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Synthesis and Photophysical Properties of Pyrrole/Polycyclic Aromatic Units Hybrid Fluorophores

Chang-Shun Li, Ya-Hsuan Tsai, Wei-Chen Lee, and Wen-Jang Kuo*

Department of Applied Chemistry, National University of Kaohsiung, Kaohsiung, Taiwan 811

wjkuo@nuk.edu.tw

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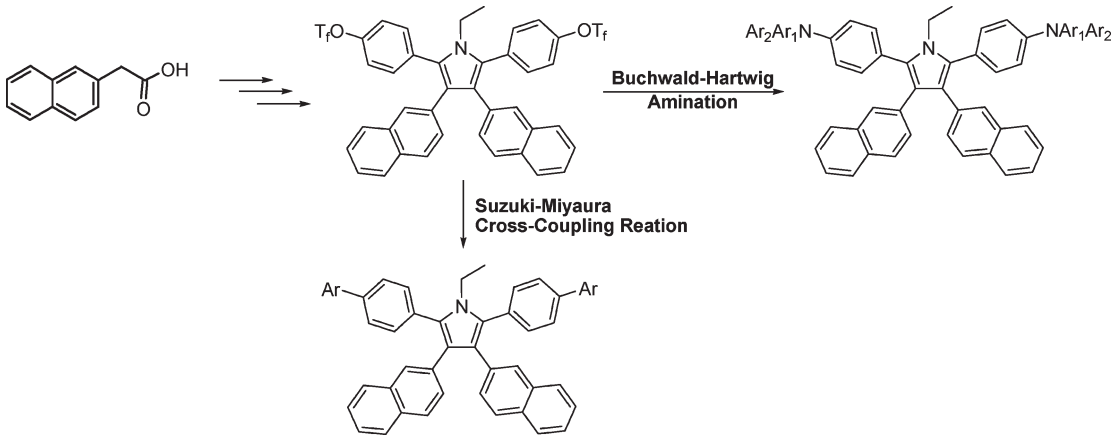

A series of pyrrole/polycyclic aromatic unit hybrid fluorophores was developed by a two-stage synthetic strategy. Their central aryl-substituted pyrrole cores were constructed by a Paal−Knorr pyrrole synthesis reaction. The reaction conditions and mechanism are also discussed in detail. End-capping triflate onto the central pyrrole core enables the core to incorporate various polycyclic aromatic units. The Buchwald−Hartwig amination reaction and the Suzuki−Miyaura cross-coupling reaction were adopted to incorporate the triflate end-capping pyrrole with *N*-phenylnaphthalen-1-amine and various polycyclic aromatic units to form the hybrid fluorophores. The photophysical properties and thermal properties of the fluorophores were characterized. Most of the pyrrole fluorophores emitted blue light and exhibited high quantum efficiency. The fluorescence properties of these pyrrole fluorophores were induced by manipulating the surrounding polycyclic aromatic units. When the central pyrrole core was incorporated with amino or naphthalene moieties, the fluorescence efficiency and thermal stability of fluorophores **1** and **2** were low ($\phi_f < 0.35$, $T_g < 140$ °C). Rigid and highly fluorescent moieties (such as pyrenyl, 9,9-dimethylfluorenyl, 9,9-diphenylfluorenyl, and spirofluorenyl groups) were grafted onto the pyrrole. Fluorophores **3**−**6** had high fluorescence efficiency ($\phi_f > 0.99$) and stable glassy morphology (the T_g value of the fluorophore **6** was as high as 220 °C). Results of this study demonstrate that the sterically induced fluorescence of crowded pyrrole and the fluorescent polycyclic aromatic units significantly affect the emission properties of the hybrid fluorophores.

Introduction

Organic materials have been extensively applied in light-emitting diodes because of their versatility and color-tunability. Quantum efficiency, film-forming properties, and temporal stability of the fluorophores remain challenges in science and engineering. To improve the aforementioned fluorescence and film-forming properties, fluorophores were introduced as sterically crowded substituents on their periphery[1] or made into starburst- and dendron-type conjugated molecules.[2] Such congested structures prevent these compounds from their aggregation/excimer formation and render them strong emission and amorphous characteristics in the film state.[1d,2a,3] A variety of palladium-catalyzed reactions, such as Suzuki−Miyaura cross-coupling,[1b,d,4] Stille cross-coupling,[5] and Buchwald−Hartwig amination,[6] are used to construct the congested structures. However, the Pd-catalyzed coupling reaction has some limitations.[1a,7] The first is that a large amount of palladium

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catalyst and excess arylboronic acids are required to form the multifunctionalized fluorophores. The Pd-catalyzed arylation reaction is a useful tool for mono- or difunctionalization with little steric effect. As the amount of steric substituents increases, the coupling reaction is inhibited. Therefore, more palladium and arylboronic acid are required to increase the coupling yield. Another question regarding the palladium-catalyzed arylation reaction concerns the purification of the multifunctionalized products. One or two substituents were introduced to the periphery of the central core in a palladium-catalyzed coupling reaction; products can be obtained in high yield and purified easily.[1a,4a,b,8] As the amount of peripheral aryl substituents increases, the activity of the arylation reaction decreases, and some byproducts with fewer substituents appear. The target product is difficult to isolate from these side products. This reaction is less effective than the preceding one in forming asymmetric aryl substituents on the periphery of the structure. To solve the aforementioned problems, Paal−Knorr condensation was used in the laboratory to generate a variety of asymmetric aryl-substitued pyrroles.[9] Not only do these fluorophores produce fluorescence in the solid state, but also their intrinsic electrical, optical, and morphological properties can be tuned by modifying the peripheral aryl groups. To increase the fluorescence efficiency, some fluorescence-active polycyclic aromatic units such as fluorene, pyrene, and hole-transporting moieties, such as diarylamine, are introduced. The trflate-capping pyrrole is the key intermediate to incorporate with these fluorescence-active polycyclic aromatic units and hole-transporting moieties. Aryl triflates are a very attractive alternative to aryl halides in the palladium-catalyzed reaction.[10] They can be easily synthesized from readily available phenolic derivatives.[11] Aryl triflate has been widely adopted to extend the aromatic ring in a palladium-catalyzed reaction. However, few works have been published on the synthesis of fluorescent materials.

In this work, a two-stage synthetic strategy is adopted to generate a variety of asymmetric pyrrole/polycyclic aromatic unit hybrid fluorophores. The factors that affect and the optimal conditions for the Paal−Knorr condensation reaction that yields the aryl-substituted pyrrole core are discussed herein. The pyrrole core was further transformed into triflate end-capping pyrrole. Many palladium-catalyzed coupling reactions were further examined by incorporating with a series of polycyclic aromatic units into the triflate end-capping pyrrole core.

Results and Discussion

Synthesis. Chart 1 presents the chemical structure of the pyrrole/polycyclic aromatic units' hybrid fluorophores. In this work, Paal−Knorr condensation was adopted to construct a functionalized aryl-substituted pyrrole core as a key intermediate **11b**. The methoxy-capping pyrrole **11b** was hydrated and further formed triflate end-capping pyrrole **12b**. Incorporating *N*-phenylnaphthalen-1-amine or the synthesized aromatic boronic acids **13**−**17** into the triflate **12b** by the Buchwald−Hartwig amination reaction or the Suzuki−Miyaura cross-coupling reaction yielded pyrrole/polycyclic aromatic units hybrid fluorophores **1**−**6**.

(1) (a) Huang, D. F.; Moorthy, J. M.; Natarajan, P.; Venkatakrishnan, P.; Chow, T. J. *Org. Lett*. **2007**, *25*, 5215–5218. (b) Huang, W.; Tang, C.; Liu, F.; Xia, Y. J.; Xie, L. H.; Wei, A.; Li, S. B.; Fan, Q. L. *J. Mater. Chem*. **2006**, *16*, 4074–4080. (c) Yu, G.; Jiao, S. B.; Liao, Y.; Xu, X. J.; Wang, L. P.; Wang, L. M.; Su, Z. M.; Ye, S. H.; Liu, L. Q. *Adv. Funct. Mater*. **2008**, *18*, 2335–2347. (d) Shen, W. J.; Dodda, R.; Wu, C. C.; Wu, F.; Liu, T. H.; Chen, H. H.; Chen, Ch. H.; Shu, C. F. *Chem. Mater*. **2004**, *16*, 930–934. (e) Lee, J.; Liu, Q. D.; Bai, D. R.; Kang, Y.; Tao, Y.; Wang, S. *Organometallics* **2004**, *23*, 6205–6213. (f) Chen, C. T.; Chiang, C. L.; Lin, Y. C.; Chan, L. H.; Huang, C. H.; Tsai, Z. W.; Chen, C. T. *Org. Lett*. **2003**, *5*, 1261–1264.

(2) (a) Setayesh, S.; Grimsdale, A. C.; Weil, T.; Enkelmann, V.; Mu1llen, K.; Meghdadi, F.; List, E. J. W.; Leising, G. *J. Am. Chem. Soc*. **2001**, *123*, 946–953. (b) Gronheid, R.; Hofkens, J.; Kohn, F.; Weil, T.; Reuther, E.; Müllen, K.; De Schryver, F. C. *J. Am. Chem. Soc*. **2002**, *124*, 2418–2419. (c) Freeman, A. W.; Koene, S. C.; Malenfant, P. R. L.; Thompson, M. E.; Frechet, J. M. J. *J. Am. Chem. Soc*. **2000**, *122*, 12385–12386. (d) Justin Thomas, K. R.; Thompson, A. L.; Sivakumar, A. V.; Bardeen, C. J.; Thayumanavan, S. *J. Am. Chem. Soc*. **2005**, *127*, 373–383. (e) Kwon, T. W.; Alam, M. M.; Jenekhe, S. A. *Chem. Mater*. **2004**, *16*, 4657–4666. (f) Chen, C. H.; Lin, J. T.; Yeh, M. C. P. *Org. Lett*. **2006**, *8*, 2233–2236. (g) Lupton, J. M.; Samuel, I. D. W.; Beavington, R.; Burn, P. L.; Bassler, H. *Adv. Mater*. **2001**, *13*, 258–261. (h) Lo, S. C.; Male, N. A. H.; Markham, J. P. J.; Magennis, S. W.; Burn, P. L.; Salata, O. V.; Samuel, I. D. W. *Adv. Mater*. **2002**, *14*, 975–979. (i) Anthopoulos, T. D.; Frampton, M. J.; Namdas, E. B.; Burn, P. L.; Samuel, I. D. W. *Adv. Mater*. **2004**, *16*, 557–560.

