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Core-Perfluoroalkylated Perylene Diimides and Naphthalene Diimides: Versatile Synthesis, Solubility, Electrochemistry, and Optical Properties

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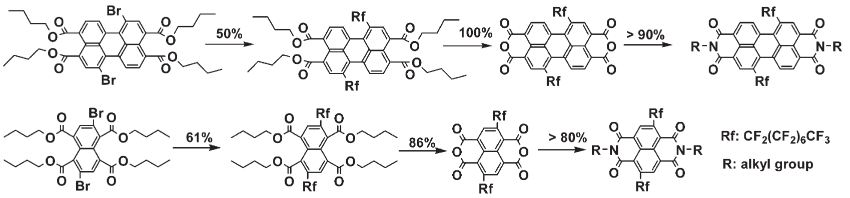

By a strategy featuring perfluoroalkylation of the highly soluble intermediates and their further efficient transformations to target compounds, a versatile synthesis of core-perfluoroalkylated perylene diimides (PDIs) and naphthalene diimides (NDIs) was developed, and PDIs perfluoroalkylated at 1-position or 1,6-positions and core-perfluoroalkylated NDIs were first obtained. By esterification, perfluoroalkylation, hydrolysis, and condensation with amine, 1-perfluorooctyl-PDIs (**7b**, **7c**, and **7e**), 1,7-bis(perfluorooctyl)-PDIs (**8a**−**c** and **8e**−**g**), 1,6-bis(perfluorooctyl)-PDIs (**8′e**), a mixture of 1,7-bis(trifluoromethyl)-PDIs and 1,6-bis(trifluoromethyl)-PDIs (**11b** and **11′b**, **11d** and **11′d**, in a ratio of 19:1), 2-perfluorooctyl-NDIs (**20a**−**d**), and 2,6-bis(perfluorooctyl)-NDIs (**21a**−**21d**) were efficiently synthesized. Five valuable intermediates—1-perfluorooctylperylene dianhydride (**5**), 1,7-bis(perfluorooctyl)perylene dianhydride (**6**) 1,6-bis(perfluorooctyl)perylene dianhydride (**6′**), 2-perfluorooctylnaphthalene dianhydride (**18**), and 2,6-bis(perfluorooctyl) naphthalene dianhydride (**19**)—were also obtained, and they can condense with many amines to produce PDIs containing different functional side chains on the imide nitrogen atoms. Solubility, electrochemistry, and optical properties of the above core-perfluoroalkylated PDIs and NDIs were investigated. Core-perfluoroalkylated **8e**, **8f**, **8′e**, mixture of **11d** and **11′d**, **20b**, and **20d** with excellent solubility in common organic solvents are competitive as candidates as solution processable semiconductors. Core-perfluoroalkylated PDIs and NDIs with experimental LUMO energy of 4.04−4.34 eV demonstrate strong electron accepting ability. For core-perfluoroalkylated PDIs, the maximum absorptions display blue shifts of 6−18 nm and the maximum molar extinction coefficients decrease obviously relative to those of unsubstituted PDIs, and they inherit the strong fluorescence from the PDIs family, which makes them promising fluorescent dyes.

Introduction

Organic semiconductors are an important class of electronic materials that offer intriguing prospects for high throughput, low-cost electronic circuitry on flexible substrates.[1,2] High-performance n-type (electron-transporting) semiconductors are still rare compared to their high-efficiency p-type (hole-transporting) counterparts, so one of the major challenges in the field of organic semiconductors is the development of high-mobility and environmentally stable n-type materials.[3] Perylene diimides (PDIs), naphthalene diimides (NDIs), and their derivatives, with compact and electron deficient cores, have demonstrated great potential as n-type semiconductors in organic field-effect transistors (OFETs).[4−6] PDIs and their derivatives also

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(1) Chen, H. Y.; Hou, J. H.; Zhang, S. Q.; Liang, Y. Y.; Yang, G. W.; Yang, Y.; Yu, L. P.; Wu, Y.; Li, G. *Nat. Photonics* **2009**, *3*, 649–653.

(2) Ma, W. L.; Yang, C. Y.; Gong, X.; Lee, K.; Heeger, A. J. *Adv. Funct. Mater.* **2005**, *15*, 1617–1622.

(3) Oh, J. H.; Sun, Y. S.; Schmidt, R.; Toney, M. F.; Nordlund, D.; Konemann, M.; Wurthner, F.; Bao, Z. A. *Chem. Mater.* **2009**, *21*, 5508–5518.

(4) Chen, Z. H.; Zheng, Y.; Yan, H.; Facchetti, A. *J. Am. Chem. Soc.* **2009**, *131*, 8–9.

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demonstrate wide applications in organic solar cells,[7−9] light harvesting systems,[10,11] and fluorescent dyes.[12−14] Though *N*,*N*′-alkyl substituted PDIs and NDIs display electron mobility as high as 2.1 and 6.2 cm^2 V^{-1} s^{-1}, respectively, in OFETs,[15−19] devices made from them are not air stable, which hampers their further applications. At present, two kinds of important and environmentally stable n-type materials were obtained via introducing electron-withdrawing groups (such as F, C_nF_{2n+1}, CN, etc.) to aromatic cores or nitrogen atoms of PDIs and NDIs.[20−25]

As electron-withdrawing substituents in particular perfluoroalkyl groups can efficiently increase air stability and electron mobility in many organic semiconductor platforms,[26−29] and perfluoroalkyl groups were introduced to the imide sites of PDIs and NDIs in an earlier period, which resulted in good devices performance.[20−22,24,30] Then, in 2007, almost at the same time, we[31] and Wang et al.[32] attached two perfluoroalkyl groups to the bay area of PDIs′ core via directly coupling dibromo-substituted PDIs with perfluoroalkyl iodide and obtained air-stable n-type semiconductors. However, this method just succeeded in a limited amount. First, as is well-known, common PDIs including dibromo-substituted PDIs have poor solubility in organic solvents due to $\pi-\pi$ stacking, so only dibromo-PDIs with a large alkyl group at nitrogen atoms can be perfluoroalkylated effectively. Second, this method encounters a common problem in the synthesis of all the bay-modified PDIs. The precursor dibromo-PDIs contained two regioisomers (1,6- and 1,7-diromo-PDIs), and they are difficult, if not impossible, to isolate on a relatively large scale, due to their poor solubility as well as their similar polarity. Thus, further transformations will also produce a mixture of isomeric products which are difficult to purify. Although in some cases isomerically pure 1,7-bis-substituted PDIs were purified via repeated crystallization,[33] the corresponding 1,6-isomers were rarely obtained.[34]

Core-perfluoroalkylated NDIs are also intriguing, because NDIs have even stronger electron accepting ability than PDIs. However, Core-perfluoroalkylated NDIs have not been available in the literature due to synthetic challenges. So it is interesting to develop a methodology suitable for the syntheses of both core-perfluoroalkylated PDIs and the corresponding NDIs. Ideally, the products can be manufactured on larger scale and the regioisomers can be effectively isolated. Since direct pefluoroalkylation of PDIs and NDIs with small alkyl groups at nitrogen atoms is impractical due to their bad solubility, a new strategy should be adopted.

In a recent communication, by a new strategy featuring trifluoromethylation of a highly soluble intermediate and its further efficient transformation to target compounds, we synthesized three regioisomerically pure bis(trifluoromethyl)-substituted 3,4,9,10-perylene tetracarboxylic bis(benzimidazoles) and obtained the key intermediate mixture of 1,7-bis(trifluoromethyl)perylene dianhydride and 1,6-bis(trifluoromethyl)perylene dianhydride (**10** and **10′**, in a ratio of 10:1).[35] In this paper, we extended the work to perfluorooctyl group substituted PDIs and NDIs, and a mixture of 1,7-bis(trifluoromethyl)-PDIs and 1,6-bis(trifluoromethyl)-PDIs which were prepared with a mixture of **10** and **10′** as the reactant. With the above versatile synthesis, 1-perfluorooctyl-PDIs (**7b**, **7c**, and **7e**), 1,7-bis(perfluorooctyl)-PDIs (**8a−c**, **8e−g**), 1,6-bis(perfluorooctyl)-PDIs (**8′e**), a mixture of 1,7-bis(trifluoromethyl)-PDIs and 1,6-bis(trifluoromethyl)-PDIs (**11b** and **11′b**, **11d** and **11′d**, in a ratio of 19:1), 2-perfluorooctyl-NDIs (**20a−d**), and 2,6-bis(perfluorooctyl)-NDIs (**21a−d**) were synthesized, as shown in Schemes 1, 3, and 4. Herein, PDIs perfluoroalkylated at 1-position or 1,6-positions and core-perfluoroalkylated NDIs were first reported. Meanwhile, five valuable intermediates 1-perfluorooctylperylene dianhydride (**5**), 1,7-bis(perfluorooctyl)perylene dianhydride (**6**), 1,6-bis(perfluorooctyl)perylene dianhydride (**6′**), 2-perfluorooctylnaphthalene dianhydride (**18**), and 2,6-bis(perfluorooctyl) naphthalene dianhydride (**19**) were also

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(5) Schmidt-Mende, L.; Fechtenkotter, A.; Mullen, K.; Moons, E.; Friend, R. H.; MacKenzie, J. D. *Science* **2001**, *293*, 1119–1122.

(6) Zhan, X. W.; Tan, Z. A.; Domercq, B.; An, Z. S.; Zhang, X.; Barlow, S.; Li, Y. F.; Zhu, D. B.; Kippelen, B.; Marder, S. R. *J. Am. Chem. Soc.* **2007**, *129*, 7246–7247.

