimmerman, S. C. *Nat. Chem.* **2013**, *5*, 692.
(5) (a) Mao, M.; Wang, J.-B.; Xiao, Z.-F.; Dai, S.-Y.; Song, Q.-H. *Dyes Pigments* **2012**, *94*, 224. (b) Usta, H.; Yilmaz, M. D.; Avestro, A.-J.; Boudinet, D.; Denti, M.; Zhao, W.; Stoddart, J. F.; Facchetti, A. *Adv. Mater.* **2013**, *25*, 4327. (c) Bonnier, C.; Machin, D. D.; Abdi, O.; Koivisto, B. D. *Org. Biomol. Chem.* **2013**, *11*, 3756.
(6) (a) Akoudad, S.; Roncali, J. *Chem. Commun.* **1998**, 2081. (b) Apperloo, J. J.; Groenendaal, L.; Verheyen, H.; Jayakannan, M.; Janssen, R. A. J.; Dkhissi, A.; Beljonne, D.; Lazzaroni, R.; Bredas, J. L. *Chem.—Eur. J.* **2002**, *8*, 2384.
(7) Akoudad, S.; Frere, P.; Mercier, N.; Roncali, J. *J. Org. Chem.* **1999**, *64*, 4267.
(8) Nielsen, C. B.; Angerhofer, A.; Abboud, K. A.; Reynolds, J. R. *J. Am. Chem. Soc.* **2008**, *130*, 9734.
(9) (a) Algi, M.; Tirkes, S.; Ertan, S.; Ergun, E.; Cihaner, A.; Algi, F. *Electrochim. Acta* **2013**, *109*, 766. (b) Yilmaza, M. D.; Aytunb, T.; Frasconia, M.; Stupp, S. I.; Stoddart, J. F. *Synth. Met.* **2014**, *197*, 52. (c) Cortizo-Lacalle, D.; Howells, C. T.; Gambino, S.; Vilela, F.; Vobecka, Z.; Findlay, N. J.; Inigo, A. R.; Thomson, S. A. J.; Skabara, P. J.; Samuel, D. W. *J. Mater. Chem.* **2012**, *22*, 14119.
(10) Coskun, A.; Yilmaz, M. D.; Akkaya, E. U. *Org. Lett.* **2007**, *9*, 607.
(11) (a) Baruah, M.; Qin, W. W.; Basaric, N.; De Borggraeve, W. M.; Boens, N. *J. Org. Chem.* **2005**, *70*, 4152. (b) Rohand, T.; Qin, W.; Boens, N.; Dehaen, W. *Eur. J. Org. Chem.* **2006**, 4658.
(12) Peña-Cabrera, E.; Aguilar-Aguilar, A.; González-Domínguez, M.; Lager, E.; Zamudio-Vázquez, R.; Godoy-Vargas, J.; Villanueva-García, F. *Org. Lett.* **2007**, *9*, 3985.
(13) (a) Alberico, D.; Scott, M. E.; Lautens, M. *Chem. Rev.* **2007**, *107*, 174. (b) Chen, X.; Engle, K. M.; Wang, D.-H.; Yu, J.-Q. *Angew. Chem., Int. Ed.* **2009**, *48*, 5094. (c) Tamba, S.; Okubo, Y.; Tanaka, S.; Monguchi, D.; Mori, A. *J. Org. Chem.* **2010**, *75*, 6998. (d) Lapointe, D.; Markiewicz, T.; Whipp, C. J.; Toderian, A.; Fagnou, K. *J. Org. Chem.* **2011**, *76*, 749. (e) Schipper, D. J.; Fagnou, K. *Chem. Mater.* **2011**, *23*, 1594. (f) Ackermann, L.; Vicente, R.; Kapdi, A. R. *Angew. Chem., Int. Ed.* **2009**, *48*, 9792.
(14) (a) Thivierge, C.; Bandichhor, R.; Burgess, K. *Org. Lett.* **2007**, *9*, 2135. (b) Chen, J.; Mizumura, M.; Shinokubo, H.; Osuka, A. *Chem.—Eur. J.* **2009**, *15*, 5942. (c) Verbelen, B.; Leen, V.; Wang, L.; Boens, N.; Dehaen, W. *Chem. Commun.* **2012**, *48*, 9129.
(15) (a) Liu, C.-Y.; Zhao, H.; Yu, H.-h. *Org. Lett.* **2011**, *13*, 4068. (b) Zhao, H.; Liu, C.-Y.; Luo, S.-Y.; Zhu, B.; Wang, T.-Y.; Hsu, H.-F.; Yu, H.-h. *Macromolecules* **2012**, *45*, 7783. (c) Wang, Q. F.; Takita, R.; Kikuzaki, Y.; Ozawa, F. *J. Am. Chem. Soc.* **2010**, *132*, 11420. (d) Wakioka, M.; Ichihara, N.; Kitano, Y.; Ozawa, F. *Macromolecules* **2014**, *47*, 626. (e) Berrouard, P.; Najari, A.; Pron, A.; Gendron, D.; Morin, P.; Pouliot, J.; Veilleux, J.; Leclerc, M. *Angew. Chem., Int. Ed.* **2012**, *51*, 2068. (f) Fujinami, Y.; Kuwabra, J.; Lu, W.; Hayashi, H.; Kanbara, T. *ACS Macro. Lett.* **2012**, *1*, 67.
(16) Schmitt, A.; Hinkeldey, B.; Wild, M.; Jung, G. *J. Fluoresc.* **2009**, *19*, 755−758.
(17) Chong, H.; Nie, C.; Zhu, C.; Yang, Q.; Liu, L.; Lv, F.; Wang, S. *Langmuir* **2012**, *28*, 2091.
(18) Leung, C. W. T.; Hong, Y.; Chen, S.; Zhao, E.; Lam, J. W. Y.; Tang, B. Z. *J. Am. Chem. Soc.* **2013**, *135*, 62.
(19) Lin, V. S.; Chang, C. J. *Curr. Opin. Chem. Biol.* **2012**, *16*, 595.
(20) Masanta, G.; Heo, C. H.; Lim, C. S.; Bae, S. K.; Cho, B. R.; Kim, H. M. *Chem. Commun.* **2012**, *48*, 3518.
(21) Lim, Y.; Park, Y.-S.; Kang, Y.; Jang, D. Y.; Kim, J. H.; Kim, J.-J.; Sellinger, A.; Yoon, D. Y. *J. Am. Chem. Soc.* **2011**, *133*, 1375.
(22) Lin, H.-Y.; Huang, W.-C.; Chen, Y.-C.; Chou, H.-H.; Hsu, C.-Y.; Lin, J. T.; Lin, H.-W. *Chem. Commun.* **2012**, *48*, 8913.

DOI: 10.1021/acs.orglett.5b00875
Org. Lett. 2015, 17, 3198−3201