

# Coronenediimides Synthesized via ICI-Induced Cyclization of Diethynyl Perylenediimides

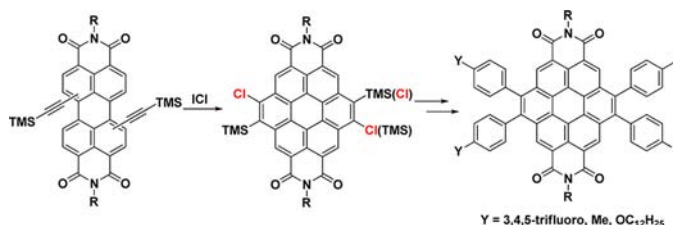
Qifan Yan, Kang Cai, Chenhao Zhang, and Dahui Zhao\*

Beijing National Laboratory of Molecular Sciences, Department of Applied Chemistry and the Key Laboratory of Polymer Chemistry and Physics of the Ministry of Education, College of Chemistry, Peking University, Beijing 100871, China

dhzhao@pku.edu.cn

Received July 29, 2012

## ABSTRACT



Treating diethynyl-substituted perylenediimides with ICI successfully induced an annulation reaction and generated a series of coronenediimide derivatives. Instead of the expected iodine-substituted cyclization product, chlorine-substituted analogues were produced. The mechanism of this annulation reaction thus necessarily involved a chlorine addition step prior to the aromatic substitution reaction. With facile subsequent transformations, various tetraaryl coronenediimides could be obtained via the annulated chloro-substituted coronenediimide.

Large, electron-deficient polycyclic aromatic molecules are attractive synthetic targets because of their unique applications as electron-transport organic semiconductive materials.<sup>1</sup> Perylenediimide (PDI) and its derivatives are among the most intensively studied candidates for their appealing optical properties, electron-accepting and -transporting ability, self-assembly propensity, as well as the ready availability of the synthetic raw material, perylene tetracarboxylic dianhydride.<sup>2–5</sup> Moreover, PDI

derivatives are also versatile synthetic precursors to larger aromatic hydrocarbons, even graphene ribbons. Various annulative transformations, such as the intramolecular Heck reaction,<sup>6</sup> Diels–Alder addition,<sup>7</sup> Ullman reaction,<sup>8</sup> and oxidative dehydrogenation, have been applied for such purposes.<sup>9</sup> Coronene, a closely related structure to perylene, with two additional annulated ethynylene units, has also been widely investigated and exploited for its semiconductive and supramolecular capabilities.<sup>10</sup> Despite the structural correlation, methodologies for transforming perylene derivatives to coronene analogues via annulation processes are limited.<sup>6,7</sup> Synthetic protocols for attaining

- (1) (a) Dong, H.; Wang, C.; Hu, W. *Chem. Commun.* **2010**, 46, 5211. (b) Huang, C.; Barlow, S.; Marder, S. R. *J. Org. Chem.* **2011**, 76, 2386. (2) (a) Würthner, F. *Chem. Commun.* **2004**, 1564. (b) Langhals, H. *Helv. Chim. Acta* **2005**, 88, 1309. (c) Wasielewski, M. R. *J. Org. Chem.* **2006**, 71, 5051. (d) Zhan, C.; Li, A. D. Q. *Curr. Org. Chem.* **2011**, 15, 1314. (3) For recent example, see: (a) Golubkov, G.; Weissman, H.; Shirman, E.; Wolf, S. G.; Pinkas, I.; Rybtchinski, B. *Angew. Chem., Int. Ed.* **2009**, 48, 926. (b) Ke, D.; Zhan, C.; Xu, S.; Ding, X.; Peng, A.; Sun, J.; He, S.; Li, A. D. Q.; Yao, J. *J. Am. Chem. Soc.* **2011**, 133, 11022. (c) Wu, H.; Xue, L.; Shi, Y.; Chen, Y.; Li, X. *Langmuir* **2011**, 27, 3074. (4) (a) Kamm, V.; Battagliarin, G.; Howard, I. A.; Pisula, W.; Mavrinskiy, A.; Li, C.; Müllen, K.; Laquai, F. *Adv. Energy Mater* **2011**, 1, 297. (b) Battagliarin, G.; Zhao, Y.; Li, C.; Müllen, K. *Org. Lett.* **2011**, 13, 3399. (5) For example, see: (a) Molinari, A. S.; Alves, H.; Chen, Z.; Facchetti, A.; Morpurgo, A. F. *J. Am. Chem. Soc.* **2009**, 131, 2462. (b) Würthner, F.; Hanke, B.; Lysetska, M.; Lambright, G.; Harms, G. S. *Org. Lett.* **2005**, 7, 967.