(7) Shibano, Y.; Umeyama, T.; Matano, Y.; Imahori, H. *Org. Lett.* **2007**, *9*, 1971–1974.

(8) Imahori, H.; Umeyama, T.; Ito, S. *Acc. Chem. Res.* **2009**, *42*, 1809–1818.

(9) Tang, C. *Appl. Phys. Lett.* **1986**, *48*, 183.

(10) Li, X. Y.; Sinks, L. E.; Rybtchinski, B.; Wasielewski, M. R. *J. Am. Chem. Soc.* **2004**, *126*, 10810–10811.

(11) Yilmaz, M. D.; Bozdemir, O. A.; Akkaya, E. U. *Org. Lett.* **2006**, *8*, 2871–2873.

(12) Langhals, H.; Karolin, J.; Johansson, L. B. A. *J. Chem. Soc., Faraday Trans.* **1998**, *94*, 2919–2922.

(13) Langhals, H. *New J. Chem.* **2008**, *32*, 21–23.

(14) Herrmann, A.; Weil, T.; Sinigersky, V.; Wiesler, U. M.; Vosch, T.; Hofkens, J.; De Schryver, F. C.; Mullen, K. *Chem.—Eur. J.* **2001**, *7*, 4844–4853.

(15) Chesterfield, R. J.; McKeen, J. C.; Newman, C. R.; Ewbank, P. C.; da Silva, D. A.; Bredas, J. L.; Miller, L. L.; Mann, K. R.; Frisbie, C. D. *J. Phys. Chem. B* **2004**, *108*, 19281–19292.

(16) Malenfant, P. R. L.; Dimitrakopoulos, C. D.; Gelorme, J. D.; Kosbar, L. L.; Graham, T. O.; Curioni, A.; Andreoni, W. *Appl. Phys. Lett.* **2002**, *80*, 2517–2519.

(17) Tatemichi, S.; Ichikawa, M.; Koyama, T.; Taniguchi, Y. *Appl. Phys. Lett.* **2006**, *89*, 112108–112110.

(18) Katz, H.; Johnson, J.; Lovinger, A.; Li, W. *J. Am. Chem. Soc.* **2000**, *122*, 7787–7792.

(19) Shukla, D.; Nelson, S. F.; Freeman, D. C.; Rajeswaran, M.; Ahearn, W. G.; Meyer, D. M.; Carey, J. T. *Chem. Mater.* **2008**, *20*, 7486–7491.

(20) Jones, B. A.; Ahrens, M. J.; Yoon, M. H.; Facchetti, A.; Marks, T. J.; Wasielewski, M. R. *Angew. Chem., Int. Ed.* **2004**, *43*, 6363–6366.

(21) Schmidt, R.; Oh, J. H.; Sun, Y. S.; Deppisch, M.; Krause, A. M.; Radacki, K.; Braunschweig, H.; Konemann, M.; Erk, P.; Bao, Z. A.; Wurthner, F. *J. Am. Chem. Soc.* **2009**, *131*, 6215–6228.

(22) Weitz, R. T.; Amsharov, K.; Zschieschang, U.; Villas, E. B.; Goswami, D. K.; Burghard, M.; Dosch, H.; Jansen, M.; Kern, K.; Klauk, H. *J. Am. Chem. Soc.* **2008**, *130*, 4637–4645.

(23) Jones, B. A.; Facchetti, A.; Marks, T. J.; Wasielewski, M. R. *Chem. Mater.* **2007**, *19*, 2703–2705.

(24) Kao, C.; Lin, P.; Lee, C.; Wang, Y.; Ho, J.; Shen, Y. *Appl. Phys. Lett.* **2007**, *90*, 212101–212103.

(25) Chen, H. Z.; Ling, M. M.; Mo, X.; Shi, M. M.; Wang, M.; Bao, Z. *Chem. Mater.* **2007**, *19*, 816–824.

(26) Facchetti, A.; Mushrush, M.; Katz, H. E.; Marks, T. J. *Adv. Mater.* **2003**, *15*, 33–38.

(27) Facchetti, A.; Yoon, M. H.; Stern, C. L.; Hutchison, G. R.; Ratner, M. A.; Marks, T. J. *J. Am. Chem. Soc.* **2004**, *126*, 13480–13501.

(28) Bao, Z. A.; Lovinger, A. J.; Brown, J. *J. Am. Chem. Soc.* **1998**, *120*, 207–208.

(29) Di, C. A.; Li, J.; Yu, G.; Xiao, Y.; Guo, Y. L.; Liu, Y. Q.; Qian, X. H.; Zhu, D. B. *Org. Lett.* **2008**, *10*, 3025–3028.

(30) Katz, H. E.; Lovinger, A. J.; Johnson, J.; Kloc, C.; Siegrist, T.; Li, W.; Lin, Y. Y.; Dodabalapur, A. *Nature* **2000**, *404*, 478–481.

(31) Xiao, Y.; Yuan, Z. *Chinese Patent*, Appl. No. CN200710012728, 2007.

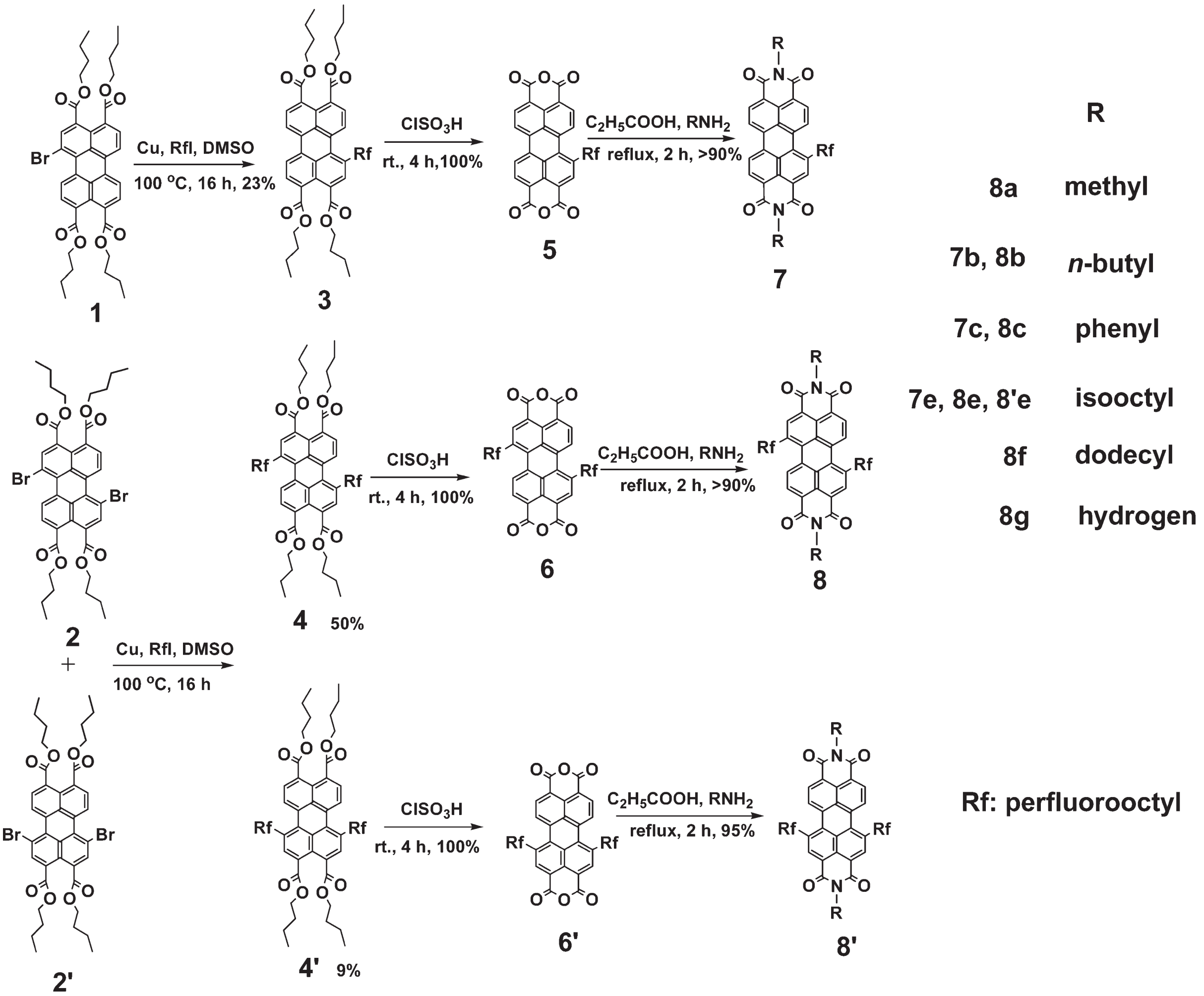
(32) Li, Y.; Tan, L.; Wang, Z. H.; Qian, H. L.; Shi, Y. B.; Hu, W. P. *Org. Lett.* **2008**, *10*, 529–532.

(33) Wurthner, F.; Stepanenko, V.; Chen, Z. J.; Saha-Moller, C. R.; Kocher, N.; Stalke, D. *J. Org. Chem.* **2004**, *69*, 7933–7939.

(34) Ahrens, M.; Tauber, M.; Wasielewski, M. *J. Org. Chem.* **2006**, *71*, 2107–2114.

(35) Yuan, Z.; Xiao, Y.; Li, Z.; Qian, X. *Org. Lett.* **2009**, *11*, 2808–2811.

