ORGANIC LETTERS

XXXX
Vol. XX, No. XX
000–000

Synthesis of Pyridine-Fused Perylene Imides with an Amidine Moiety for Hydrogen Bonding

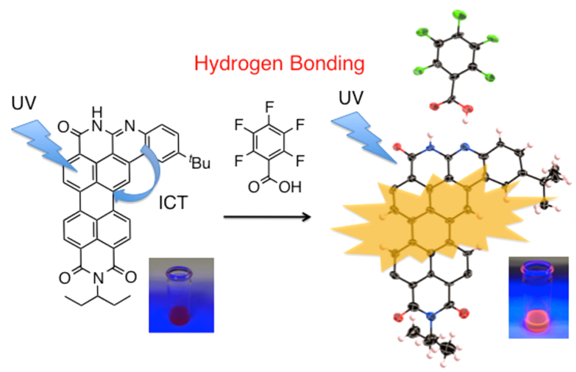
Satoru Ito, Satoru Hiroto, and Hiroshi Shinokubo*

Department of Applied Chemistry, Graduate School of Engineering, Nagoya University, Furo-cho, Chikusa-ku, Nagoya, Aichi, 464-8603, Japan

hshino@apchem.nagoya-u.ac.jp

Received May 11, 2013

ABSTRACT



Pyridine-fused perylene tetracarboxylic acid bisimides (PBIs) were synthesized via Suzuki–Miyaura coupling and acid condensation. The fused PBIs with electron-donating substituents exhibited an intramolecular charge transfer interaction. One of the *N*-alkyl substituents was selectively removed with BBr_3 to create an amidine guest binding site. A hydrogen bonding interaction with pentafluorobenzoic acid changed the absorption spectra and enhanced fluorescence.

Perylene tetracarboxylic acid bisimide (PBI) is an important class of dyes and pigments for widespread use in both academia and industry.[1] Since PBIs have unique photophysical properties such as efficient visible light absorption, strong emission, and high stability against light and air, they have received much attention in wide areas of material science such as organic solar cells,[2] organic light-emitting diodes,[3] single molecule spectroscopy,[4] field effect transistors,[5] and biomedical sensors.[6] PBIs are also a building block of supramolecules, constructing optically active H- or J-aggregated structures by a $\pi-\pi$ stacking interaction with cooperating hydrogen-bonding interaction.[7]

To control electronic and photophysical characteristics of PBIs, a number of studies on functionalization of PBIs have been conducted.[8] In particular, extension of the PBI core with fused structures is a current hot topic.[9] Such core extension has been mostly achieved at the 1,6,7,12-positions, so-called "bay-areas." In contrast, there are few

(1) For reviews on PBIs: (a) Li, C.; Wonneberger, H. *Adv. Mater.* **2012**, *24*, 613. (b) Huang, C.; Barlow, S.; Marder, S. R. *J. Org. Chem.* **2011**, *76*, 2386. (c) Würthner, F. *Chem. Commun.* **2004**, *14*, 1564. (d) Langhals, H. *Heterocycles* **1995**, *40*, 477.

(2) (a) Rajaram, S.; Shivanna, R.; Kandappa, S. K.; Narayan, K. S. *J. Phys. Chem. Lett.* **2012**, *3*, 2405. (b) Raj, M. R.; Anandan, S.; Solomon, R. V.; Venuvanalingam, P.; Lyer, S. S. K.; Ashokkumer, M. *J. Photochem. Photobiol. A* **2012**, *247*, 52. (c) Keivanidis, P. E.; Kamm, V.; Zhang, W.; Floudas, G.; Laquai, F.; McCulloch, I.; Bradley, D. D. C.; Nelson, J. *Adv. Funct. Mater.* **2012**, *22*, 2318. (d) Liang, Z.; Cormier, R. A.; Nardes, A. M.; Gregg, B. A. *Synth. Met.* **2011**, *161*, 1014. (e) Zhan, X.; Facchetti, A.; Barlow, S.; Marks, T. J.; Ratner, M. A.; Wasielewski, M. R.; Marder, S. R. *Adv. Mater.* **2011**, *23*, 268.

(3) (a) Grozema, F.; Andrienko, D.; Kremer, K.; Müllen, K. *Nat. Chem.* **2009**, *8*, 421. (b) Kraft, A.; Grimsdale, A. C.; Holmes, A. B. *Angew. Chem., Int. Ed.* **1998**, *37*, 402. (c) Pan, J.; Zhu, W.; Li, S.; Zeng, W.; Cao, Y.; Tian, H. *Polymer* **2005**, *46*, 7658.

(4) Rohr, U.; Schlichting, P.; Böhm, A.; Gross, M.; Meerholz, K.; Bräuchle, C.; Müllen, K. *Angew. Chem., Int. Ed.* **1998**, *37*, 1434.