- (6) Müller, S.; Müllen, K. *Chem. Commun.* **2005**, 4045. (7) Alibert-Fouet, S.; Seguy, I.; Bobo, J.-F.; Destruel, P.; Bock, H. *Chem.—Eur. J.* **2007**, 13, 1746. (8) (a) Qian, H.; Wang, Z.; Yue, W.; Zhu, D. *J. Am. Chem. Soc.* **2007**, 129, 12664. (b) Qian, H.; Qian, Z.; Negri, F.; Wang, C.; Wang, Z. *J. Am. Chem. Soc.* **2008**, 130, 17970. (c) Shi, Y.; Qian, H.; Li, Y.; Yue, W.; Wang, Z. *Org. Lett.* **2008**, 10, 2337. (d) Zhen, Y.; Wang, C.; Wang, Z. *Chem. Commun.* **2010**, 46, 1926. (9) (a) Li, Y.; Zheng, H.; Li, Y.; Wang, S.; Wu, Z.; Liu, P.; Gao, Z.; Liu, H.; Zhu, D. *J. Org. Chem.* **2007**, 72, 2878. (b) Li, Y.; Li, Y.; Li, J.; Li, C.; Liu, X.; Yuan, M.; Liu, H.; Wang, S. *Chem.—Eur. J.* **2006**, 12, 8378. (c) Li, Y.; Xu, L.; Liu, T.; Yu, Y.; Liu, H.; Li, Y.; Zhu, D. *Org. Lett.* **2011**, 13, 5692. (d) Yuan, Z.; Xiao, Y.; Qian, X. *Chem. Commun.* **2010**, 46, 2772.

coronenediimide (CDI) from PDI are particularly meager. One example was shown by Müllen and co-workers, who carried out a DBU-induced cyclization reaction with a dialkynyl PDI and obtained a dialkyl CDI.<sup>10a</sup> Here, we present our recent investigation into an ICl-mediated cyclization of diethynyl PDI derivatives. The reaction led to a series of dichlorinated CDIs that could then be conveniently transformed into various tetraaryl CDIs. The developed methodology can be of great value for electron-transport organic material syntheses, and the mechanism of the reaction is rather intriguing.

ICl is a widely employed latent  $[I^+]$  reagent that has been observed to induce iodocyclization of ethynyl groups with a number of different substrates. For instance, Larock et al. applied this iodocyclization strategy to prepare a number of polycyclic aromatic molecules such as benzofurans, benzothiophenes, indoles, quinolines, isoquinolines, isocoumarins,  $\alpha$ -pyrones, naphthalenes, etc.<sup>11</sup> Using a different form of  $[I^+]$ , Swager and co-workers accomplished iodocyclization with a series of phenylethynyl-substituted polyphenylenes and obtained unique ladder-type conjugated polymers.<sup>12</sup> Similar methodologies were also used for synthesizing dibenzo[*g,p*]chrysenes and dibenzo[*a,j*]anthracene.<sup>13,14</sup> In these previous examples, only electron-rich aromatic systems were reported to be suitable substrates for this cyclization transformation. To the best of our knowledge, no previous example has shown this methodology being successfully applied to electron-deficient aromatic molecules. The challenge is understandable, since the cyclization mechanism entails an electrophilic

aromatic substitution (EAS) step, following an electrophilic addition of  $[I^+]$  to the carbon–carbon triple bond and generation of an iodonium intermediate, which serves as the electrophile in subsequent EAS.