SCHEME 1. Synthesis of Perfluorooctylated Perylene Diimides

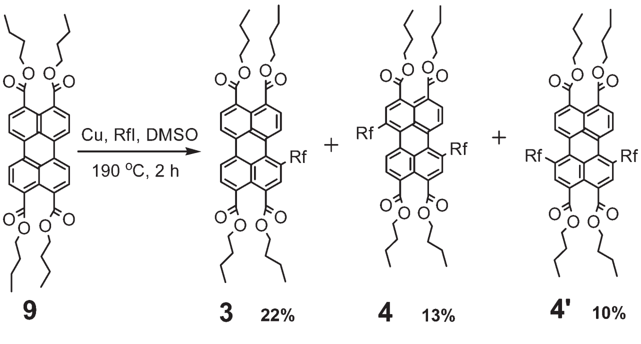


obtained, and they can condense with many amines to produce PDIs containing different functional side chains on the imide nitrogen atoms. In addition, the perfluorooctyl group was introduced to 3,4,9,10-tetra(*n*-butoxycarbonyl)perylene (**9**) directly in the presence of copper bronze as catalyst for the first time, as shown in Scheme 2. Solubility, electrochemistry, and optical properties of the above core-perfluoroalkylated PDIs and NDIs were also investigated.

Results and Discussion

Synthesis. As shown in Scheme 1, to increase the solubility of reactants used in the perfluoroalkylation, the highly soluble intermediates 1-bromo-3,4,9,10-tetra(*n*-butoxycarbonyl)perylene (**1**) and a mixture of 1,7-dibromo-3,4,9,10-tetra(*n*-butoxycarbonyl)perylene and 1,6-dibromo-3,4,9,10-tetra(*n*-butoxycarbonyl)perylene (**2** and **2′**, in a ratio of 4:1) were selected as starting materials. After perfluorooctylation with a mixture of **2** and **2′** as reactant, we found regioisomers 1,7-bis(perfluorooctyl)-3,4,9,10-tetra(*n*-butoxycarbonyl)perylene (**4**) and 1,6-bis(perfluorooctyl)-3,4,9,10-tetra(*n*-butoxycarbonyl)perylene (**4′**) can be separated through silica gel column chromatography, and they can be differentiated by ^{1}H NMR (Figure 1).

SCHEME 2. Perfluorooctylation of 3,4,9,10-Tetra(*n*-butoxycarbonyl)perylene



Rf: perfluorooctyl

The coupling reaction of **1** with perfluorooctyl iodide in DMSO at 100 °C in the presence of copper bronze as catalyst led to **3** in 23% yield. To our surprise, compounds **4** and **4′** were also found in the above reaction mixture. The finding suggested that perfluorooctylation of **9** may be done by reacting perfluorooctyl iodide directly with **9**. After many attempts, it was found that the reaction between perfluorooctyl iodide and **9** can occur quickly in DMSO in the presence of copper bronze at high temperature. For example, **9** can be converted to **3**, **4**, and **4′** in 22%, 13%, and 10% yield, respectively, at 190 °C in 2 h (Scheme 2). However,

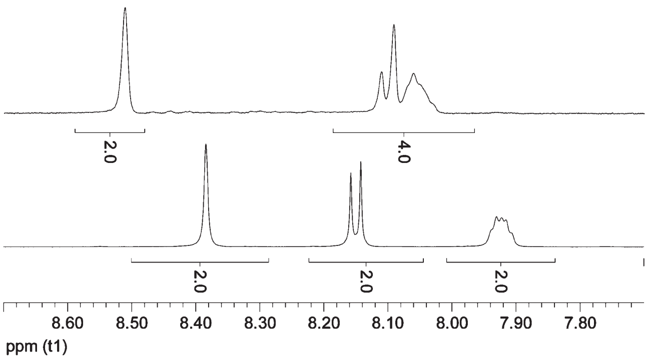
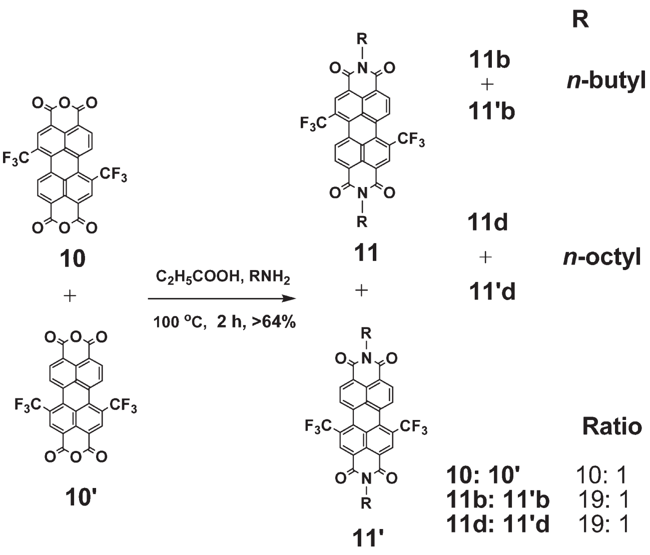


FIGURE 1. Low-field section of the ^{1}H NMR spectrum (400 MHz, in $CDCl_3$) of **4** (bottom) and **4′**(top).

SCHEME 3. Synthesis of Bis(trifluoromethyl)-Substituted Perylene Diimides



perfluorooctylation of PDIs under the above conditions occurs very slowly. Compounds **4** and **4′** can also be synthesized in 50% and 9% yield, respectively, by the coupling reaction of a mixture of **2** and **2′** with perfluorooctyl iodide.

Hydrolysis of **3**, **4**, and **4′** in chlorosulfonic acid was carried out smoothly at room temperature, and resulted in 100% yield of the corresponding 1-perfluorooctylperylene dianhydride (**5**), 1,7-bis(perfluorooctyl)perylene dianhydride (**6**), and 1,6-bis(perfluorooctyl)perylene dianhydride (**6′**). The products can be easily obtained just by adding the reaction mixture to ice and filtering.

The condensation of **5**, **6**, and **6′** with primary amines in propanoic acid at reflux satisfactorily led to **7b** (97%), **7c** (96%), **7e** (97%), **8a** (90%), **8b** (96%), **8c** (92%), **8e** (99%), **8f** (91%), **8g** (99%), and **8′e** (95%). One should notice that the intermediates **5**, **6**, and **6′** can condense with many other amines to produce PDIs containing different functional side chains on the imide nitrogen atoms, so they are valuable platforms.

A mixture of 1,7-bis(trifluoromethyl)perylene dianhydride and 1,6-bis(trifluoromethyl)perylene dianhydride (**10** and **10′**, in a ratio of 10:1) was synthesized according to our published work.[35] The condensation of a mixture of **10** and **10′** with primary amines in propanoic acid at 100 °C led to bis(trifluoromethyl)-PDIs mixtures (**11b** and **11′b** in a 64% yield, **11d** and **11′d** in a 70% yield, Scheme 3). 1,7-Bis(trifluoromethyl)-PDIs and 1,6-bis(trifluoromethyl)-PDIs cannot be separated through silica gel column chromatography, but can be differentiated by ^{1}H NMR (Figure 2), and a 19:1 ratio (**11b**:**11′b**, **11d**:**11′d**) was indicated by 400 MHz NMR spectroscopy.

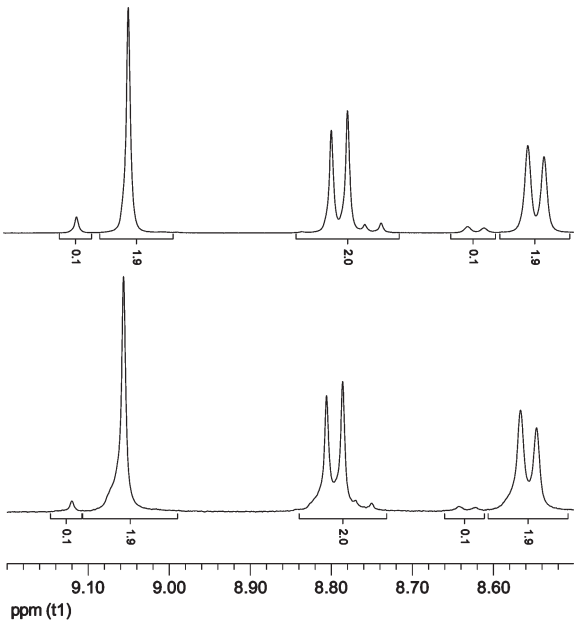
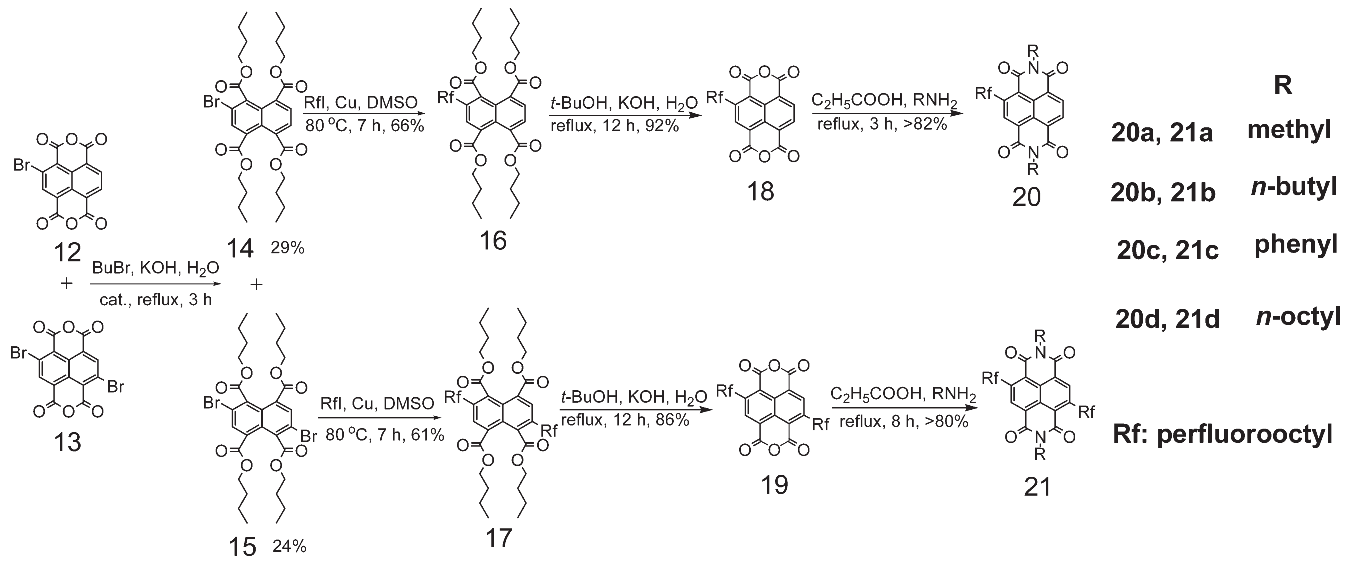