(3) (a) Gensch, T.; Hofkens, J.; Heirmann, A.; Tsuda, K.; Verheijen, W.; Vosch, T.; Crist, T.; Basche, T.; Mullen, K.; De Schryver, F. C. *Angew. Chem., Int. Ed*. **1999**, *38*, 3752–3756. (b) Pogantsch, A.; Wenl, E. G.; List, E. J. W.; Leising, G.; Mullen, K. *Adv. Mater*. **2002**, *14*, 1061–1064. (c) Wu, R. L.; Schumm, J. S.; Pearson, D. L.; Tour, J. M. *J. Org. Chem*. **1996**, *61*, 6906–6921. (d) Tour, J. M.; Wu, R.; Schumm, J. S. *J. Am. Chem. Soc*. **1990**, *112*, 5662–5663. (e) Wong, K. T.; Chien, Y. Y.; Chen, R. T.; Wang, C. F.; Lin, Y. T.; Chiang, H. H.; Hsieh, P. Y.; Wu, C. C.; Chou, C. H.; Su, Y. O.; Lee, G. H.; Peng, S. M. *J. Am. Chem. Soc*. **2002**, *124*, 11576–11577. (f) Xia, C. J.; Advincula, R. C. *Macromolecules* **2001**, *34*, 5854–5859. (g) Steuber, F.; Staudigel, J.; Stossel, M.; Simmerer, J.; Winnacker, A.; Spreitzer, H.; Weissortel, F.; Salbeck, J. *Adv. Mater*. **2000**, *12*, 130–133. (h) Oldham, W. J., Jr.; Lachicotte, R. J.; Bazan, G. C. *J. Am. Chem. Soc*. **1998**, *120*, 2987–2988.

(4) (a) Kanibolotsky, A. L.; Berridge, R.; Skabara, P. J.; Perepichka, I. F.; Bradley, D. D. C.; Koeberg, M. *J. Am. Chem. Soc*. **2004**, *126*, 13695–13702. (b) Sonntag, M.; Kreger, K.; Hanft, D.; Strohriegl, P. *Chem. Mater*. **2005**, *17*, 3031–3039. (c) Lyu, Y. Y.; Kwak, J.; Jeon, W. S.; Byun, Y.; Lee, H. S.; Kim, D.; Lee, C.; Char, K. *Adv. Funct. Mater*. **2009**, *19*, 420–427. (d) Culligan, S. W.; Chen, A. C. A.; Wallace, J. U.; Klubek, K. P.; Tang, C. W.; Chen, S. H. *Adv. Funct. Mater*. **2006**, *16*, 1481–1487. (e) Geng, Y.; Katsis, D.; Culligan, S. W.; Ou, J. J.; Chen, S. H.; Rothberg, L. J. *Chem. Mater*. **2002**, *14*, 463–470.

(5) (a) Sotgiu, G.; Zambianchi, M.; Barbarella, G.; Aruffo, F.; Cipriani, F.; Ventola, A. *J. Org. Chem*. **2003**, *68*, 1512–1520. (b) Su, Y. Z.; Lin, J. T.; Tao, Y. T.; Ko, C. W.; Lin, S. C.; Sun, S. S. *Chem. Mater*. **2002**, *14*, 1884–1890. (c) Barbarella, G.; Favaretto, L.; Zanelli, A.; Gigli, G.; Mazzeo, M.; Anni, M.; Bongini, A. *Adv. Funct. Mater*. **2005**, *15*, 664–670. (d) Radke, K. R.; Ogawa, K.; Rasmussen, S. C. *Org. Lett*. **2005**, *7*, 5253–5256.

(6) (a) Lee, Y. T.; Chiang, C. L.; Chen, C. T. *Chem. Commun*. **2008**, 217–219. (b) Palayangoda, S. S.; Cai, X.; Adhikari, R. M.; Neckers, D. C. *Org. Lett*. **2008**, *10*, 281–284. (c) Lai, M. Y.; Chen, C. H.; Huang, W. S.; Lin, J. T.; Ke, T. H.; Chen, L. Y.; Tsai, M. H.; Wu, C. C. *Angew. Chem., Int. Ed*. **2008**, *47*, 581–585. (d) Huang, T. H.; Lin, J. T.; Chen, L. Y.; Lin, Y. T.; Wu, C. C. *Adv. Mater*. **2006**, *18*, 602–606. (e) Shen, J. Y.; Yang, X. L.; Huang, T. H.; Lin, J. T.; Ke, T. H.; Chen, L. Y.; Wu, C. C.; Yeh, M. C. P. *Adv. Funct. Mater*. **2007**, *17*, 983–995.

(7) (a) Dang, T. T.; Ahmad, R.; Dang, T. T.; Reinke, H.; Langer, P. *Tetrahedron Lett*. **2008**, *49*, 1698–1700. (b) Sun, X.; Liu, Y.; Chen, S.; Qiu, W.; Yu, G.; Ma, Y.; Qi, T.; Zhang, H.; Xu, X.; Zhu, D. *Adv. Funct. Mater*. **2006**, *16*, 917–925.

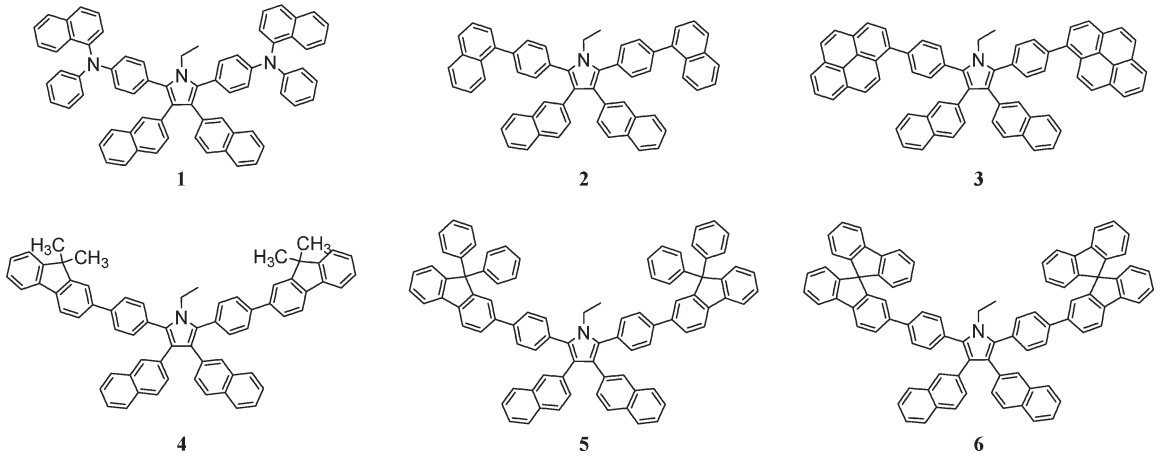
(8) (a) Tao, S.; Peng, Z.; Zhang, X.; Wang, P.; Lee, C. S.; Lee, S. T. *Adv. Funct. Mater*. **2005**, *15*, 1716–1721. (b) Li, Y.; Ding, J.; Day, M.; Tao, Y.; Lu, J.; D'iorio, M. *Chem. Mater*. **2004**, *16*, 2165–2173. (c) Kim, Y. H.; Shin, D. C.; Kim, S. H.; Ko, C. H.; Yu, H. S.; Chae, Y. S.; Kwon, S. K. *Adv. Mater*. **2001**, *13*, 1690–1693. (d) Wu, Q.; Lavigne, J. A.; Tao, Y.; D'Iorio, M.; Wang, S. *Chem. Mater*. **2001**, *13*, 71–77.

(9) Kuo, W. J.; Chen, Y. H.; Jeng, R. J.; Chan, L. H.; Lin, W. P.; Yang, Z. M. *Tetrahedron* **2007**, *63*, 7086–7096.

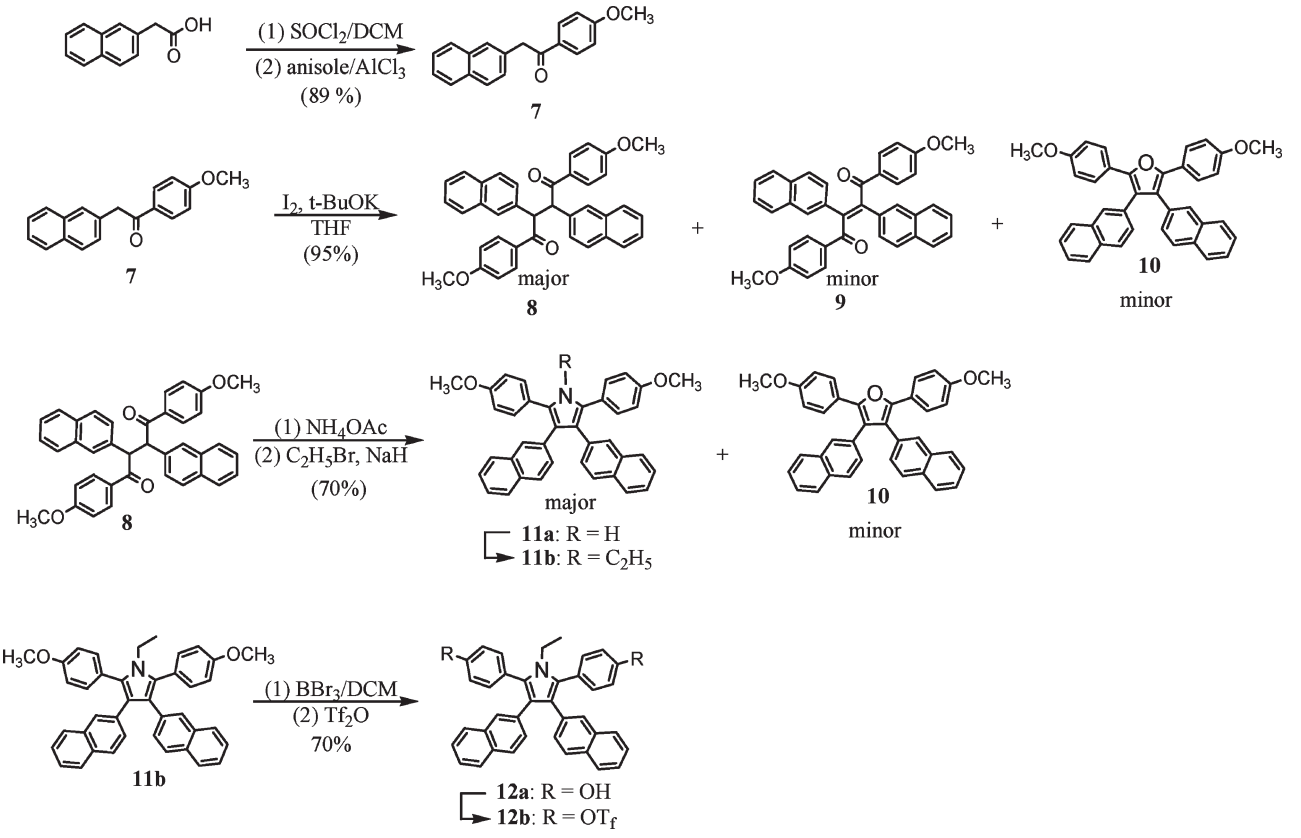
(10) (a) Miyaura, N.; Suzuki, A. *Chem. Rev*. **1995**, *95*, 2457–2483. (b) Oh-e, T.; Miyaura, N.; Suzuki, A. *Synlett* **1990**, 221. (c) Oh-e, T.; Miyaura, N.; Suzuki, A. *J. Org. Chem*. **1993**, *58*, 2201–2208. (d) Riggleman, S.; DeShong, P. *J. Org. Chem*. **2003**, *68*, 8106–8109. (e) Seganish, W. M.; DeShong, P. *J. Org. Chem*. **2004**, *69*, 1137–1143. (f) Furstner, A.; Grabowski, J.; Lehmann, C. W. *J. Org. Chem*. **1999**, *64*, 8275–8280. (g) Bringmann, G.; Götz, R.; Keller, P. A.; Walter, R.; Boyd, M. R.; Lang, F.; Garcia, A.; Walsh, J. J.; Tellitu, I.; Bhaskar, K. V.; Kelly, T. R. *J. Org. Chem*. **1998**, *63*, 1090–1097. (h) Malapel-Andrieu, B.; Merour, J.-Y. *Tetrahedron* **1998**, *54*, 11079–11094.