Interested in new aromatic molecules with electron-transport capacity, we examined the reaction between ICl and a series of ethynyl-substituted PDIs. The results showed that the cyclization was achievable with such electron-deficient substrates. However, dichloro-substituted cyclization products instead of diiodo-substituted analogues were obtained. The mechanism of this unexpected substitution is thus proposed to involve the addition of the chloride anion to the iodonium intermediate. Evidence suggested that the following elimination of a halogen atom and annulative aromatic substitution likely proceeded via a radical-mediated mechanism. As a demonstration of the potential use of the obtained dichloro-CDI in functional material syntheses, the molecule was subsequently converted into a series of tetraphenyl CDIs having various side chains via facile transformations.

The syntheses of the CDI derivatives are depicted in Scheme 1. Sonogashira coupling of isomeric mixture of 1,6- and 1,7-dibromo-PDI<sup>15</sup> with trimethylsilylacetylene afforded corresponding isomer mixture of PDI derivative **1**. Similar to previously reported analogues, the 1,7-isomers of dibromo-PDI and **1** were the major components of the mixtures.<sup>16</sup> As the regioisomer separation procedure was rather tedious and inefficient, we applied the mixture of **1** to subsequent reactions without separation and planned to eliminate the isomerism by further functionalizing the products. Based on previous studies, exposing a proper substrate containing 2-ethynylbiphenyl moiety to ICl would first initiate an electrophilic addition of  $[I^+]$  to the triple bond, and the generated iodonium intermediate would then undergo an EAS on the adjacent phenyl ring, offering an iodine-substituted phenanthrene derivative. With our current substrate of **1**, we were hoping that in addition to iodocyclization, in the presence of an excess amount of ICl, further substitution of TMS by  $[I^+]$  could proceed with the cyclization product in one pot. Namely, if the above-described iodocyclization were to take place, diiodo-substituted CDI **2** or even the highly symmetric tetraiodo-substituted CDI **3** was anticipated.

However, treating **1** with an excess amount of ICl did not trigger the expected cascade reactions and furnish **3**. Instead, a pair of isomers of lower molecular symmetry emerged, and the two TMS groups were still present in the products according to the <sup>1</sup>H NMR spectrum. At first, we assumed the only problem might be that the substitution of TMS by iodine did not take place. Hence, a further reaction of the isolated products was carried out with newly added ICl at room temperature. Although the TMS groups were successfully removed upon further reaction with ICl as expected, the resulting product still exhibited isomerism and a set of <sup>1</sup>H NMR resonances indicating a lower molecular symmetry

(10) (a) Rohr, U.; Schlichting, P.; Böhm, A.; Gross, M.; Meerolz, K.; Bräuchle, C.; Müllen, K. *Angew. Chem., Int. Ed.* **1998**, *37*, 1434. (b) Rohr, U.; Kohl, C.; Müllen, K.; van de Craats, A.; Warman, J. J. *Mater. Chem.* **2001**, *11*, 1789. (c) An, Z.; Yu, J.; Domercq, B.; Jones, S. C.; Barlow, S.; Kippelen, B.; Marder, S. R. *J. Mater. Chem.* **2009**, *19*, 6688. (d) Adachi, M.; Nagao, Y. *Chem. Mater.* **2001**, *13*, 662. (e) Samori, P.; Severin, N.; Simpson, C. D.; Müllen, K.; Rabe, J. P. *J. Am. Chem. Soc.* **2002**, *124*, 9454. (f) Franceschin, M.; Alvino, A.; Ortaggi, G.; Bianco, A. *Tetrahedron Lett.* **2004**, *45*, 9015. (g) Nolde, F.; Pisula, W.; Müller, S.; Kohl, C.; Müllen, K. *Chem. Mater.* **2006**, *18*, 3715. (h) Avlasevich, Y.; Müller, S.; Erk, P.; Müllen, K. *Chem.—Eur. J.* **2007**, *13*, 6555. (i) Franceschin, M.; Alvino, A.; Casagrande, V.; Mauriello, C.; Pascucci, E.; Savino, M.; Ortaggi, G.; Bianco, A. *Bioorg. Med. Chem.* **2007**, *15*, 1848. (j) Bai, Q.; Gao, B.; Ai, Q.; Wu, Y.; Ba, X. *Org. Lett.* **2011**, *13*, 6484. (k) Eversloh, C. L.; Li, C.; Müllen, K. *Org. Lett.* **2011**, *13*, 4148. (l) Avlasevich, Y.; Li, C.; Müllen, K. *J. Mater. Chem.* **2010**, *20*, 3814.