FIGURE 2. Low-field section of the ^{1}H NMR spectrum (400 MHz, in $CDCl_3$) for a mixture of **11b** and **11′b** (bottom) and a mixture of **11d** and **11′d** (top).

A mixture of 2-bromonaphthalene dianhydride (**12**) and 2,6- dibromonaphthalene dianhydride (**13**), with poor solubility in common organic solvents, was synthesized by bromination of naphthalene dianhydride according to a literature method.[23] As shown in Scheme 4, highly soluble intermediates 2-bromo-1,4,5,8-tetra(*n*-butoxycarbonyl)naphthalene (**14**) and 2,6-dibromo-1,4,5,8-tetra(*n*-butoxycarbonyl)naphthalene (**15**) were synthesized by reaction of a mixture of **12** and **13** with 1-bromobutane in a 29% and 24% yield, respectively (overall for bromination and esterification), in aqueous KOH in the presence of tetraoctyl ammonium bromide as phase transfer catalyst. After purification through silica gel column chromatography, intermediate **15** as a viscous liquid still contained several impurities, and HPLC results indicated that **15** with chromatographic purity 83% included at least six impurities (see the Supporting Information), and it was used directly in the next reaction without further purification; with preparative HPLC, we successfully obtained a small amount of pure **15**, which was satisfactorily characterized by NMR.

The coupling reaction of **14** or **15** with perfluorooctyl iodide in DMSO at 80 °C in the presence of copper bronze as catalyst led to **16** or **17** in a 66% or 61% yield, respectively. However direct perfluorooctylation of 1,4,5,8-tetra(*n*-butoxycarbonyl)naphthalene in the presence of copper bronze and perfluorooctyl iodide at high temperature was inaccessible. Introduction of a trifluoromethyl group to 1,4,5,8-tetra(*n*-butoxycarbonyl)naphthalene with **14** or **15** as reactant under previous conditions[35] also failed.

SCHEME 4. Synthesis of Perfluorooctylated Naphthalene Diimides



Hydrolysis of **16** and **17** in a *tert*-butyl alcohol–water mixed solvent (10:1, v/v) solution of KOH at reflux led to 2-perfluorooctylnaphthalene dianhydride (**18**) and 2,6-bis(perfluorooctyl)naphthalene dianhydride (**19**) as a white solid in 92% and 86% yield, respectively. But hydrolysis in chlorosulfonic acid at room temperature cannot lead to pure **18** or **19**.

The condensation of **18** and **19** with primary amines in propanoic acid at reflux led to **20a** (92%), **20b** (87%), **20c** (92%), **20d** (82%), **21a** (86%), **21b** (82%), **21c** (89%), and **21d** (80%). Intermediates **18** and **19** can also condense with many other amines to produce NDIs containing different functional side chains on the imide nitrogen atoms, so they are also valuable intermediates.

Due to poor solubility, intermediates **18** and **19** were only characterized by HRMS, target compound **8g** was characterized by ^{1}H NMR and HRMS, target compound **21a** was characterized by ^{1}H–^{19}F NMR and HRMS, and target compound **21c** was characterized by ^{1}H–^{13}C NMR and HRMS. The other 25 new compounds containing fluorine in this study were all well characterized by ^{1}H–^{19}F ^{13}C NMR and HRMS, and the intermediate **14** and **15** without fluorine were well characterized by ^{1}H–^{13}C NMR and HRMS.

Solubility. Common PDIs have poor solubility in organic solvents due to π–π stacking. For example, *N*,*N*′-bis(isooctyl)-PDIs show very poor solubility in common organic solvents (solubility less than 1 mg/mL in CH_2Cl_2). For another example, Deyama et al. investigated the solubility of several kinds of PDIs containing perfluoroalkyl groups and found *cis*-*N*,*N*′-bis[2-(1*H*,1*H*-perfluoroheptyl)phenyl]-PDIs have the maximum solubility of 14 mg/mL in chloroform.[36] In a review, Langhals summarized the solubility of PDIs with two unbranched alkyl groups attached to nitrogen atoms and concluded that the solubility of those compounds is lower than 0.1 mg/mL in $CHCl_3$. Poor solubility restricts their potential applications as solution processable semiconductors, laser dyes in liquid solution, and soluble fluorescent dyes and so on. Interestingly, the solubility of perfluorooctyl-substituted PDIs can be adjusted conveniently by changing the size of the groups attached to nitrogen atoms. Taking 1,7-bis(perfluorooctyl)-substituted PDIs for example, **8e** or **8f** with two isooctyl or dodecyl groups attached to nitrogen atoms exhibits excellent solubility (over 200 mg/mL in CH_2Cl_2) in common solvents such as toluene, CH_2Cl_2, *n*-hexane, THF, etc. The solubility of **8a** with two methyl groups is only about 2 mg/mL in CH_2Cl_2 and it is slightly soluble in THF and insoluble in *n*-hexane. The solubility of **8c** with two phenyl groups is about 6 mg/mL in CH_2Cl_2. Compound **8g** with no alkyl group is insoluble in common organic solvents and only slightly soluble in trifluoroacetic acid. The solubility of 1-perfluorooctyl-PDIs has a similar rule. For example, the solubility of **7b** with two butyl groups is about 10 mg/mL in CH_2Cl_2, while **7e** with two octyl groups shows a solubility of about 50 mg/mL in CH_2Cl_2. 1,6-Bis(perfluorooctyl)-PDIs **8′e** as well as the two mixtures of bis(trifluoromethyl)-PDIs (**11b** and **11′b**, **11d** and **11′d**) have good solubility in common solvents such as toluene, CH_2Cl_2, and THF. The mixture of **11d** and **11′d** (in CH_2Cl_2) shows much better solubility than **11b** and **11′b** (120 mg/mL for the former, 8 mg/mL for the latter, in CH_2Cl_2).

Compounds **20a**, **21a**, **20c**, and **21c** with two methyl or phenyl groups attached to nitrogen atoms of core-perfluorooctylated NDIs exhibit poor solubility in common solvents (about 1.3, 3.2, 2.4, and 1.8 mg/mL for the four compounds, respectively, in CH_2Cl_2). 2-Perfluorooctyl-NDIs **20b** and **20d** with two butyl or octyl groups show good solubility in common solvents (about 30 mg/mL for **20b** and 160 mg/mL for **20d**, in CH_2Cl_2), while 2,6-bis(perfluorooctyl)-NDIs **21b** and **21d** show much poorer solubility (lower than 8 mg/mL for **20b** and lower than 12 mg/mL for **20d**, in CH_2Cl_2).

In a word, the solubility of core-perfluoroalkylated PDIs or NDIs can be adjusted conveniently by changing the size of the alkyl groups attached to nitrogen atoms. Core-perfluoroalkylated **8e**, **8f**, **8′e**, mixture of **11d** and **11′d**, **20b**, and **20d** with excellent solubility in common organic solvents are competitive as candidates for solution processable semiconductor.

Electrochemistry. The electrochemical properties of **7b**, **7c**, **7e**, **8b**, **8c**, **8e**, **8′e**, **20a–d**, **21a**, **21b**, mixture of **11b** and **11′b**,

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(36) Deyama, K.; Tomoda, H.; Muramatsu, H.; Matsui, M. *Dyes Pigm.* **1996**, *30*, 73–78.

(37) Thompson, B. C.; Kim, Y. G.; McCarley, T. D.; Reynolds, J. R. *J. Am. Chem. Soc.* **2006**, *128*, 12714–12725.