(11) (a) Littke, A. F.; Dai, C.; Fu, G. C. *J. Am. Chem. Soc*. **2000**, *122*, 4020–4028. (b) Marion, N.; Navarro, O.; Mei, J.; Stevens, E. D.; Scott, N. M.; Nolan, S. P. *J. Am. Chem. Soc*. **2006**, *128*, 4101–4111.

CHART 1. Chemical Structures of the Pyrrole/Polycyclic Aromatic Unit Hybrid Fluorophores



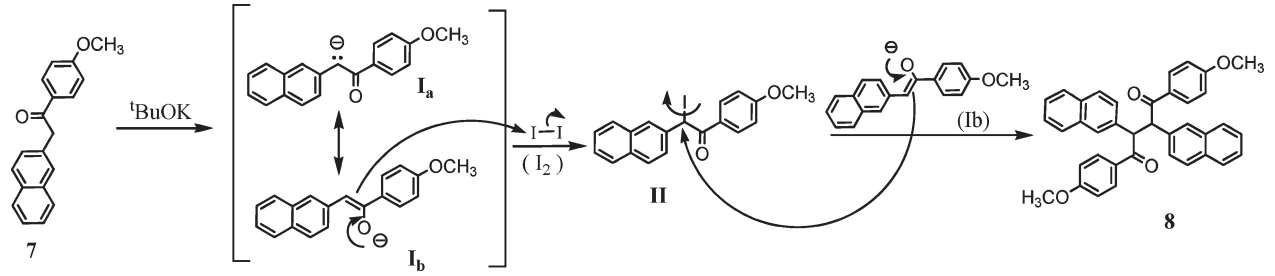
SCHEME 1. Synthesis of the Triflate End-Capping Pyrrole 12b



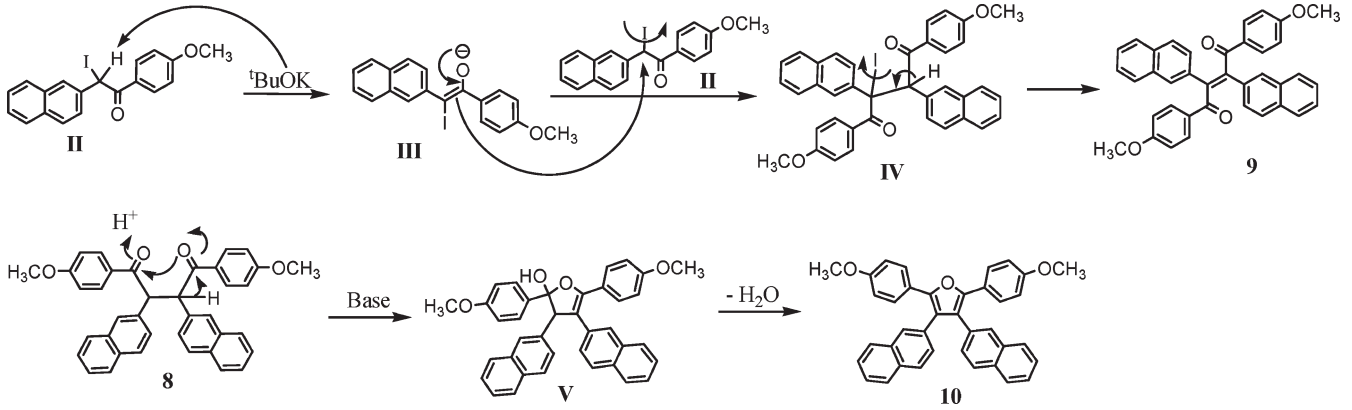
Scheme 1 presents the route for synthesizing the triflate end-capping pyrrole **12b**. In the first step, anisole was incorporated into 2-naphthylacetic acid chloride, which was synthesized from 2-naphthylacetic acid or purchased commercially, using the Friedel−Crafts acylation to yield intermediate **7**. Base ^{t}BuOK and I_2 were used to dimerize **7** and thus obtain intermediate **8**. Notably, the yield of the dimerization depended strongly on the doses of I_2 and ^{t}BuOK and on the reaction time.

Scheme 2 shows the mechanism by which intermediate **8** is formed. In the general procedure, equivalent base ^{t}BuOK abstracted the α-H of **7** to yield resonance forms $\mathbf{I_a}$ and $\mathbf{I_b}$. The intermediates $\mathbf{I_a}$ and $\mathbf{I_b}$ reacted with 0.5 equiv of I_2 and afforded 0.5 equiv of **II**. The intermediate **II** further reacted with the remaining 0.5 equiv of $\mathbf{I_b}$ to yield **8**. However, excess base and I_2 decrease the yield of intermediate **8**. A large amount of intermediate **II** and a few of byproducts of **10** were obtained when 0.5 equiv of I_2 and an excessive amount of base was added. Moreover, large amounts of byproduct **9** generate when excess I_2 and base were added. Scheme 3 proposes the mechanism of the formation of the side products. Intermediate **II** further reacted with excess ^{t}BuOK to generate **III**. The intermediate formation inhibited the enolate $\mathbf{I_b}$ to react with **II** when an excessive amount of base was

SCHEME 2. Formation Mechanism of Intermediate 8



SCHEME 3. Mechanism of the Formation of the Side Product



added. Once an excess of I_2 ($I_2 > 0.5$ equiv) was added in the reaction, a competition reaction between enolates **III** and $\mathbf{I_b}$ to react with **II** led to formation of the byproduct **9**. Lengthening the reaction time also caused intermediate **8** to undergo Paar−Knorr furan cyclization to yield byproduct **10**. Experimental results indicate that the optimal conditions for the synthesis of intermediate **8** are refluxing the intermediate **7** with 1 equiv of ^{t}BuOK and 0.5 equiv of I_2 in THF solution for 4 h.

Intermediate **8** further reacted with ammonium acetate and acetic acid by the Paal−Knorr condensation reaction to afford pyrrole intermediate **11a** (See Scheme 1). The competitive Paal−Knorr furan condensation reaction also proceeded, generating the byproduct **10**. The concentration of ammonium acetate in acetic acid is a key factor in the inhibition of the side reaction. Reaction of intermediate **8** with saturated ammonium acetate solution yielded the greatest possible amount of the pyrrole intermediate **11a**. To prevent the high activity of N−H in the following reaction and to improve the fluorescent characteristics, pyrrole **11a** was ethylated under strong base NaH and bromoethane to yield intermediate **11b**. To transform the methoxy end-capping pyrrole **11b** into a hydroxyl form, attempts were made to apply various demethylation methods. Simple methods based on Lewis acid $AlCl_3$ in toluene[12] or HBr in HOAc[13] gave a low yield of demethylated product, despite many trials. Demethylation of **11b** with BBr_3 in CH_2Cl_2 at −78 °C gave the corresponding phenolic intermediate **12a** in an excellent yield (~99%).[14] The crude phenolic intermediate **12a** was directly esterified with triflic anhydride in CH_2Cl_2 at 0 °C to give triflate end-capping pyrrole **12b** in 70% isolated yield (two steps). Palladium-catalyzed Suzuki cross-coupling was adopted to incorporate the triflate end-capping pyrrole **12b** with the aromatic boronic acids **13**−**17** to yield the hybrid fluorophores **2**−**6**.

Aromatic boronic acids, pyreneboronic acid **14**, and 9,9′-spirobifluorenylboronic acid **17** were purchased commercially. 2-Naphthylboronic acid **13**, 9,9′-dimethylfluorenylboronic acid **15**, and 9,9′-diphenylfluorenylboronic acid **16** were synthesized as described in the literature.[8b,15] The detailed synthetic route and experiment are depicted in the Supporting Information (see Scheme S1).

To establish an efficient protocol for Suzuki−Miyaura cross-coupling, several ligands and reaction conditions were adopted in the reaction between bistriflate **12b** and naphthylboronic acid **13**. Table 1 lists the reaction conditions of the Suzuki−Miyaura cross coupling under argon atmosphere. Phosphine ligands PCy_3[10c,11a] and SPhos[16] were applied under various conditions in the reaction between 1-naphthylboronic acid and bistriflate **12b**, but the coupling yield was low.

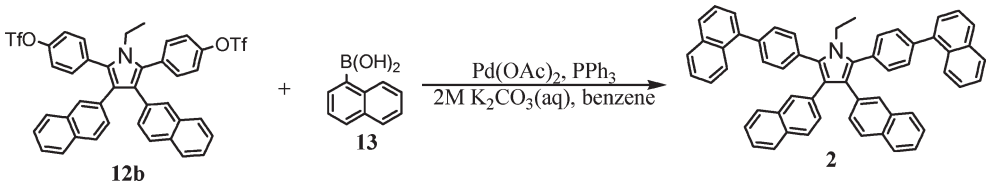
(12) (a) Mensonides−Harsema, M. M.; Liao, Y.; Böttcher, H.; Bartoszyk, G. D.; Greiner, H. E.; Jürgen Harting, P.; de Boer; Wikström, H. V. *J. Med. Chem.* **2000**, *43*, 432–439. (b) Lednicer, D.; Grostic, M. F. *J. Org. Chem.* **1967**, *32*, 3251–3253.