(11) (a) Larock, R. C.; Yue, D. *Tetrahedron Lett.* **2001**, *42*, 6011. (b) Yue, D.; Larock, R. C. *J. Org. Chem.* **2002**, *67*, 1905. (c) Flynn, B. L.; Verdier-Pinard, P.; Hamel, E. *Org. Lett.* **2001**, *3*, 651. (d) Zhang, X.; Campo, M. A.; Yao, T.; Larock, R. C. *Org. Lett.* **2005**, *7*, 763. (e) Huang, Q.; Hunter, J. A.; Larock, R. C. *J. Org. Chem.* **2002**, *67*, 3437. (f) Yao, T.; Larock, R. C. *Tetrahedron Lett.* **2002**, *43*, 7401. (g) Yao, T.; Larock, R. C. *J. Org. Chem.* **2003**, *68*, 5936. (h) Yao, T.; Campo, M. A.; Larock, R. C. *Org. Lett.* **2004**, *6*, 2677. (i) Yao, T.; Yue, D.; Larock, R. C. *J. Org. Chem.* **2005**, *70*, 9985.

(12) (a) Goldfinger, M. B.; Swager, T. M. *J. Am. Chem. Soc.* **1994**, *116*, 7895. (b) Goldfinger, M. B.; Crawford, K. B.; Swager, T. M. *J. Am. Chem. Soc.* **1997**, *119*, 4578.

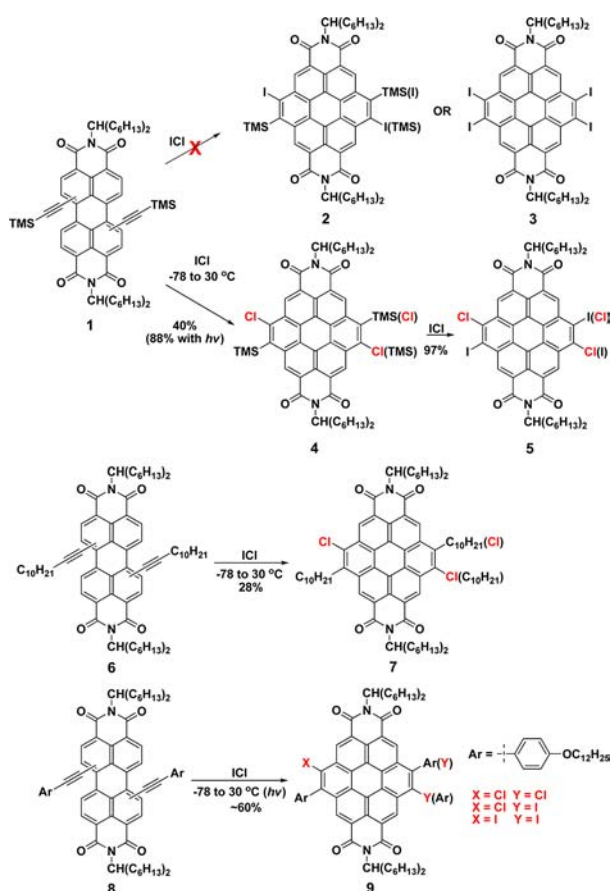
(13) (a) Li, C.-W.; Wang, C.-I.; Liao, H.-Y.; Chaudhuri, R.; Liu, R.-S. *J. Org. Chem.* **2007**, *72*, 9203. (b) Chaudhuri, R.; Hsu, M.-Y.; Li, C.-W.; Wang, C.-I.; Chen, C.-J.; Lai, C.-K.; Chen, L.-Y.; Liu, S.-H.; Wu, C.-C.; Liu, R.-S. *Org. Lett.* **2008**, *10*, 3053. (c) Mukherjee, A.; Pati, K.; Liu, R.-S. *J. Org. Chem.* **2009**, *74*, 6311. (d) Chen, T.-A.; Liu, R.-S. *Org. Lett.* **2011**, *13*, 4644. (e) Chen, T.-A.; Liu, R.-S. *Chem.—Eur. J.* **2011**, *17*, 8023. (f) Lee, S.-L.; Huang, M.-J.; Chen, C.-h.; Wang, C.-I.; Liu, R.-S. *Chem. Asian J.* **2011**, *6*, 1181.