TABLE 1. **Half-Wave Reduction Potentials (in V vs Fc/Fc$^+$) and LUMO Energy of 7b, 7c, 7e, 8b, 8c, 8e, 8′e, 11b, 11d, RPDIs, 20a−d, 21a, and 21b**

	E (M/M^{-1})^a	*E* (M^{-1}/M^{-2})^a	exptl LUMO (eV)^b	theoretical LUMO (eV)^c
7b	−0.98	−1.22	4.10	3.92
7c	−0.89	−1.13	4.19	3.89
7e	−0.92	−1.15	4.16	3.89
8b^d	−0.82	−1.09	4.26	4.16
8c	−0.75	−1.03	4.33	4.13
8e	−0.81	−1.08	4.27	4.16
8′e	−0.82	−1.12	4.26	4.19
11b^e	−0.84	−1.11	4.24	4.11
11d^f	−0.80	−1.05	4.28	4.11
RPDIs	−1.09	−1.29	3.99	3.62
20a	−0.90	−1.51	4.18	4.08
20b	−1.04	−1.74	4.04	4.03
20c	−0.91	−1.51	4.17	4.00
20d	−1.00	−1.49	4.08	4.00
21a	−0.74	−1.41	4.34	4.46
21b	−0.83	−1.41	4.25	4.35

[a] Measured in 0.05 M solution of Bu_4NPF_6 in CH_2Cl_2 with a scan rate of 100 mV/s. [b] On the basis of the assumption that the energy of Fc/Fc$^+$ is 5.08 eV relative to vacuum.[37] [c] DFT method, Gaussian 03 programs. [d] The two reduction potentials of *N*,*N*′-bis(butyl)-1,7-bis(perfluorobutyl) PDIs are −0.72 and −0.98 V, respectively, in ref 32. [e] Mixture of **11b** and **11′b**. [f] Mixture of **11d** and **11′d**.

mixture of **11d** and **11′d**, and reference compound *N*,*N*′-bis(isooctyl)perylene diimides (RPDIs) were investigated by cyclovoltammetry, and their reduction potentials, experimental LUMO (E-LUMO) energy, and theoretical LUMO (T-LUMO) energy are shown in Table 1. All the above compounds show two reversible reduction peaks, indicating they can accept two electrons, whereas within the accessible scanning range in CH_2Cl_2 no oxidation waves can be detected. Figure 3 shows reductive cyclic voltammograms of **7e**, **8c**, **8′e**, mixture of **11b** and **11′b**, **20d**, and **21b**. For core-perfluoroalkylated PDIs, both the first and the second reduction waves are at higher potentials than those of RPDIs, indicating that the perfluoroalkyl-substituted PDIs receive electrons more easily. The E-LUMO energy of 1-perfluorooctyl-PDIs (**7b**, **7c**, and **7e**, 4.10−4.19 eV) is 0.11−0.20 V lower than that of RPDIs (3.99 eV), and the LUMO energy of 1,7-bis(perfluorooctyl)-PDIs (**8b**, **8c**, and **8e**, 4.26−4.33 eV), 1,6-bis(perfluorooctyl)-PDIs (**8′e**, 4.26 eV), and bis(trifluoromethyl)-PDIs (mixture of **11b** and **11′b** and mixture of **11d** and **11′d**, 4.24−4.28 eV) is 0.27−0.34 eV lower than that of RPDIs, which indicates obviously stronger electron accepting ability of core-perfluoroalkylated PDIs relative to unsubstituted PDIs and stronger electron accepting ability of bis(perfluorooctyl)-PDIs (**8b**, **8c**, **8e**, and **8′e**) relative to 1-perfluorooctyl-PDIs (**7b**, **7c**, and **7e**). 1,6-Bis(perfluorooctyl)-PDIs (**8′e**) with E-LUMO energy of 4.26 eV is similar to those of 1,7-bis(perfluorooctyl)-PDIs (**8b**, **8c**, and **8e**, 4.26−4.33 eV). For core-perfluorooctylated NDIs, the E-LUMO energy of two perfluorooctyl groups substituted NDIs (**21a**, **21b**, 4.25−4.34 eV) is 0.07−0.30 eV lower than that of one perfluorooctyl group substituted NDIs (**20a**−**d**, 4.04−4.18 eV).

For **8′e**, **20b**, and **20d**, T-LUMO energy is very close to E-LUMO energy (lower than 0.1 eV difference), and for the other compounds the difference between T-LUMO energy and E-LUMO energy is in the range of 0.1−0.3 eV. A clear trend for T-LUMO energy is that T-LUMOs of 1-perfluorooctyl-PDIs and 1,7-bis(perfluoroalkyl)-PDIs are 0.27−0.3 and 0.49−0.57 eV lower than that of RPDIs, respectively.

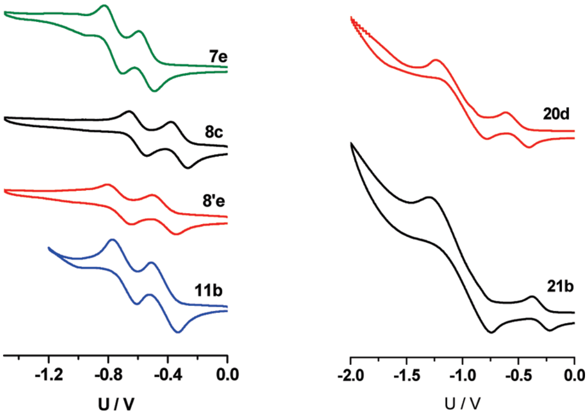

FIGURE 3. Reductive cyclic voltammograms of **7e**, **8c**, **8′e**, mixture of **11b** and**11′b**, **20d**, and **21b** in CH_2Cl_2 (vs Ag/AgCl).

TABLE 2. **Optical Data of 7c, 7e, 8b, 8c, 8e, 8′e, Mixture of 11b and 11′b, Mixture of 11d and 11′d, 20b−d, 21a, 21b, RPDIs, and RNDIs in CH_2Cl_2**

	λ_{abs} (nm)	ε (M^{-1} cm^{-1})	λ_{em} (nm)	S^a (nm)	$\varphi_{fl}/\lambda_{ex}{}^b$ (nm)
7c	519	47500	542	23	0.92/485
7e	518	48700	540	22	0.73/485
8b	508	53100	527	19	1.0/475
8c	509	57400	529	20	0.81/475
8e	508	49800	526	19	0.97/475
8′e	509	39200	535	26	0.67/477
11b^c	506	60700	521	15	0.97/473
11d^d	506	73600	524	18	0.92/474
RPDIs	524	89800	533	9	1.0/447
20b	384	13500			
20c	383	21200			
20d	384	13900			
21a	387	15900			
21b	388	12500			
RNDIs^e	382	14500			

[a] Stokes shifts. [b] Determined with rhodamine 6G as reference.[40] [c] Mixture of **11b** and **11′b**. [d] Mixture of **11d** and **11′d**. [e] The data of RNDIs (*N*,*N*′-bis(octyl)naphthalene diimides) is from the literature.[41]

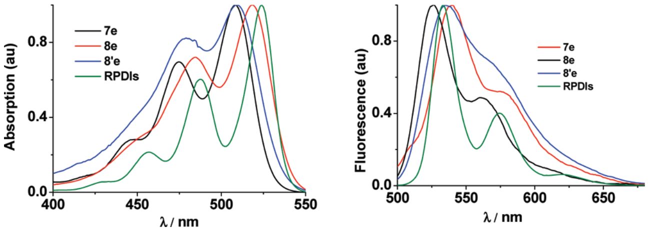

FIGURE 4. UV−vis absorption (left) and fluorescence emission (right) spectrum of **7e**, **8e**, **8′e**, and RPDIs in CH_2Cl_2.

That is, electron-withdrawing perfluoroalkyl groups can effectively lower the LUMO energy of PDIs and the more electron-withdrawing groups the lower the LUMO energy, which is consistent with the trend for E-LUMOs. The above trend also exists in the NDIs series; for example, T-LUMOs of 2,6-bis(perfluorooctyl)-NDIs are 0.32−0.46 eV lower than those of 2-perfluorooctyl-NDIs, and the trend is consistent with that of E-LUMOs. The HOMO energy and HOMO and LUMO electron density for all compounds in Table 1 were also calculated, and the results are given in the Supporting Information.

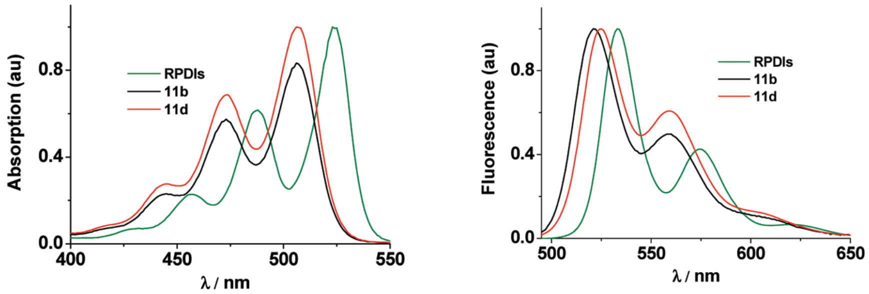

FIGURE 5. UV−vis absorption (left) and fluorescence emission (right) spectrum for a mixture of **11b** and **11′b**, a mixture of **11d** and **11′d**, and RPDIs in CH_2Cl_2.

All these compounds with E-LUMO energy between 4.04 and 4.34 eV demonstrate strong electron-accepting ability, and their E-LUMO energy is similar to that of extensively used and expensive n-type semiconductor PCBM (4.2 eV), which makes these core-perfluoroalkylated PDIs or NDIs potential substitutes for PCBM.