(13) (a) Reichwagen, J.; Hopf, H.; Guerzo, A.; Belin, C.; Bouas−Laurent, H.; Desvergne, J. P. *Org. Lett.* **2005**, *7*, 971–974. (b) Sittisombut, C.; Boutefnouchet, S.; Trinhvan−Dufat, H.; Tian, W.; Michel, S.; Koch, M.; Tillequin, F.; Pfeiefer, B.; Pierre, A. *Chem. Pharm. Bull.* **2006**, *54*, 1113–1118. (c) Grethe, G.; Toome, V.; Lee, H. L.; Uskokovic, M.; Brossi, A. *J. Org. Chem.* **1968**, *33*, 504–508.

(14) Kawaguchi, K.; Nakano, K.; Nozaki, K. *Org. Lett.* **2008**, *10*, 11991–202.

(15) (a) Katsis, D.; Geng, Y. H.; Ou, J. J.; Culligan, S. W.; Trajkovska, A.; Chen, S. H.; Rothberg, L. J. *Chem. Mater.* **2002**, *14*, 1332–1339. (b) Li, Z. H.; Wong, M. S.; Fukutani, H.; Tao, Y. *Chem. Mater.* **2005**, *17*, 5032–5040. (c) Rehahn, M.; Schluter, A. D.; Wegner, G.; Feast, W. J. *Polymer* **1989**, *30*, 1060–1062. (d) Vahlenkamp, T.; Wegner, G. *Macromol. Chem. Phys.* **1994**, *195*, 1933–1952. (e) Ding, J.; Day, M.; Robertson, G.; Roovers, J. *Macromolecules* **2002**, *35*, 3474–3483. (f) Li, Z. H.; Wong, M. S.; Tao, Y.; Lu, J. *Chem.—Eur. J.* **2005**, *11*, 3285–3293.

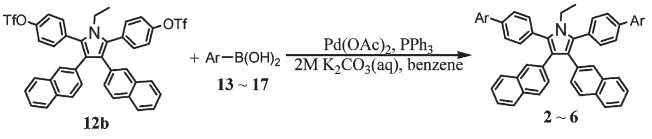
TABLE 1. Screen of Ligands and Bases for Suzuki−Miyaura Cross-Coupling Reactions of Naphthalen-1-yl-1-boronic Acid with Triflate 12b[a]

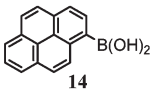
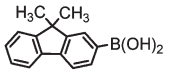
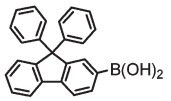
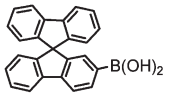


entry	Pd	ligand	base (6 equiv)	temp (°C)	solvent	yield[b] (%)
1	$Pd(OAc)_2$	PCy_3	KF	rt	THF	trace
2	$Pd(OAc)_2$	PCy_3	KF	40	THF	trace
3	$Pd(OAc)_2$	PCy_3	KF	reflux	THF	trace
4	$Pd(OAc)_2$	SPhos	K_3PO_4	rt	THF	trace
5	$Pd(OAc)_2$	PPh_3	K_2CO_3	reflux	benzene	74

[a]Reaction conditions: 1 equiv of aryl trflate **12b**, 2.5 equiv of boronic acid, 6 equiv of base, 2 mol % of $Pd(OAc)_2$, and 9 mol % of ligand. [b]Isolated yield based upon an average of two runs.

TABLE 2. Suzuki−Miyaura Cross-Coupling Reactions of Arylboronic Acid with Triflate 12b[a]

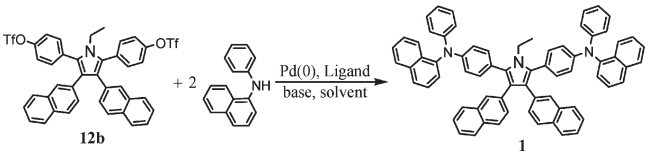


entry	Ar-OT_f	Aryl boronic acid	Product	Yield (%)[b]
1	**12b**	 **13**	**2**	74
2	**12b**	 **14**	**3**	70
3	**12b**	 **15**	**4**	79
4	**12b**	 **16**	**5**	72
5	**12b**	 **17**	**6**	82

[a]Reaction conditions: 1 equiv of aryl trflate **12b**, 2.5 equiv of boronic acid, 6 equiv of base, 2 mol % of $Pd(OAc)_2$, and 9 mol % of ligand. [b]Isolated yield based upon an average of two runs.

The highest yield of 70% was obtained when 2 mol % of $Pd(OAc)_2$, 9 mol % of triphenylphosphine, and 6 equiv of K_2CO_3 (2 M) were used as the base in a heterogeneous solution of benzene and degassed water.[17]

TABLE 3. Screen of Ligands and Bases for Buchwald−Hartwig Amination Reactions of Triflate 12b[a]



entry	Pd(0)	ligand	base	solvent	yield[b] (%)
1	$Pd_2(dba)_3$	$P(tBu)_3$	tBuONa	toluene	trace
2	$Pd_2(dba)_3$	DPPF	tBuONa	toluene	trace
3	$Pd_2(dba)_3$	BINAP	tBuONa	toluene	10
4	$Pd_2(dba)_3$	$BPCy_2$	tBuONa	toluene	70

[a]Reaction conditions: 1 equiv of aryl trflate **12b**, 2.05 equiv of amine, 2 equiv of base, 3 mol % of Pd_2dba_3, and 6 mol % of ligand. [b]Isolated yield based upon an average of two runs.

Table 2 presents the synthesis of target fluorophores via a Suzuki−Miyaura cross-coupling reaction. All of the fluorophores dissolved in common organic solvents such as *n*-hexane, toluene, CH_2Cl_2, and acetonitrile. Therefore, they were purified by silica gel column chromatography and characterized using ^1H and ^{13}C NMR spectroscopy as well as HRMS.

To establish another efficient method for the production of fluorophores **1** by Buchwald−Hartwig amination, various ligands were used in the coupling of bistriflate **12b** with *N*-naphthyl-*N*-phenylamine.[14,16a,18] Table 3 presents the Buchwald−Hartwig amination of the bistriflate **12b** with *N*-naphthyl-*N*-phenylamine examined in the presence of 3 mol % of $Pd_2(dba)_3$, 9 mol % of ligand, and 2 equiv of ^{t}BuONa in toluene solution. The amination with ligands $P(tBu)_3$,[6c−e,19] DPPF,[20] and BINAP[21] is inefficient. The

(16) (a) Martin, R.; Buchwald, S. L. *Acc. Chem. Res.* **2008**, *41*, 1461–1473. (b) Barder, T. E.; Walker, S. D.; Martinelli, J. R.; Buchwald, S. L. *J. Am. Chem. Soc.* **2005**, *127*, 4685–4696. (c) Barder, T. E.; Buchwald, S. L. *Org. Lett.* **2007**, *9*, 137–139. (e) Billingsley, K.; Buchwald, S. L. *J. Am. Chem. Soc.* **2007**, *129*, 3358–3366.

(17) Bouchard, J.; Wakim, S.; Leclerc, M. *J. Org. Chem.* **2004**, *69*, 5705–5711.

(18) (a) Wolfe, J. P.; Tomori, H.; Sadighi, J. P.; Yin, J.; Buchwald, S. L. *J. Org. Chem.* **2000**, *65*, 1158–1174. (b) Anderson, K. W.; Mendez-Perez, M.; Priego, J.; Buchwald, S. L. *J. Org. Chem.* **2003**, *68*, 9563–9573. (c) Tundel, R. E.; Anderson, K. W.; Buchwald, S. L. *J. Org. Chem.* **2006**, *71*, 430–433. (d) Rostovtsev, V. V.; Bryman, L. M.; Junk, C. P.; Harmer, M. A.; Carcani, L. G. *J. Org. Chem.* **2008**, *73*, 711–714.

(19) (a) Thomas, K. R. J.; Lin, J. T.; Tao, Y. T.; Ko, C. W. *J. Am. Chem. Soc.* **2001**, *123*, 9404–9411. (b) Yamamoto, T.; Nishiyama, M.; Koie, Y. *Tetrahedron Lett.* **1998**, *39*, 2367–2370. (c) Hartwig, J. F. *Angew. Chem., Int. Ed.* **1998**, *37*, 2046–2067.

(20) (a) Louie, J.; Driver, M. S.; Hamann, B. C.; Hartwig, J. F. *J. Org. Chem.* **1997**, *62*, 1268–1273. (b) Li, J.; Ma, C.; Tang, J.; Lee, C. S.; Lee, S. *Chem. Mater.* **2005**, *17*, 615–619.