(14) (a) Chen, H.-B.; Yin, J.; Wang, Y.; Pei, J. *Org. Lett.* **2008**, *10*, 3113. (b) Long, Y.; Chen, H.; Yang, Y.; Wang, H.; Yang, Y.; Li, N.; Li, K.; Pei, J.; Liu, F. *Macromolecules* **2009**, *42*, 6501.

(15) Yan, Q.; Zhao, D. *Org. Lett.* **2009**, *11*, 3426.

(16) Würthner, F.; Stepanenko, V.; Chen, Z.; Saha-Möller, C. R.; Kocher, N.; Stalke, D. *J. Org. Chem.* **2004**, *69*, 7933.

**Scheme 1.** Syntheses of CDIs via ICl-Induced Cyclization of Ethynyl-Substituted PDIs



than that of expected **3**. Even more surprisingly, subsequent mass spectroscopy characterization revealed that the product from two consecutive reactions with ICl was dichloro-diiodo-substituted CDI **5**. Naturally, we went back and further examined the product from the first reaction of ICl with **1**. The structure was proven to be dichloro-substituted CDI **4** rather than **2** by mass spectroscopy. These results unambiguously indicated that the two chlorine atoms were introduced to CDI derivatives during the reaction between ethynyl-PDIs and ICl. Importantly, exposing the mixture of **1** and ICl to sunlight irradiation could substantially improve the yield of **4** from ca. 40% to 88%.

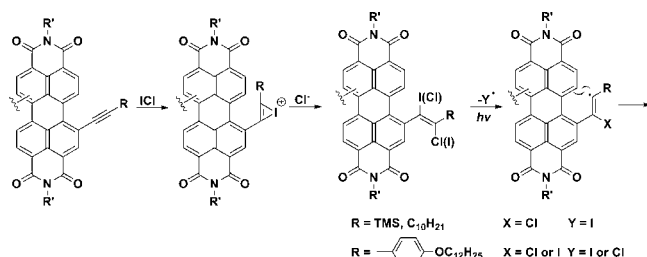
To find out whether such a peculiar chlorocyclization was unique to **1** or if it also occurred with other ethynyl-substituted PDIs, we carried out a reaction by subjecting dialkylethynyl-PDI **6** to ICl. NMR and mass spectroscopies confirmed that the major products from this reaction were dichloro-CDI isomers **7** (Scheme 1). Notably, bearing 4-alkoxyphenylethynyl groups, PDI **8** afforded both iodo- and chloro-cyclization products under similar conditions. On the basis of  $^1\text{H}$  NMR and mass spectroscopy, the product mixture **9** was rather complex, comprising a number of CDI analogues with three different molecular formulas,

(17) Based on the NMR spectrum and elemental analysis of the mixture, chlorination and iodination took place at a ratio of approximately 1:3.

corresponding to dichloro-, diiodo-, and monochloromonoiodo-CDIs (see the Supporting Information).<sup>17</sup>