Optical Properties. Compound **7c**, **7e**, **8b**, **8c**, **8e**, **8′e**, mixture of **11b** and **11′b**, mixture of **11d** and **11′d**, **20b−d**, **21a**, **21b**, RPDIs, and *N*,*N*′-bis(octyl)naphthalene diimides (RNDIs) were selected as representative samples in an optical test, and their optical data was listed in Table 2. Figure 4 shows absorption and fluorescence emission of **7e**, **8e**, **8′e**, and RPDIs in CH_2Cl_2. Figure 5 shows absorption and fluorescence emission for a mixture of **11b** and **11′b**, a mixture of **11d** and **11′d**, and RPDIs in CH_2Cl_2. Figure 6 shows the absorption of **20b**, **20c**, **21a**, and **21b** in CH_2Cl_2.

As shown in Figure 4, the maximum absorptions of core-perfluorooctylated PDIs **7e**, **8e**, and **8′e** (located at 518, 508, and 509 nm) display blue shifts of 6, 16, and 15 nm, respectively, relative to that of unsubstituted RPDIs. Meanwhile, their maximum molar extinction coefficients (48 700, 49 800, and 39 200, respectively) decrease remarkably relative to that of RPDIs (89 800). A twist of the perylene core exists in many previous core-substituted perylene biimides.[33,38] And it is likely that the twist also exists in the above perfluorooctyl-substituted molecules, which partly causes the blue shifts and decreased extinction coefficients.

As shown in Figure 5, similar to those of core-perfluorooctylated PDIs, the maximum absorptions of core-trifluoromethylated PDIs (mixture of **11b** and **11′b** and mixture of **11d** and **11′d**, located at 506 nm) display blue shifts of 18 nm relative to that of RPDIs. And their maximum molar extinction coefficients (**11b**: 60 700; **11d:** 73 600) also decrease obviously compared to that of RPDIs.

In this study, all the core-perfluoroalkylated PDIs inherit the strong fluorescence from the PDIs family, and their fluorescence quantum yields are higher than 0.67, which makes them promising fluorescent dyes. Core-perfluoroalkylated PDIs possess bigger Stokes shifts (15−26 nm) relative to that of RPDIs (9 nm), and this indicates their stronger molecular vibration, which may be partly responsible for a little lower fluorescence quantum yields of some core-perfluoroalkylated PDIs. 1,6-Bis(perfluorooctyl)-PDIs (**8′e**) with Stoke shifts 26 nm and fluorescence quantum yield 0.67 is different from 1,7-bis(perfluorooctyl)-PDIs (**8b**, **8c**, and **8e**, with Stoke shifts 19−20 nm and fluorescence quantum yield 0.81−1.0). Though 1,7-bis(perfluoroalkyl)-PDIs were proved to be air-stable n-type organic semiconductors, the properties of 1,6-bis(perfluoroalkyl)-PDIs have not been studied. So it is worth investigating the applications of 1,6-bis(perfluoroalkyl)-PDIs in electronic devices in the future.

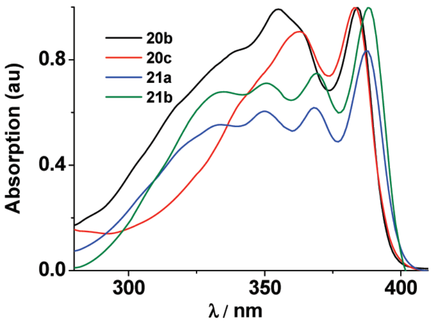

FIGURE 6. UV−vis absorption of **20b**, **20c**, **21a**, and **21b** in CH_2Cl_2.

As shown in Figure 6, in the range of 300−400 nm, one perfluorooctyl group substituted NDIs (**20b** and **20c**) exhibits two absorption bands with nearly equal intensity, while two perfluorooctyl groups substituted NDIs (**21a** and **21b**) show a strongest peak and another three strong peaks with similar intensity. The different absorption profiles may be attributed to different numbers of electron-withdrawing substitutes.[39] The maximum absorptions of **20b** and **20c** (located at 384 and 383 nm) are almost the same as that of RNDIs (located at 382 nm), and the maximum absorptions of **21a** and **21b** (located at 387 and 388 nm) display a little blue shift of 5 and 6 nm, respectively. The maximum absorptions of NDIs are almost unaffected by introduction of perfluorooctyl groups to their cores. In this study, the fluorescence of core-perfluorooctylated NDIs and RNDIs is very weak, so they were not investigated here.

Conclusions

A versatile synthesis of core-perfluoroalkylated perylene diimides (PDIs) and naphthalene diimides (NDIs) was developed, and PDIs perfluoroalkylated at 1-position or 1,6-positions and core-perfluoroalkylated NDIs were first

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(38) Wurthner, F.; Osswald, P.; Schmidt, R.; Kaiser, T. E.; Mansikkamaki, H.; Konemann, M. *Org. Lett.* **2006**, *8*, 3765–3768.

(39) Wurthner, F.; Ahmed, S.; Thalacker, C.; Debaerdemaeker, T. *Chem.—Eur. J.* **2002**, *8*, 4742–4750.

(40) Fischer, M.; Georges, J. *Chem. Phys. Lett.* **1996**, *260*, 115–118.

(41) Chopin, S.; Chaignon, F.; Blart, E.; Odobel, F. *J. Mater. Chem.* **2007**, *17*, 4139–4146.

obtained. The perfluorooctyl group was introduced to 3,4,9,10-tetra(*n*-butoxycarbonyl)perylene directly in the presence of copper bronze as catalyst for the first time. 1-Perfluorooctyl-PDIs (**7b**, **7c**, and **7e**), 1,7-bis(perfluorooctyl)-PDIs (**8a**−**c** and **8e**−**g**), 1,6-bis(perfluorooctyl)-PDIs (**8′e**), a mixture of 1,7-bis(trifluoromethyl)-PDIs and 1,6-bis(trifluoromethyl)-PDIs (**11b** and **11′b**, **11d** and **11′d**, in a ratio of 19:1), 2-perfluorooctyl-NDIs (**20a**−**d**), and 2,6-bis(perfluorooctyl)-NDIs (**21a**−**d**) were efficiently synthesized. Five valuable intermediates **5**, **6**, **6′**, **18**, and **19** were also obtained, and they can condense with many kinds of amines to produce core-perfluoroalkylated PDIs or NDIs containing different functional side chains on the imide nitrogen atoms. The solubility of core-perfluoroalkylated PDIs or NDIs can be adjusted conveniently by changing the size of groups attached to the nitrogen atoms. Core-perfluoroalkylated **8e**, **8f**, **8′e**, mixture of **11d** and **11′d**, **20b**, and **20d** with excellent solubility in common organic solvents are competitive as candidates for solution processable semiconductor. Core-perfluoroalkylated PDIs and NDIs with experimental LUMO energy 4.04−4.34 eV demonstrate strong electron accepting ability, and their experimental LUMO energy is similar to that of extensively used and expensive n-type semiconductor PCBM (4.2 eV), which makes them potential substitutes for PCBM. For core-perfluoroalkylated PDIs, the maximum absorptions display blue shifts of 6−18 nm relative to unsubstituted PDIs, the maximum molar extinction coefficients decrease obviously relative to unsubstituted PDIs, and they inherit the strong fluorescence from PDIs family, which makes them promising fluorescent dyes. The applications of these compounds are in progress.

Experimental Section

Compound **9** was synthesized by a literature method.[42] Compound **1** and the mixture of **2** and **2′** were synthesized according to our previous work.[35,43] The other reactants were purchased from commercial sources. NMR spectra were measured with use of TMS as internal standard for ^{1}H NMR and ^{13}C NMR and with $CFCl_3$ as reference for ^{19}F NMR. Cyclic voltammetry (CV) was performed with a standard commercial electrochemical analyzer in a three-electrode single-component cell under argon with a scan rate of 100 mV/s. Working electrode: glassy carbon; reference electrode: Ag/AgCl; auxiliary electrode: Pt disk; supporting electrolyte: tetrabutylammonium hexafluorophosphate (Bu_4NPF_6); internal standard: ferrocene (Fc).

There are two synthetic routes for **3**, **4** and **4′**.

Synthesis of 3 According to Scheme 1. A mixture of **1** (150 mg, 0.20 mmol), perfluorooctyl iodide (200 μL, 0.75 mmol), and copper bronze (66 mg, 1.0 mmol) was stirred at 100 °C in 1 mL of DMSO for 16 h under argon. After cooling to room temperature, the reaction was quenched by addition of water and CH_2Cl_2, washed three times with water, dried over $MgSO_4$, and purified through silica gel column chromatography. Compound **3** was obtained as a viscous oil (49 mg, 23%). HRMS calcd for $C_{48}H_{43}O_8F_{17}Na$ 1093.2584, found 1093.2538 ($[M + Na]^+$, ESI); ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.00 (m, 12H), 1.49 (m, 8H), 1.79 (m, 8H), 4.36 (m, 8H), 7.94 (d, 1H), 8.03 (d, 1H), 8.16 (d, 1H), 8.21 (d, 1H), 8.33 (m, 2H), 8.40 ppm (s, 1H); ^{19}F NMR (376.5 MHz, $CDCl_3$) δ −126.08, −122.65, −121.78, −121.55, −121.06, −115.63, −97.35, −80.75 ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ 13.9, 19.4, 29.9, 66.1, 122.6, 123.0, 127.7, 128.8, 129.1, 129.3, 129.6, 129.9, 130.1, 130.4, 130.5, 130.8, 130.9, 131.9, 132.0, 133.4, 136.9, 167.8, 168.8 ppm.