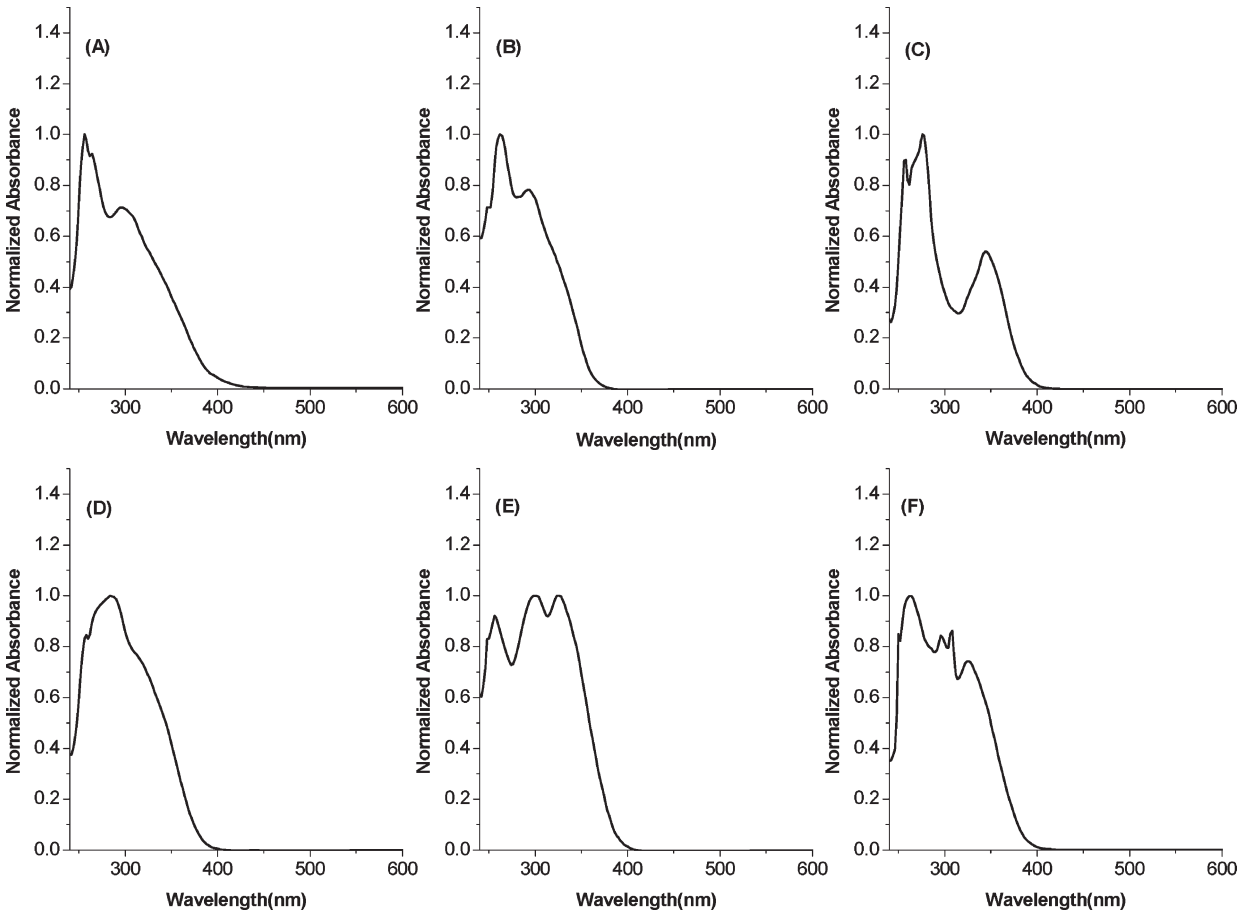


FIGURE 1. Absorption spectra of the hybrid fluorophores **1** (A), **2** (B), **3** (C), **4** (D), **5** (E), and **6** (F) in ethyl acetate. The concentrations were controlled in 1×10^{-5} M.

steric effect of the secondary amine and bulky triflate restrict the formation of fluorophore **1**.[20a,21a] The more active catalyst $BPCy_2$ gives a high yield.[22] The fluorophore **1** was also dissolved in common organic solvents, purified by silica gel column chromatography, and then characterized using ^1H and ^{13}C NMR spectroscopy as well as HRMS.

Photophysical Properties. Figure 1 shows the absorption spectra of the hybrid fluorophores **1**−**6** in ethyl acetate. The absorption around 286 nm was caused by the $\pi-\pi^*$ excitation of the pyrrole cores,[9] and the longest absorption around 290−350 nm was caused by the $\pi-\pi^*$ excitation of the hybrid fluorophores. As shown in Figure 1, the maximum absorption wavelength of the hybrid fluorophores was greatly shifted by the terminal polycyclic aromatic units. Introducing arylamino or naphthylenyl groups to the terminus gave the shortest maximum absorption wavelength of fluorophores **1** and **2**, of 292−296 nm. As the terminal polycyclic aromatic unit such as pyrene, or fluorene, was introduced, the maximum absorption wavelength of the fluorophores **4**−**6** was red-shifted to 320−340 nm.

Table 4 summarizes the absorption wavelength and the corresponding molar extinction coefficient, which was determined by linear regression of the data using Beer's law (see the Supporting Information, Figure S1). When excited with the maximum absorption wavelength, these hybrid fluorophores emitted blue light.

Figure 2 presents the fluorescence spectra of the fluorophores in ethyl acetate solution and solid films. The inset photographs display the photoluminescence of the fluorophores in dichloromethane solution and solid film. Table 4 also summarizes the fluorescence data. The fluorescence data demonstrate that the terminal polycyclic aromatic units strongly affected the quantum efficiency of the fluorophores. Pyrroles bearing naphthylphenylamino and naphthyl groups had quantum efficiency of 30 and 35%. The fluorescent characteristic may have resulted from the sterically inhibiting π-stacking of the crowded pyrrole core.[1a,9] Naphthylphenylamino and naphthyl groups slightly increase the quantum efficiency. However, the quantum efficiency of the hybrid fluorophores **3**−**6** is markedly increased to 99%, when the fluorophores bear polycyclic aromatic units such as pyrene and fluorene derivative moieties. The combination of the sterically inhibiting π-stacking of the crowded pyrrole and the highly fluorescent polycyclic units gives the hybrid fluorophores **3**−**6** possessing high quantum efficiency. Bright blue emission in the solid film makes fluorophores **3**−**6** highly promising as blue emitters or phosphorescence hosts.

Electrochemical Properties and Energy Levels. To examine the electrochemical behavior of the hybrid fluorophores,

(21) (a) Wolfe, J. P.; Buchwald, S. L. *J. Org. Chem.* **1997**, *62*, 1264–1267. (b) Ahman, J.; Buchwald, S. L. *Tetrahedron Lett.* **1997**, *38*, 6363–6366. (c) Zhang, W.; Nagashima, T. *J. Fluorine Chem.* **2006**, *127*, 588–591.

(22) Old, D. W.; Wolfe, J. P.; Buchwald, S. L. *J. Am. Chem. Soc.* **1998**, *120*, 9722–9723.

TABLE 4. Thermal and Photophysical Characteristics of the Hybrid Fluorophores 1−6

	11b	NPANPy[9]	1	2	3	4	5	6
λ_{max}^{abs}/nm (log ε)[a,b]	259 (3.85)	309 (4.73)	256 (4.75) 296 (4.65)	263 (4.71) 292 (4.61)	276 (5.07) 344 (4.91)	284 (4.79) 320 (4.77)	301 (4.78) 325 (4.76)	307 (4.87) 326 (4.80)
$\lambda_{max,solution}^{em}$/nm[a,d] (fwhm/cm^{-1})	404 (5920)	453 (3420)	434 (3660)	429 (3580)	460 (3470)	442 (3530)	441 (3240)	441 (3220)
Stokes shift (cm^{-1})	13860	10290	11460	11080	7310	8600	8090	8000
Φ_f[c]	0.04	0.40	0.30	0.35	>0.99	>0.99	>0.99	>0.99
$\lambda_{max,film}^{em}$/nm[a,d] (fwhm/cm^{-1})	416 (4200)	461 (4340)	462 (2710)	428 (3400)	463 (2970)	445 (2920)	446 (2780)	445 (2890)
$E_{1/2}^{0}$/eV[e]	0.93	0.79, 1.04	0.71, 0.85	1.05	1.05	1.01	1.01	1.03
E_{gap}/eV[f]	3.47	2.61	3.13	3.41	3.16	3.25	3.20	3.23
HOMO/eV[f]	5.26	5.05	5.04	5.38	5.38	5.34	5.34	5.36
LUMO/eV[e]	1.79	2.44	1.91	1.97	2.22	2.09	2.14	2.09
T_g/°C[g]	89	118	137	122	162	158	191	220
T_m/°C[g]	234		277	269	303			
T_{dec}/°C[g]	325	419	525	512	522	515	530	540

[a]Photophysical properties of the molecules were examined by UV−vis and fluorescence in ethyl acetate solution. The concentrations of the fluorophores were controlled in 1×10^{-5} M and 5×10^{-8} M in ethyl acetate for UV−vis and fluorescence, respectively. [b]The molar extinction coefficient; ε was determined by means of a linear regression fit of the data to Beer's law. [c]Quantum yield; Φ_f was determined with reference to EA solution of coumarin **1**. [d]Full width at half-maximum of PL spectra given in parentheses. [e]Measured in CH_2Cl_2. All of the potentials (E_{ox}) are reported relative to ferrocene (E_{Fc}). The concentrations of the compounds were 1×10^{-3} M, and the scan rates were 100 mV/s. [f]HOMO calculated from CV potentials [HOMO = 4.8 + ($E_{ox} - E_{Fc}$)]. LUMO = HOMO)− E_{gap}. Energy gap (E_{gap}) estimated from absorption on-set energy. [g]Glass transition temperatures; T_gs, and melting temperatures; T_m's were measured from DSC at heating rate of 10 °C/min under N_2, T_{dec}'s were defined as weight loss at 5 wt % which was measured by TGA at heating rate of 10 °C/min under N_2.

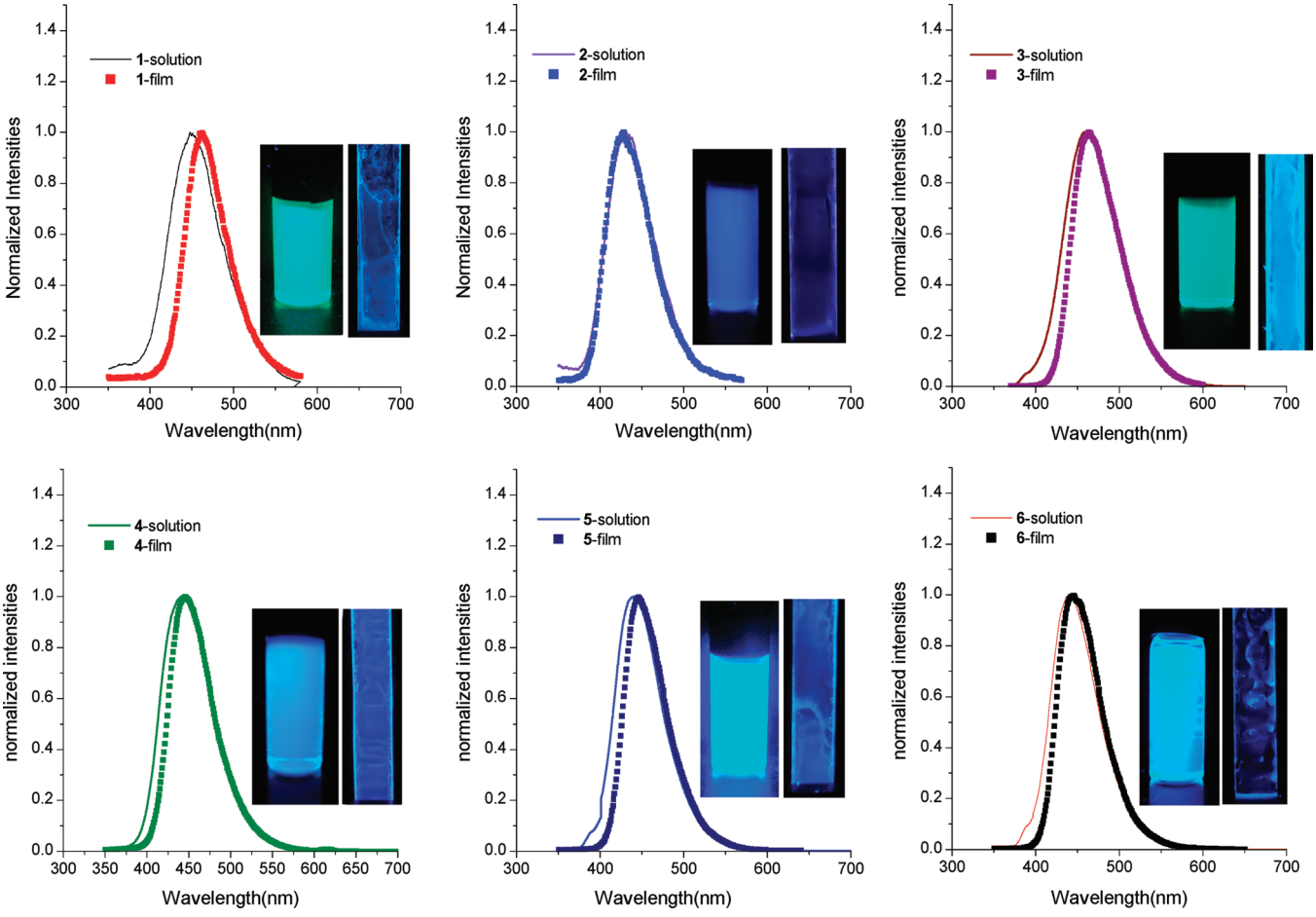


FIGURE 2. Emission spectra of the hybrid fluorophores **1**−**6** in ethyl acetate and solid films. The concentrations were controlled in 5×10^{-8} M. Inset: photo of the hybrid fluorophores luminescence in solutions and solid films.