A possible mechanism for the above reaction was suggested (Scheme 2). The reaction between ICl and the carbon-carbon triple bond should have proceeded properly, producing the iodonium intermediate, just like in conventional iodocyclization reactions with electron-rich substrates.<sup>11</sup> However, because of the electron-deficiency of PDI moiety, this iodonium was not competent for bringing about the intramolecular EAS reaction. Subsequently, the addition by chloride anion occurred. Since the reaction yield was noticeably improved by sunlight irradiation, it is highly possible that the subsequent elimination of a halogen atom and the aromatic substitution steps involved radical intermediates. The reason why iodo-cyclization was only observed with substrate **8** was likely that the alkoxyphenyl group facilitated the elimination of chlorine atom, which is more inert than iodine and does not leave in other cases. Nonetheless, although less plausible, the possibility of EAS taking place with the halonium intermediates<sup>18</sup> could not be excluded completely.

**Scheme 2.** Proposed Mechanism of ICl-Induced Cyclization of Ethynyl-PDI



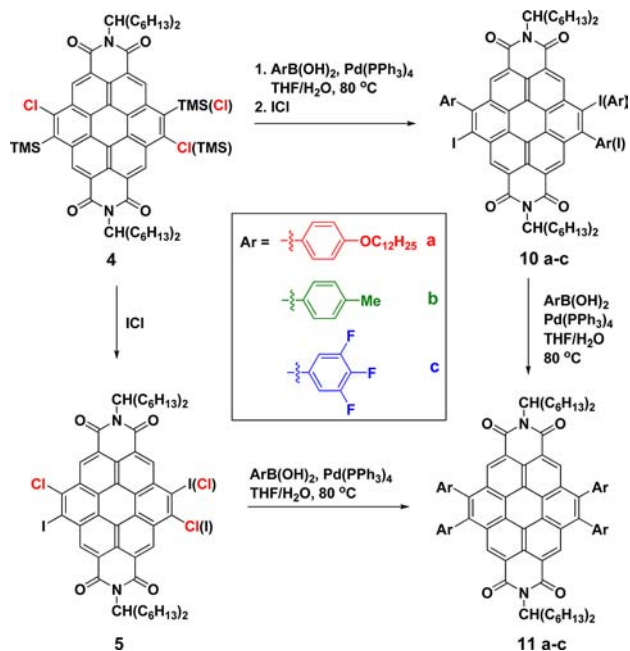
We later found that compound **5** could indeed be directly obtained from **1** via a one-pot reaction, provided a large excess of ICl was supplied. Additional reaction time was also necessary after the reaction mixture was warmed to room temperature. Such a one-pot procedure afforded a slightly lower yield of **5** compared to the two-step process with isolation of intermediate **4**.

With compounds **4** and **5** available, we subsequently demonstrated that other CDI derivatives can be prepared from these precursors. Since aryl chlorides are competent substrates for Suzuki coupling reaction, three phenylboronic acids bearing substituents of different electronic characteristics, i.e., *p*-dodecyloxy, *p*-methyl, and 3,4,5-trifluoro groups, were then examined for coupling with **4**. All three reactions proceeded smoothly, affording corresponding diaryl-bisTMS-CDIs in high yields (Scheme 3). By reacting with ICl, the TMS groups in these diaryl CDIs were converted into iodide. Via another round of Suzuki coupling with corresponding phenylboronic acids, three different tetraphenyl CDIs (**11a–c**) were acquired.

(18) A chloronium might be formed if iodide acted as a leaving group in the chloroiodovinyl substituted PDI derivative, possibly leading to chloro-substituted CDIs via EAS.