Synthesis of 4 and 4′ According to Scheme 1. A mixture of the mixture of **2** and **2′** (750 mg, 0.93 mmol), perfluorooctyl iodide (1 mL, 3.7 mmol), and copper bronze (430 mg, 6.7 mmol) was stirred at 100 °C in 5 mL of DMSO for 16 h under argon. After cooling to room temperature, the reaction was quenched by addition of water and CH_2Cl_2, washed three times with water, dried over $MgSO_4$, and purified through silica gel column chromatography.

Compound **4** was obtained as a slightly green solid (700 mg, 50%). Mp 159−161 °C; HRMS calcd for $C_{56}H_{42}O_8F_{34}Na$ 1511.2234, found 1511.2178 ($[M + Na]^+$, ESI); ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.00 (m, 12H), 1.52 (m, 8H), 1.81 (m, 8H), 4.40 (m, 8H), 7.92 (m, 2H), 8.14 (d, 2H), 8.38 (s, 2H); ^{19}F NMR (376.5 MHz, $CDCl_3$) δ −126.13, −122.69, −121.83, −121.58, −121.06, −116.63, −97.47, −80.88 ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ 13.7, 19.3, 30.6, 66.0, 118.4, 124.4, 127.6, 129.4, 130.2, 130.5, 130.6, 131.2, 131.4, 134.6, 167.4, 167.8 ppm.

Compound **4′** was obtained as a yellow solid (125 mg, 9%). Mp 167−168 °C; HRMS calcd for $C_{56}H_{42}O_8F_{34}Na$ 1511.2167, found 1511.2234 ($[M + Na]^+$, ESI); ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.00 (m, 12H), 1.52 (m, 8H), 1.80 (m, 8H), 4.39 (m, 8H), 8.06 (m, 2H), 8.10 (d, 2H), 8.51 ppm (s, 2H); ^{19}F NMR (376.5 MHz, $CDCl_3$) δ −126.50, −123.08, −122.22, −121.97, −121.50, −115.86, −97.35, −81.20 ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ 13.9, 19.4, 30.7, 66.4, 66.5, 113.3, 125.4, 126.4, 129.0, 129.4, 130.8, 131.2, 132.2, 135.8, 167.4, 168.7 ppm.

Synthesis of 3, 4, and 4′ According to Scheme 2. A mixture of **9** (1.5 g, 2.3 mmol), perfluorooctyl iodide (2.5 mL, 9.2 mmol), and 3 g of copper bronze was stirred at 190 °C in 7.5 mL of DMSO in a sealed autoclave for 3 h. After cooling to room temperature, the reaction was quenched by addition of water and CH_2Cl_2, washed three times with water, dried over $MgSO_4$, and purified by silica gel column chromatography. Compounds **3** (0.55 g, 22%), **4** (0.44 g, 13%), and **4′** (0.35 g, 10%) were obtained.

Synthesis of 5. Compound **3** (1 g, 0.93 mmol) was added to 5 mL of stirring chlorosulfonic acid gradually and the mixture was stirred for 4 h at room temperature. Then the mixture was added to ice. After filtration, compound **5** was obtained as a brown solid (0.75 g, 100%). Mp > 300 °C; HRMS calcd for $C_{32}H_7O_6F_{17}$ 809.9971, found 810.0010 (M^-, MALDI-TOF); ^{1}H NMR (400 MHz, CF_3COOD) δ 8.45 (m, 1H), 8.61 (d, 1H), 8.70 (m, 3H), 8.74 (d, 1H), 8.90 ppm (s, 1H); ^{19}F NMR (376.5 MHz, $CDCl_3$) δ −126.30, −122.88, −121.97, −121.69, −121.26, −115.22, −97.88, −81.14 ppm; ^{13}C NMR (100 MHz, CF_3COOD) δ 119.6, 120.1, 120.2, 121.0, 125.6, 126.0, 126.2, 126.9, 127.3, 128.1, 129.7, 129.8, 129.9, 130.1, 131.8, 132.8, 133.6, 134.6, 135.0, 135.3, 135.4, 136.0, 136.4, 137.3, 138.2, 140.6 ppm.

Synthesis of 6. Compound **4** (1.8 g, 1.21 mmol) was added to 5 mL of stirring chlorosulfonic acid gradually and the mixture was stirred for 4 h at room temperature. Then the mixture was added to ice. After filtration, compound **6** was obtained as a brown solid (1.47 g, 100%). Mp 269−270 °C; HRMS calcd for $C_{40}H_6O_6F_{34}$ 1227.9621, found 1227.9598 (M^-, MALDI-TOF); ^{1}H NMR (400 MHz, CF_3COOD) δ 8.37 (m, 2H), 8.68 (d, 2H), 8.93 ppm (s, 2H); ^{19}F NMR (376.5 MHz, $CDCl_3$) δ −126.53, −123.10, −122.21, −121.96, −121.46, −116.17, −98.2, −81.14 ppm; ^{13}C NMR (100 MHz, CF_3COOD) δ 119.9, 120.2, 129.7, 129.8, 131.3, 134.6, 134.8, 135.1, 135.2, 138.2 ppm.

Synthesis of 6′. Compound **4′** (400 mg, 0.27 mmol) was added to 5 mL of stirring chlorosulfonic acid gradually and the mixture was stirred for 4 h at room temperature. Then the mixture was added to ice. After filtration, compound **6′** was obtained as a brown solid (330 mg, 100%). Mp 275−276 °C; HRMS calcd for $C_{40}H_6O_6F_{34}$ 1227.9621, found 1227.9637 (M^-, MALDI-TOF); ^{1}H NMR (400 MHz, CF_3COOD) δ 8.45 (m, 2H), 8.63 (d, 2H),

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(42) Mo, X.; Chen, H. Z.; Shi, M. M.; Wang, M. *Chem. Phys. Lett.* **2006**, *417*, 457–460.

(43) Yuan, Z.; Xiao, Y.; Qian, X. *Chem. Commun.* **2010**. DOI: 10.1039/b925605a.

8.96 ppm (s, 2H); ^{19}F NMR (376.5 MHz, $CDCl_3$) δ −126.47, −123.03, −122.12, −121.87, −121.48, −115.32, −98.92, −81.10 ppm; ^{13}C NMR (100 MHz, CF_3COOD) δ 122.0, 128.7, 131.1, 131.4, 132.3, 134.0, 134.7, 140.6 ppm.

Synthesis of 14 and 15. A mixture of KOH (1.4 g, 25 mmol), 200 mL of water, and a mixture of **12** and **13** (2.13 g) was stirred at room temperature for about 0.5 h, and then 1-bromobutane (5 mL, 46 mmol) and tetraoctyl ammonium bromide (2 g) were added to the reaction mixture. The reaction continued at reflux for another 3 h. After purification through silica gel chromatography (with a mixture of CH_2Cl_2 and petroleum ether as eluent), compounds **14** and **15** was obtained as a light yellow and viscous liquid.

14 (1 g, a29% overall yield for bromination and esterification): HRMS calcd for $C_{30}H_{39}O_8NaBr$ 629.1726, found 629.1710 ([M + Na]$^+$, ESI); ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.98 (m, 12H), 1.49 (m, 8H), 1.73 (m, 8H), 4.31 (m, 8H), 7.87 (d, 1H), 8.01 (d, 1H), 8.19 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 13.7, 19.2, 19.3, 30.3, 30.5, 65.7, 65.9, 66.0, 66.1, 121.2, 127.7, 128.9, 129.0, 129.7, 133.1, 133.3, 133.5, 134.2, 134.4, 166.7, 166.8, 167.6, 167.8 ppm.

15 (0.96 g, 24% overall yield for bromination and esterification): HRMS calcd for $C_{30}H_{38}O_8NaBr_2$ 707.0831, found 707.0846 ([M + Na]$^+$, ESI); ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.97 (m, 12H), 1.48 (m, 8H), 1.78 (m, 8H), 4.31 (t, 8H), 8.05 (d, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 13.7, 19.2, 19.3, 30.3, 30.4, 66.2, 121.2, 128.5, 132.8, 134.4, 134.5, 166.4, 166.5 ppm.

Synthesis of 16. A mixture of **14** (1.07 g, 1.76 mmol), perfluorooctyl iodide (1.1 mL, 4 mmol), and copper bronze (520 mg, 8.13 mmol) was stirred at 80 °C in 2 mL of DMSO for 7 h under argon. After purification through silica gel column chromatography, compound **16** was obtained as a light yellow and viscous oil (1.09 g, 66%). HRMS calcd for $C_{38}H_{39}O_8F_{17}Na$ 969.2271, found 969.2238 ([M + Na]$^+$, ESI); ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.95 (m, 12H), 1.46 (m, 8H), 1.77 (m, 8H), 4.30 (m, 8H), 7.85 (d, 1H), 8.12−8.15 (m, 2H); ^{19}F NMR (376.5 MHz, $CDCl_3$) δ −126.08, −122.66, −121.87, −121.69, −121.43, −177.91, −103.75, −80.74 ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ 13.8, 14.3, 19.1, 19.3, 22.9, 19.6, 29.9, 30.6, 32.1, 66.0, 66.2, 66.3, 67.0, 127.8, 128.4, 129.2, 130.3, 130.9, 133.0, 133.2, 135.0, 135.6, 166.7, 167.1, 167.5, 167.9 ppm.