cyclic voltammetry (CV) experiments were carried out in a three-electrode cell setup with 0.10 M of tetrabutylammonium perchlorate (TBAP) in anhydrous CH_2Cl_2 solution. The oxidation potentials were determined to be 0.71−1.05 V. All of the

hybrid fluorophores undergo a reversible oxidation process around 1.03 V, except for fluorophore **1**. These oxidation potentials exhibited insignificant variations by modifying the peripheral aryl substituents. The results exhibit the oxidation process corresponding to the removal of electrons from the pyrrole core to form radical cations. On the other hand, the hybrid fluorophore **1** shows two reversible oxidation processes at 0.71 and 0.85 V. In contrast to other hybrid fluorophores, the two lower oxidation processes correspond to the sequential removal of electrons from the two arylamine segments.[9] The absence of central pyrrole oxidation in the fluorophore **1** is attributed to the destabilization of the two cation radicals formed from the peripheral arylamine segments.[19a,23] Based on the oxidation potential and the band gap which was determined from the optical absorption threshold, the HOMO and LUMO energy levels of the fluorophores were estimated with regard to the energy level of the ferrocene reference (4.8 eV below the vacuum level).[24] The results are tabulated in Table 1. The peripheral substituents also affected the energy levels of the hybrid fluorophores. Upon the incorporation of diarylamino end-caps, the HOMO level of fluorophore **1** is raised to 5.04 eV. Such a high HOMO level makes it a candidate for hole-transporting/injection material.

Thermal Properties. To enhance morphological stability and prevent aggregation/excimer formation for the pyrrole-based fluorophores, a variety of polycyclic aromatic units were attached onto the phenyl group at the C2- and C5-positions in the pyrrole core. Table 1 summarized the thermal properties of the hybrid fluorophores by using differential scanning calorimetry (DSC) and thermogravimetric analyzer (TGA). The DSC traces of the second heating run are shown in the Supporting Information (Figure S2). All of the hybrid fluorophores exhibit stable amorphous morphologies. They have distinct glass transition temperatures (T_g), some even (fluorophores **1**−**3**) have melting points in the first heating run. It is important to note that the hybrid fluorophores bearing rigid and bulky flurenyl substituents exhibit high T_g values of 191 and 220 °C for fluorophores **5** and **6**, respectively. Furthermore, all of the hybrid fluorophores show improved thermal stabilities, with decomposition temperatures, T_{dec}'s, in the range 512−540 °C. These results suggest that the incorporation of rigid and bulky fluorenyl moieties at the ends of pyrroles may be used as a tool to induce morphologically stable amorphous thin-film formation.

Conclusion

In this study, a series of highly bright luminescent fluorophores **1**−**6** were constructed using two-stage synthetic methods. In the first stage, the central aryl-substituted pyrrole core was formed in a Paal−Knorr condensation reaction. Studies of the reaction mechanism and experimental testing revealed that the amounts of some side products, such as furan derivatives **10** and but-2-ene1,4-dione derivatives **9**, can be minimized by controlling the stoichiometric dosage, the addition sequence, and the reaction time. This study also confirmed that bulky triflate can undergo a palladium-catalyzed reaction. After the terminal methoxy group in the crowded pyrrole core was transferred into triflate moieties, a palladium-active intermediate **12b** was obtained. A Buchwald−-Hartwig amination reaction and a Suzuki−Miyaura cross-coupling reaction were performed using the triflate end-capping intermediate **12b** as the key intermediate to yield the fluorophores **1**−**6**. The aforementioned studies of the optical properties and thermal properties revealed that the fluorescence efficiency and morphological stability of these fluorophores **3**−**6** can be markedly enhanced by incorporating the sterically induced fluorescence of crowded pyrrole into the fluorescent polycyclic aromatic units. These hybrid fluorophores have great potential as blue fluorescence emitters or phosphorescence hosts.

Experimental Section

Preparation of Pyrrole Precursors. 1-(4-Methoxyphenyl)-2-(naphthalen-6-yl)ethanone (7). 2-Naphthylacetic acid (10 g, 53.7 mmol) was dissolved in 200 mL of anhydrous dichloromethane in a 250 mL two-neck round-bottom flask that was equipped with a condenser, a magnetic stirrer, and a hot plate. After 30 mL of thionyl chloride was added, the mixture was refluxed for 6 h. Excess thionyl chloride and dichloromethane were evaporated, and the residue viscous liquid was dried under a vacuum. Fresh anhydrous dichloromethane (250 mL) and anisole (8.8 mL, 81.3 mmol) were added. The mixture solution was cooled in an ice bath. Aluminum chloride (9 g, 68.3 mmol) was added in small portions for a period of 30 min. The solution changed from brown to dark red after all of the aluminum chloride was added. The solution was stirred for another 24 h after the temperature recovered to room temperature. Adding 100 mL of 1 M aqueous HCl to terminate this reaction caused the dark red solution to recover its brown color. The mixed solution was extracted with ethyl acetate three times (100 mL × 3). The combined organic solution was then washed with water and dried over anhydrous $MgSO_4$. After the $MgSO_4$ powder was filtered off and the filtrate was condensed, a dark crude solid was left. Further purification by column chromatography on silica gel gave 13.7 g of product **7** in the form of white powder in a yield of 89%: ^{1}H NMR(300 MHz, $CDCl_3$, δ) 3.85 (s, 3H), 4.40 (s, 2H), 6.93 (d, J = 9.0 Hz, 2H), 7.39−7.49 (m, 3H), 7.73 (s, 1H), 7.77−7.82 (m, 3H), 8.04 (d, J = 9.0 Hz, 2H); ^{13}C NMR(75 MHz, $CDCl_3$, δ) 45.4, 55.4, 113.8, 125.6, 126.0, 127.5, 127.6, 127.6, 127.9, 128.2, 129.6, 131.0, 132.3, 132.5, 133.5, 163.5, 196.2; HRMS (FAB) m/z calcd for $C_{19}H_{17}O_2$ 277.1229 ($[M + H]^+$), found 277.1227 ($[M + H]^+$).

1,4-Bis(4-methoxyphenyl)-2,3-di(naphthalen-2-yl)butane-1,4-dione (8). Compound **7** (5 g, 18.1 mmol) was dissolved in 100 mL of anhydrous THF in an ice bath in a 250 mL two-neck round-bottom flask that was equipped with a magnetic stirrer. Potassium *tert*-butoxide (4.061 g, 36.2 mmol) was added in small portions over a period of 20 min. The transparent solution became orange when the potassium *tert*-butoxide was added. After 10 min of stirring, a solution of iodine (2.2965 g, 9.05 mmol) in 50 mL of anhydrous THF was added dropwise. During the addition process, the red solution turned to brown. The solution continued to be stirred in an ice bath for another 4 h. Aqueous sodium bisulfite was added to remove excess iodine. The mixed solution was extracted with ethyl acetate (100 mL × 3). The combined organic solution was then dried over anhydrous $MgSO_4$. After the $MgSO_4$ powder was filtered off and the filtrate was condensed, a dark crude solid was left. Further purification by column chromatography on silica gel gave 4.7 g of the

(23) (a) Justin Thomas, K. R.; Lin, J. T.; Tao, Y.-T.; Ko, C.-W. *Adv. Mater.* **2000**, *12*, 1949–1951. (b) Ko, C.-W.; Tao, Y.-T.; Lin, J. T.; Thomas, K. R. J. *Chem. Mater.* **2002**, *14*, 357–361. (c) Justin Thomas, K. R.; Lin, J. T.; Tao, Y.-T.; Ko, C.-W. *Chem. Mater.* **2002**, *14*, 1354–1361.

(24) Anderson, J. D.; McDonald, E. M.; Lee, P. A.; Anderson, M. L.; Ritchie, E. L.; Hall, H. K.; Hopkins, T.; Mash, E. A.; Wang, J.; Padias, A.; Thayumanavan, S.; Barlow, S.; Marder, S. R.; Jabbour, G. E.; Shaheen, S.; Kippelen, B.; Peyghambarian, N.; Wightman, R. M.; Armstrong, N. R. *J. Am. Chem. Soc.* **1998**, *120*, 9646–9655.

product **8** as a white powder in a yield of 95%: ^{1}H NMR (300 MHz, $CDCl_3$, δ) 3.76 (s, 3H), 5.66 (s, 2H), 6.83 (d, J = 9.3 Hz, 2H), 7.12 (dd, J = 8.4, 1.8 Hz, 2H), 7.34−7.38 (m, 2H), 7.52 (d, J = 8.4 Hz, 1H), 7.59−7.67 (m, 3H), 8.05 (d, J = 9.0 Hz, 2H); ^{13}C NMR (75 MHz, $CDCl_3$, δ) 55.3, 58.1, 113.6, 125.7, 125.9, 126.8, 127.5, 127.6, 127.7, 128.3, 129.4, 131.2, 132.3, 133.3, 134.4, 163.3, 197.9; HRMS (FAB) m/z calcd for $C_{38}H_{31}O_4$ 551.2222 ([M + H] $^+$), found 551.2234 ([M + H] $^+$).