To eliminate the regioisomerism, we used the same boronic acids in the two Suzuki couplings and prepared the highly symmetrical tetraaryl CDIs. Apparently, if a pure regioisomer of **1** was used in prior reactions with ICl, with proper installment of different boronic acids in separate steps, two isomeric CDI molecules with controlled spatial arrangement of two different aryl substituents can be attained, exhibiting mirror plane or  $C_2$  symmetry, respectively. Obviously, a more efficient approach to obtaining CDIs bearing identical aryl groups is through intermediate **5**. Directly treating **5** with 4 equiv of phenylboronic acids also generated tetraaryl CDIs in optimal yields.

### Scheme 3. Syntheses of Tetraphenyl CDIs

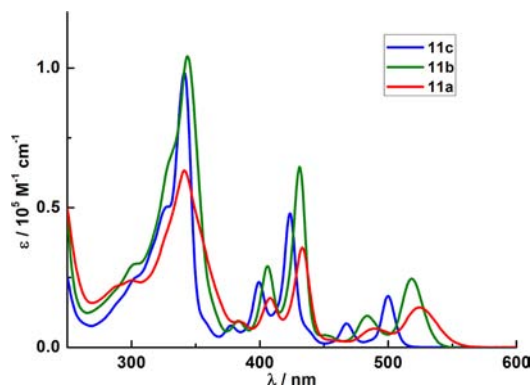


The structures of all prepared tetraaryl CDIs were characterized by NMR, mass spectroscopy, and elemental analyses. As such CDI derivatives could potentially exhibit useful electronic and/or photonic functions, we then characterized their electronic properties, particularly with a focus on the effect of the aryl substituents on the central polycyclic structure. All of the CDI molecules manifested three absorption bands between 300 and 550 nm in their UV–vis spectra (Figure 1). Their absorption features were very similar to those of previously reported dialkyl CDI analogues,<sup>10b</sup> suggesting that all corresponding electronic transitions mainly originated from the central CDI framework. Nonetheless, substituents on the phenyl rings clearly exerted pronounced influences over the electronic transitions of CDI core, even though the four phenyl groups adopted significant dihedral angles with respect to the CDI skeleton (see Figure S9, Supporting Information, for the

(19) It was HOMO-2 to LUMO for **11a**; see the Supporting Information for details.

nonplanar conformation of tetraaryl CDIs simulated by DFT). As demonstrated in Figure 1, the  $S_0$ – $S_1$  transition was the most sensitive to the electronic effect of the aryl groups. As the substituents changed from an electron-withdrawing 3,4,5-trifluoro to an electron-donating 4-dodecyloxy group, the corresponding absorption peak red-shifted from 500 to 526 nm. The  $S_0$ – $S_2$  transition energy manifested a similar dependence on the substituent, but to a less significant extent.

Absorption spectra simulated by TD-DFT were highly agreeable to the experimental results. The  $S_0$ – $S_1$  and  $S_0$ – $S_2$  transitions mainly corresponded to transitions from HOMO and HOMO-1<sup>19</sup> to LUMO, respectively (Figures S5–S8, Supporting Information). All relevant MOs featured predominant contributions from the CDI moiety, with a minor influence from the aryl groups (Table S2, Supporting Information).



**Figure 1.** Absorption spectra of tetraaryl-CDIs **11a–c** recorded in  $\text{CH}_2\text{Cl}_2$  at  $1.0 \times 10^{-5}$  M.

In summary, coronenediimides of varied substitutions were prepared through a facile synthetic protocol, i.e., an ICl-induced cyclization of diethynyl-PDI derivatives. Instead of forming iodo-substituted products, such electron-deficient substrates uniquely afforded chloro-substituted CDIs, indicating a reaction pathway altered from that of electron-rich analogues. Subsequent transformation of dichloro-bis-TMS-CDI into tetraaryl CDIs bearing different substituents demonstrated the great versatility of this intermediate for syntheses of related functional molecules.

**Acknowledgment.** This work is supported by the National Natural Science Foundation of China (Project Nos. 21174004 and 51073002).

**Supporting Information Available.** Syntheses, emission spectra, electrochemical characterizations, and calculation details. This material is available free of charge via the Internet at <http://pubs.acs.org>.

The authors declare no competing financial interest.