Synthesis of 17. A mixture of **15** (0.66 g, 0.97 mmol), perfluorooctyl iodide (1.0 mL, 3.63 mmol), and copper bronze (750 mg, 11.7 mmol) was stirred at 80 °C in 2 mL of DMSO for 7 h under argon. After purification through silica gel column chromatography, compound **17** was yielded as a white solid (0.8 g, 61%). Mp 137−138 °C; HRMS calcd for $C_{46}H_{38}O_8F_{34}Na$ 1387.1921, found 1387.1970 ([M + Na]$^+$, ESI); ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.95 (m, 12H), 1.46 (m, 8H), 1.77 (m, 8H), 4.25 (t, 4H), 4.33 (t, 4H), 7.98 (s, 1H); ^{19}F NMR (376.5 MHz, $CDCl_3$) δ −126.07, −122.64, −121.85, −121.65, −121.39, −177.82, −103.97, −80.73 ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ 13.6, 19.0, 19.1, 29.7, 30.3, 66.6, 67.1, 127.3, 127.7, 129.6, 134.5, 134.6, 165.8, 166.6 ppm.

Synthesis of 18. A mixture of **16** (430 mg, 0.45 mmol), KOH (500 mg, 8.9 mmol), 0.5 mL of water, and 0.5 mL of *tert*-butyl alcohol was refluxed for 12 h. After washing with water, compound **18** was obtained as a white solid (286 mg, 92%). Mp 135−138 °C; HRMS calcd for $C_{22}H_3O_6F_{17}$ 685.9658, found 685.9640 (M$^-$, MALDI-TOF).

Synthesis of 19. A mixture of **17** (200 mg, 0.15 mmol), KOH (500 mg, 8.9 mmol), 0.5 mL of water, and 0.5 mL of *teert*-butyl alcohol was refluxed for 12 h. After washing with water, compound **19** was obtained as a white solid (140 mg, 86%). Mp > 300 °C; HRMS calcd for $C_{30}H_2O_6F_{34}$ 1103.9308, found 1103.9268 (M$^-$, MALDI-TOF).

General Procedure for the Synthesis of 7b, 7c, 7e, 8a−c, 8e−g, 8′e, Mixture of 11b and 11′b, Mixture of 11d and 11′d, 20a−d, and 21a−d. A mixture of **5**, **6**, **6′**, mixture of **10** and **10′**, **18**, or **19** and primary amine was stirred in propanoic acid at 100 °C or at the boiling point of the solvent for 2−3 h. After cooling to room temperature, precipitations were filtered for **8a** and **8g**. After adding water to the reaction mixture, precipitations were also filtered for the other target compounds. For **8g**, a filter cake was pure enough to be characterized by ^{1}H NMR was obtained. The other compounds were purified by silica gel column chromatography with CH_2Cl_2 as eluent. Only the synthesis of compounds **7b**, **8a**, **8′a**, mixture of **11b** and **11′b**, **20c**, and **21d** are listed here, and detailed syntheses of the other compounds are given in the Supporting Information.

7b: Compound **5** (0.26 g, 0.32 mmol), *n*-butylamine (0.5 mL, 5.0 mmol), and 12 mL of propanoic acid led to **7b** as a red solid (0.29 g, 0.31 mmol, 97%). Mp 245−247 °C; HRMS calcd for $C_{40}H_{26}N_2O_4F_{17}$ 921.1621, found 921.1653 (M$^+$, MALDI-TOF); ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.00 (m, 6H), 1.49 (m, 4H), 1.76 (m, 4H), 4.23 (m, 4H), 8.33 (m, 1H), 8.64 (m, 3H), 8.75 (d, 1H), 8.80 (d, 1H), 8.92 ppm (s, 1H); ^{19}F NMR (376.5 MHz, $CDCl_3$) δ −126.07, −122.62, −121.71, −121.47, −121.09, −114.76, −97.48, −80.71 ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ 13.8, 20.4, 30.2, 40.5, 122.6, 122.9, 123.8, 123.9, 124.1, 124.6, 126.7, 128.3, 128.4, 129.4, 130.1, 131.0, 131.7, 132.1, 132.2, 132.5, 133.1, 135.2, 137.7, 162.6, 163.1, 163.2, 163.4 ppm.

8a: Compound **6** (0.24 g, 0.20 mmol), 30% aqueous methylamine (0.5 mL, 4.8 mmol), and 15 mL of propanoic acid led to **8a** as a red solid (0.23 g, 0.18 mmol, 90%). Mp: 218−221 °C; HRMS calcd for $C_{42}H_{12}N_2O_4F_{34}$ 1254.0254, found 1254.0139 (M$^+$, MALDI-TOF); ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.25 (s, 6H), 8.31 (m, 2H), 8.76 (d, 2H), 9.00 ppm (s, 2H); ^{19}F NMR (376.5 MHz, $CDCl_3$) δ −126.13, −122.67, −121.80, −121.56, −121.10, −115.81, −98.14, −80.71 ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ 27.4, 123.1, 123.6, 126.8, 127.9, 128.3, 131.0, 131.3, 132.4, 132.5, 135.5, 162.7, 163.0 ppm.

8′e: Compound **6′** (0.20 g, 0.16 mmol), isooctylamine (0.5 mL, 3.0 mmol), and 10 mL of propanoic acid led to **8′e** as a brown solid (0.22 g, 95%). Mp 128−131 °C; HRMS calcd for $C_{56}H_{40}N_2O_4F_{34}$ 1450.2445, found 1450.2540 (M$^+$, MALDI-TOF); ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.85−1.00 (m, 12H), 1.20−1.60 (m, 16H), 2.01 (m, 2H), 4.17 (m, 4H), 8.40 (d, 2H), 8.70 (d, 2H), 9.02 (d, 2H); ^{19}F NMR (376.5 MHz, $CDCl_3$) δ −126.07, −122.61, −121.72, −121.49, −121.11, −114.82, −98.34, −80.69 ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ 10.8, 14.3, 23.3, 24.2, 28.9, 29.9, 30.9, 37.6, 44.7, 45.0, 122.4, 125.0, 126.6, 127.0, 127.6, 129.5, 129.8, 130.1, 130.2, 131.8, 133.0, 137.3, 162.7, 163.7 ppm.

Mixture of 11b and 11′b: A mixture of **10** and **10′** (300 mg, 0.57 mmol), *n*-butylamine (831 mg, 11.4 mmol), and 15 mL of propanoic acid led to a mixture of **11b** and **10′b** as a red solid (231 mg, 64%). Mp 282−283 °C; HRMS calcd for $C_{34}H_{24}N_2O_4F_6$ 638.1640, found 638.1636 (M$^+$, MALDI-TOF); ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.99 (m, 6H), 1.51 (m, 4H), 1.75 (m, 4H), 4.25 (t, 4H), 8.56 (d, 2H), 8.79 (d, 2H), 9.06 ppm (s, 2H); ^{19}F NMR (376.5 MHz, $CDCl_3$) δ −55.81 ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ 14.0, 20.5, 30.4, 40.9, 123.5, 123.9, 128.0, 128.7, 130.3, 132.0, 132.8, 134.0, 162.7, 162.9 ppm. Only NMR signals of the main regioisomer **11b** were given.

20c: Compound **18** (200 mg, 0.29 mmol), aniline (135 mg, 1.45 mmol), and 1 mL of propanoic acid led to **20c** as a white solid (223 mg, 92%). Mp > 300 °C; HRMS calcd for $C_{34}H_{13}N_2O_4F_{17}$ 836.0604, found 836.0536 (M$^+$, MALDI-TOF); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.33 (m, 4H), 7.55 (m, 6H), 8.95 (s, 2H), 9.07 ppm (s, 1H); ^{19}F NMR (376.5 MHz, $CDCl_3$) δ −126.31, −122.88, −122.03, −121.61, −121.47, −115.38, −98.77, −81.24 ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ 126.9, 127.0, 127.8, 128.3, 128.4, 128.5, 129.3, 129.5, 129.7, 131.0, 132.7, 133.3, 134.1, 134.5, 159.9, 161.9, 162.3 ppm.

21d: Compound **19** (200 mg, 0.18 mmol), *n*-octylamine (115 mg, 0.9 mmol), and 1 mL of propanoic acid led to **21d**

as a white solid (190 mg, 80%). Mp 129−131 °C; HRMS calcd for $C_{46}H_{36}N_2O_4F_{34}$ 1326.2132, found 1326.2172 (M^-, MALDI-TOF); ^1H NMR (400 MHz, $CDCl_3$) δ 0.87 (m, 6H), 1.27−1.41 (m, 20H), 1.74 (m, 4H), 4.10 (m, 4H), 9.10 ppm (s, 2H); ^{19}F NMR (376.5 MHz, $CDCl_3$) δ −126.00, −122.57, −121.73, −121.33, −114.81, −98.73, −80.71 ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ 14.0, 22.6, 27.0, 27.9, 29.2, 29.7, 31.8, 41.7, 127.3, 127.7, 128.9, 131.4, 131.5, 134.9, 159.3, 160.7 ppm.

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Supporting Information Available: HPLC spectrum of **15**; detailed synthesis of **7c**, **7e**, **8b**, **8c**, **8e**, **8f**, **8g**, mixture of **11d** and **11′d**, **20a**, **20b**, **20d**, and **21a−c**; cyclovoltammograms of **7b**, **7c**, **8b**, **8e**, mixture of **11d** and **11′d**, **20a−c**, and **21a**; HOMO and LUMO electron density and theoretical HOMO energy of **7b**, **7c**, **7e**, **8b**, 8c, **8e**, **11b**, **11d**, RPDIs, **20a−d**, **21a**, and **21b**; absorption and fluorescence emission spectrum of **7c**, **8b**, and **8c**; absorption spectrum of **20d**; and copies of NMR spectra. This material is available free of charge via the Internet at http://pubs.acs.org.