1,4-Bis(4-methoxyphenyl)-2,3-di(naphthalen-2-yl)-2-butene-1,4-dione (9). Compound **9** (3−12%) was obtained as a byproduct in the synthesis of compound **8** according to the reaction conditions: ^{1}H NMR (300 MHz, $CDCl_3$, δ) 3.76 (s, 6H), 6.80 (d, J = 9.0 Hz, 4H), 7.23 (dd, J = 8.4, 1.8 Hz 2H), 7.36−7.44 (m, 4H), 7.56 (d, J = 8.4 Hz, 2H), 7.60−7.72 (m, 4H), 7.78 (s, 2H), 7.91 (d, J = 9.0 Hz, 4H); ^{13}C NMR (75 MHz, $CDCl_3$, δ) 55.3, 113.6, 126.2, 126.7, 127.2, 127.6, 128.2, 128.3, 129.2, 129.3, 132.6, 132.7, 132.8, 133.1, 143.4, 163.4, 195.4; HRMS (FAB) m/z calcd for $C_{38}H_{29}O_4$ 549.2066 ([M + H]$^+$), found 549.2079 ([M + H]$^+$).

2,5-Bis(4-methoxyphenyl)-3,4-di(naphthalen-2-yl)furan (10). Compound **10** (10−20%) was obtained as a byproduct in the synthesis of compound **11$_a$** (acid-catalyzed Parr−Knorr furan condensation) and 1−10% in the synthesis of compound **8** (base-catalyzed Paal−Knorr furan condensation) according to the reaction conditions: ^{1}H NMR (300 MHz, $CDCl_3$, δ) 3.78 (s, 6H), 6.80 (d, J = 8.4 Hz, 4H), 7.29 (d, J = 8.4 Hz, 2H), 7.36−7.44 (m, 4H), 7.48 (d, J = 8.7 Hz, 4H), 7.60−7.72 (m, 6H), 7.78 (d, J = 7.8 Hz, 2H); ^{13}C NMR (75 MHz, $CDCl_3$, δ) 55.1, 113.8, 123.3, 123.8, 125.8, 125.8, 127.3, 127.6, 127.9, 127.9, 128.6, 129.2, 131.0, 132.3, 133.4, 147.7, 158.8; HRMS (FAB) m/z calcd for $C_{38}H_{28}O_3$ 532.2038, found 532.2044 (M^+).

1-Ethyl-2,5-bis(4-methoxyphenyl)-3,4-di(naphthalen-2-yl)-1*H*-pyrrole (11$_b$). Compound **8** (2.5 g, 4.5 mmol) and ammonium acetate (7 g, 90.8 mmol) were dissolved in 14 mL of acetic acid in a 250 mL two-neck round-bottom flask that was equipped with a reflux condenser, a magnetic stirrer, and a hot plate. The mixed solution was refluxed for 36 h. After the reaction had run to completion, the solution was poured into icy deionic water, and white powder precipitated out. The crude powder product was filtered and washed with deionized water. It was dissolved in ethyl acetate and washed with 1 M sodium bicarbonate (100 mL × 2) and deionic water (100 mL × 2). The solution was dried over anhydrous magnesium sulfate. The magnesium sulfate was filtered off, and the filtrate was condensed and dried under a vacuum. The crude solid was dissolved in 50 mL of anhydrous DMF. The DMF solution was cooled to 0 °C, and sodium hydride (0.54 g, 60 wt % in mineral oil; 13.5 mmol) was added in small portions. After the solution was stirred for 10 min, 1.0 mL of ethyl bromide (13.5 mmol) was added. The solution recovered to room temperature and was stirred for another 12 h. During this process, the milky solution became brown. The solution was terminated by addition of ethanol until the bubbles disappeared. Excess ethyl bromide and solvent DMF were removed under a vacuum. The residue was dissolved in 100 mL of ethyl acetate and washed twice using deionized water (100 mL × 2). The organic solution was condensed after drying over anhydrous magnesium sulfate and filtered off. It was further purified by column chromatography on silica gel using dichloromethane and *n*-hexane as diluent. White powder (2.0 g) was afforded in 70% yield: ^{1}H NMR (300 MHz, $CDCl_3$, δ) 1.06 (t, J = 6.9 Hz, 3H), 3.81 (s, 6H), 3.93 (q, J = 6.9 Hz, 2H), 6.88 (d, J = 8.7 Hz, 4H), 7.12 (dd, J = 8.7, 1.5 Hz, 2H), 7.27−7.34 (m, 8H), 7.46−7.49 (m, 6H), 7.68 (d, J = 7.2 Hz, 2H); ^{13}C NMR (75 MHz, $CDCl_3$, δ) 16.7, 39.3, 55.1, 113.7, 121.6, 124.8, 125.1, 125.3, 126.6, 127.3, 127.8, 129.0, 129.7, 131.0, 131.3, 132.6, 133.3, 133.5, 158.8; HRMS (FAB) m/z calcd for $C_{40}H_{33}NO_2$ 559.2511, found 559.2497 (M^+).

1-Ethyl-2,5-bis(4-hydroxyphenyl)-3-(naphthalen-2-yl)-4-(naphthalen-3-yl)-1*H*-pyrrole (12a). Compound **11b** (1.9 g, 3.40 mmol) was dissolved in 50 mL of anhydrous dichloromethane in a 250 mL two-neck round-bottom flask that was equipped with a magnetic stirrer. Five milliliters of 1 M tribromoborane in dichloromethane was added dropwise in an ice bath. As the triboromoborane solution was added, the transparent solution became dark brown. The solution was stirred at the same temperature for another 11 h. Deionized water was added to terminate the reaction at 0 °C. After 50 mL of ethyl acetate was added, the solution was washed three times with 50 mL of deionic water. The combined organic layer was dried over anhydrous magnesium sulfate and condensed under vacuum conditions. The crude product was recrystallized from dichloromethane and *n*-hexane solution. Product **12a** (1.8 g) was obtained as a white solid in a yield of 99%: ^{1}H NMR (300 MHz, DMSO-d_6, δ) 0.91 (t, J = 6.9 Hz, 3H), 3.79 (q, J = 6.9 Hz, 2H), 6.75 (d, J = 8.1 Hz, 4H), 7.04 (d, J = 8.4 Hz, 2H), 7.20 (d, J = 8.4 Hz, 4H), 7.27−7.35 (m, 4H), 7.44−7.52 (m, 6H), 7.69 (d, J = 7.5 Hz, 2H); ^{13}C NMR (75 MHz, DMSO-d_6, δ)16.0, 114.8, 120.6, 122.6, 124.7, 125.3, 126.1, 126.9, 127.0, 128.0, 129.0, 130.5, 132.1, 132.4, 133.3, 156.5; HRMS (FAB) m/z calcd for $C_{38}H_{29}NO_2$ 531.2198, found 531.2199 (M^+).

1-Ethyl-2,5-bis(4-trifluoromethanesulfonylphenyl)-3-(naphthalen-2-yl)-4-(naphthalen-3-yl)-1*H*-pyrrole (12b). Compound **12a** (2.6 g, 4.9 mmol) and 5 mL of triethylamine were dissolved in 50 mL of anhydrous dichloromethane in a round-bottom flask. The solution was cooled in an ice bath, and 3.92 g of triflic anhydride was added dropwise. During the addition, the solution became dark brown. The solution was stirred for another 7 h. Aqueous ammonium chloride (1 M, 10 mL) was added to terminate the reaction. After 50 mL of deionic water was added, the reaction mixture was transferred to a separatory funnel, and the dichloromethane layer was separated. The aqueous phase was extracted three times (50 mL × 3). The combined organic layer was dried over anhydrous magnesium sulfate and condensed under vacuum conditions. It was further purified by column chromatography on silica gel using ethyl acetate and *n*-hexane as a diluent. Compound **12b** (2.0 g) was obtained as a white powder in a yield of 70%: ^{1}H NMR (300 MHz, $CDCl_3$, δ) 1.073 (t, J = 6.9 Hz, 3H), 3.98 (q, J = 6.9 Hz, 2H), 7.03 (dd, J = 8.4, 1.8 Hz, 2H), 7.27 (d, J = 8.7 Hz, 4H), 7.32−7.37 (m, 6H) 7.45−7.50 (m, 8H), 7.68 (d, J = 7.2 Hz, 2H); ^{13}C NMR (75 MHz, $CDCl_3$, δ) 16.6, 39.7 (112.3, 116.6, 120.8, 125.1) (q, J = 128 Hz, OT_f C), 121.4, 123.4, 125.3, 125.6, 127.1, 127.4, 127.7, 129.2, 129.2, 130.0, 131.6, 132.2, 133.1, 133.2, 133.4, 148.9; ^{19}F NMR (470 MHz, $CDCl_3$, $CFCl_3$, δ) −73.182; HRMS (FAB) m/z calcd for $C_{40}H_{27}F_6NO_6S_2$ 795.1184, found 795.1177 (M^+).

Synthesis of Hybrid Fluorophores. 1-Ethyl-2,5-bis(4-(*N*-naphthylanilino)phenyl)-3,4-bis(naphthalen-2-yl)-1*H*-pyrrole (1). A 100 mL two-necked round-bottom flask that had been dried in a vacuum was charged with compound **12b** (0.5 g, 0.63 mmol), *N*-phenylnaphthalen-1-amine (0.285 g, 1.30 mmol), tris(dibenzylideneacetone)dipalladium(0) ($Pd_2(dba)_3$, 0.028 g, 0.03 mmol), sodium *tert*-butoxide (0.151 g, 1.57 mmol), and dry toluene (2 mL). When a solution of $BPCy_2$ (2-dicyclohexylphosphino-2′-(*N*,*N*-dimethylamino)biphenyl) (0.1 M 0.628 mL) was added, the solution became dark red. The solution was warmed and refluxed for 24 h. It was then cooled to room temperature, and 50 mL of deionized water was added. The reaction mixture was transferred to a separatory funnel, and 50 mL of ethylacetate was added. After the organic layer was separated, the aqueous phase was extracted twice with ethyl acetate (50 mL × 2). The combined organic solution was dried over anhydrous magnesium sulfate, filtered, and then condensed under vacuum conditions. It was further purified by column chromatography on silica gel (EA/hexane = 10:1). Product **1** (0.32 g) was obtained as a slightly yellow powder in a yield of 70%: ^{1}H NMR (500 MHz, $CDCl_3$, δ) 1.12 (t, J = 7.0 Hz, 3H), 4.00 (q, J = 7.0 Hz, 2H), 6.94−6.98 (m, 6H), 7.05−7.12 (m, 6H), 7.20 (t, J = 7.0 Hz, 8H), 7.35−7.38 (m, 8H), 7.45−7.53 (m, 10H), 7.71 (q, J = 3.0 Hz, 2H),

7.78 (d, J = 8.0 Hz, 2H), 7.90 (d, J = 8.0 Hz, 2H), 7.95 (d, J = 8.5 Hz, 2H); ^{13}C NMR (125 MHz, $CDCl_3$, δ) 16.8, 39.4, 121.1, 121.5, 122.0, 122.2, 124.2, 124.8, 125.2, 126.0, 126.1, 126.3, 126.5, 127.2, 127.4, 127.7, 128.4, 129.0, 129.1, 129.8, 131.1, 131.2, 131.3, 132.2, 133.4, 133.4, 135.3, 143.3, 147.7, 148.1; HRMS (FAB) m/z calcd for $C_{70}H_{52}N_3$ 934.4161 ([M + H] $^+$), found 934.4160 ([M + H] $^+$).

General Procedure for Suzuki−Miyaura Cross-Coupling Reaction. In an atmosphere of argon, 1 equiv of bistriflate **12b** (0.5 g, 0.6 mmol), 2.5 equiv of arylboronic acid **13**−**17**, 2 mol % of palladium acetate (0.006 g, 0.027 mmol), and 9 mol % of triphenylphosphine (0.026 g, 0.099 mmol) were dissolved in 6 mL of benzene and 6 equiv of 2 M aqueous potassium carbonate in a 100 mL two-necked round-bottom flask. The reaction solution was warmed and refluxed for 3 days. Thirty milliliters of deionized water was added, and the solution was extracted with ethyl acetate (30 mL × 3). The combined organic solution was dried over anhydrous magnesium sulfate, filtered, and condensed under vacuum conditions. It was further purified by column chromatography using ethyl acetate and *n*-hexane as a diluent to give products **2**−**6**.

1-Ethyl-2,5-bis(4-(naphthalen-1-yl)phenyl)-3,4-(naphthalen-2-yl)-1*H*-pyrrole (2). Following the general Suzuki−Miyaura cross-coupling procedure which was described above, triflate **12b** (1 g, 1.26 mmol) and boronic acid **13** (0.54 g, 3.15 mmol) were used. The crude product was further purified using column chromatography (ethyl acetate/n-hexane = 1:10) on silica gel to give fluorophores **2** (0.70 g) as a white powder in a yield of 74%: ^{1}H NMR (500 MHz, $CDCl_3$, δ) 1.27 (t, J = 7.0 Hz, 3H), 4.22 (q, J = 7.0 Hz, 2H), 7.22 (dd, J = 8.5, 1.5 Hz, 2H), 7.34−7.39 (m, 4H), 7.42−7.57 (m, 22H), 7.73 (d, J = 7.0 Hz, 2H), 7.88 (d, J = 8.5 Hz, 4H), 7.93 (d, J = 8.0 Hz, 2H); ^{13}C NMR (125 MHz, $CDCl_3$, δ) 17.0, 39.8, 122.3, 125.0, 125.3, 125.8, 125.9, 126.1, 126.8, 126.8, 127.4, 127.7, 127.8, 128.3, 129.3, 129.8, 130.0, 131.4, 131.5, 131.5, 131.6, 132.1, 133.3, 133.4, 133.8, 139.8, 139.9; HRMS (FAB) m/z calcd for $C_{58}H_{42}N$ 752.3317 ([M + H] $^+$), found 752.3328 ([M + H] $^+$).

1-Ethyl-3,4-bis(naphthalen-2-yl)-2,5-bis(4-(pyren-1-yl)phenyl)-1*H*-pyrrole (3). According to the general Suzuki−Miyaura cross-coupling procedure described above, triflate **12b** (0.5 g, 0.63 mmol) and boronic acid **14** (0.386 g, 1.57 mmol) were used. The crude product was further purified using column chromatography (ethyl acetate/*n*-hexane = 1:10) on silica gel to give the fluorophore **3** (0.4 g) as a slightly yellow powder in a yield of 70%: ^{1}H NMR (500 MHz, $CDCl_3$, δ) 1.35 (t, J = 7.0 Hz, 3H), 4.32 (q, J = 7.0 Hz, 2H), 7.30 (dd, J = 8.5, 1.0 Hz, 2H), 7.39−7.43 (m, 4H), 7.60−7.66 (m, 14H), 7.77−7.79 (m, 2H), 8.03−8.06 (m, 6H), 8.12 (s, 4H), 8.18−8.26 (m, 8H); ^{13}C NMR (125 MHz, $CDCl_3$, δ) 17.1, 39.9, 122.5, 124.6, 124.9, 124.9, 125.0, 125.0, 125.1, 125.4, 126.0, 126.8, 127.4, 127.4, 127.5, 127.5, 127.5, 127.8, 128.5, 129.3, 129.8, 130.6, 130.6, 131.0, 131.5, 131.5, 131.6, 132.1, 133.3, 133.4, 137.3, 140.3; HRMS (FAB) m/z calcd for $C_{70}H_{46}N$ 900.3630 ([M + H] $^+$), found 900.3634 ([M + H] $^+$).

1-Ethyl-2,5-bis(4-(9,9-dimethyl-9*H*-fluoren-2-yl)phenyl)-3,4-bis(naphthalen-2-yl)-1*H*-pyrrole (4). According to the general Suzuki−Miyaura cross-coupling procedure which was described above, triflate **12b** (0.5 g, 0.63 mmol) and boronic acid **15** (0.375 g, 1.57 mmol) were used. The crude product was further purified by column chromatography (ethyl acetate/*n*-hexane = 1:10) on silica gel to afford the fluorophores **4** (0.44 g) as a slightly yellow powder in a yield of 79%: ^{1}H NMR (500 MHz, $CDCl_3$, δ) 1.16 (t, J = 7.0 Hz, 3H), 1.56 (s, 12H), 4.13 (q, J = 7.0 Hz, 2H), 7.20 (dd, J = 8.5, 1.5 Hz, 2H), 7.30−7.40 (m, 8H), 7.47−7.56 (m, 12H), 7.64 (dd, J = 8.0, 1.5 Hz, 2H), 7.69−7.72 (m, 8H), 7.77 (d, J = 6.5 Hz, 2H), 7.81 (d, J = 8.0 Hz, 2H); ^{13}C NMR (125 MHz, $CDCl_3$, δ) 16.8, 27.2, 39.7, 46.9, 120.1, 120.3, 121.1, 122.4, 122.6, 124.9, 125.2, 126.0, 126.8, 126.9, 127.0, 127.3, 127.4, 127.8, 129.2, 129.7, 131.4, 131.5, 131.8, 131.9, 133.3, 133.3, 138.6, 138.8, 139.6, 140.2, 153.9, 154.3; HRMS (FAB) m/z calcd for $C_{68}H_{54}N$ 884.4256 ([M + H] $^+$), found 884.4268 ([M + H] $^+$).

1-Ethyl-3,4-bis(naphthalen-2-yl)-2,5-bis(4-(9,9-diphenyl-9*H*-fluoren-2-yl)phenyl)-1*H*-pyrrole (5). According to the general Suzuki−Miyaura cross-coupling procedure which was described above, triflate **12b** (0.75 g, 0.94 mmol) and boronic acid **16** (0.85 g, 2.35 mmol) were used. The crude product was further purified by column chromatography (ethyl acetate/*n*-hexane = 1:10) on silica gel to give fluorophore **5** (0.70 g) as a white powder in a yield of 74%: ^{1}H NMR (500 MHz, $CDCl_3$, δ) 1.09 (t, J = 7.0 Hz, 3H), 4.04 (q, J = 7.0 Hz, 2H), 7.15 (dd, J = 8.0, 1.5 Hz, 2H), 7.23−7.33 (m, 26H), 7.40 (t, J = 7.0 Hz, 2H), 7.44−7.50 (m, 12H), 7.56 (d, J = 8.0 Hz, 4H), 7.64 (dd, J = 8.0, 1.5 Hz, 2H), 7.69 (m, 4H), 7.81 (d, J = 7.5 Hz, 2H), 7.84 (d, J = 8.0 Hz, 2H); ^{13}C NMR (125 MHz, $CDCl_3$, δ) 16.8, 39.6, 65.6, 120.2, 120.5, 122.4, 124.6, 124.9, 125.2, 126.2, 126.5, 126.6, 126.8, 126.8, 127.3, 127.5, 127.8, 127.8, 128.2, 128.2, 129.2, 129.7, 131.3, 131.4, 131.7, 132.0, 133.2, 133.3, 139.5, 139.8, 139.9, 140.0, 145.8, 151.5, 151.9; HRMS (FAB) m/z calcd for $C_{88}H_{62}N$ 1132.4882 ([M + H] $^+$), found 1132.4883 ([M + H] $^+$).

1-Ethyl-3,4-bis(naphthalen-2-yl)-2,5-bis(4-(9,9-diphenyl-9*H*-fluoren-2-yl)phenyl)-1*H*-pyrrole (6). According to the general Suzuki−Miyaura cross-coupling procedure which was described above, triflate **12b** (0.75 g, 0.94 mmol) and boronic acid **17** (0.85 g, 2.35 mmol) were used. The crude product was further purified by column chromatography (ethyl acetate/*n*-hexane = 1:10) on silica gel to give the fluorophore **6** (0.87 g) as a white powder in a yield of 82%: ^{1}H NMR (500 MHz, $CDCl_3$, δ) 0.96 (t, J = 7.0 Hz, 3H), 3.91 (q, J = 7.0 Hz, 2H), 6.76 (d, J = 7.5 Hz, 2H), 6.80 (d, J = 7.5 Hz, 4H), 7.01 (s, 2H), 7.08−7.15 (m, 8H), 7.24−7.34 (m, 8H), 7.38−7.45 (m, 16H), 7.64−7.66 (m, 4H), 7.88−7.93 (m, 8H); ^{13}C NMR (125 MHz, $CDCl_3$, δ) 16.6, 39.5, 66.0, 120.0, 120.3, 122.3, 122.3, 124.0, 124.1, 124.8, 125.2, 126.7, 126.7, 126.7, 127.3, 127.7, 127.8, 127.8, 129.1, 129.6, 131.2, 131.4, 131.5, 131.8, 133.1, 133.2, 139.5, 140.1, 141.1, 141.3, 141.8, 148.7, 149.2, 149.4; HRMS (FAB) m/z calcd for $C_{88}H_{58}N$ 1128.4569 ([M + H] $^+$), found 1128.4576 ([M + H]$^+$).

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Supporting Information Available: Experimental details, copies of ^{1}H and ^{13}C NMR spectra of all new compounds, and linear regression analysis of the absorption data. This material is available free of charge via the Internet at http://pubs.acs.org.