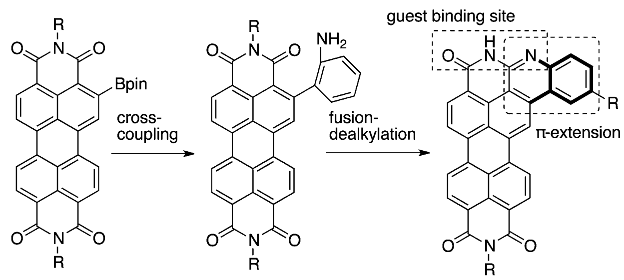
(5) (a) Dössel, L. F.; Kamm, V.; Howard, I. A.; Laquai, F.; Pisula, W.; Feng, X.; Li, C.; Takase, M.; Kudernac, T.; Feyter, S. D.; Müllen, K. *J. Am. Chem. Soc.* **2012**, *134*, 5876. (b) An, Z.; Yu, J.; Domercq, B.; Jones, S. C.; Barlow, S.; Kippelen, B.; Marder, S. R. *J. Mater. Chem.* **2009**, *19*, 6688.

(6) (a) Franceschin, M.; Alvino, A.; Casagrande, V.; Mauriello, C.; Pascucci, E.; Savino, M.; Ortaggi, G.; Bianco, A. *Bioorg. Med. Chem.* **2007**, *15*, 1848. (b) Franceschin, M.; Alvino, A.; Ortaggi, G.; Bianco, A. *Tetrahedron Lett.* **2004**, *45*, 9015.

10.1021/ol401316q

reports on fused PBIs at the 2,5,8,11-positions instead of bay areas, due to the lack of functionalization methods at these positions.[10]

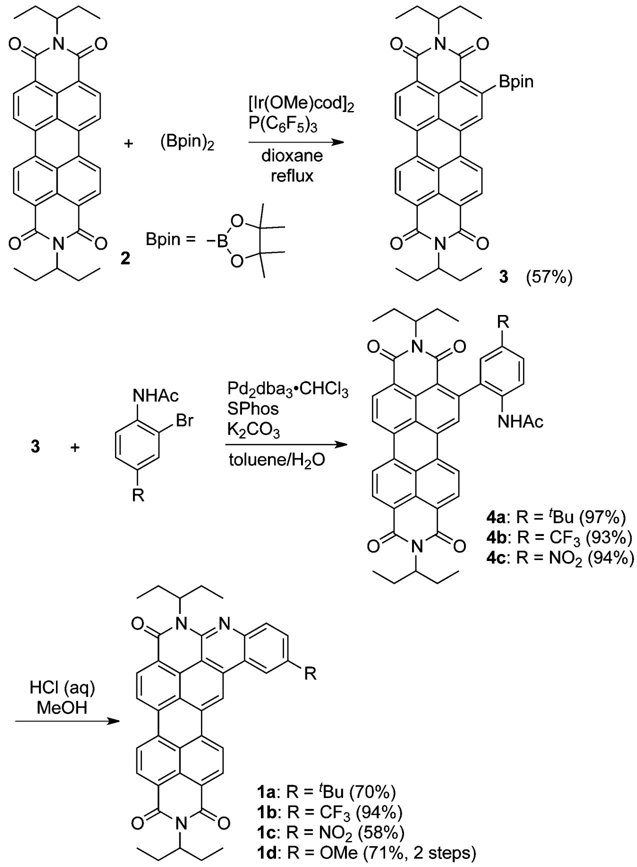
Scheme 1. Synthetic Strategy for Pyridine Fusion



Recently, direct C−H borylation of PBIs at the 2,5,8,11-positions has been accomplished under iridium and ruthenium catalyses.[11,12] The boryl group is useful for introduction various functionalities through oxidation and cross-coupling reactions[13] We now designed a novel type of core-extended PBIs, which could be prepared through Suzuki−Miyaura cross-coupling followed by dehydrative condensation of the carbonyl and amino groups (Scheme 1). The ring fusion created an amidine moiety, which served as a hydrogen bonding site. The imide moiety of PBIs has been utilized as a guest-binding site in supramolecular chemistry. However, the binding at the imide group is not generally strong.[14] Incorporation of a more basic pyridine unit would enhance the binding constant.

The synthesis of **1** began with direct C−H borylation of PBI **2** according to our previous report.[11c] The yield of monoborylated product **3** was improved up to a 57% yield

Scheme 2. Synthesis of Pyridine-Fused PBIs



by using 1.0 equiv of bis(pinacolate)diboron (Scheme 2). The cross-coupling reaction with 4-*tert*-butyl-2-bromoacetoanilide proceeded smoothly in the presence of a catalyst combination of the Pd_2dba_3−SPhos ligand to furnish **4a** in 97% yield. Deprotection and spontaneous ring fusion occurred by hydrolysis with aqueous HCl to afford pyridine-fused PBI **1a** in 70% yield. The structure of **1a** was characterized by spectroscopic analysis. Its ^{1}H NMR spectrum showed a downfield shifted singlet peak at 9.65 ppm, which is assigned as a proton on the perylene core proximal to the fused moiety. In addition, two broadened signals were observed around 6 ppm, which gradually merged into a single peak at elevated temperatures (Figure S10). These peaks are attributed to the methine protons of the 3-pentyl group, whose rotation is constrained by steric hindrance of the pyridine ring. According to the same synthetic procedure, various pyridine-fused PBIs **1b**, **1c**, and **1d** were obtained in excellent yields.

Figure 1a shows UV/vis absorption spectra of pyridine-fused PBIs in CH_2Cl_2. As compared to parent PBI **2**, no obvious change was observed for fused PBIs **1b** and **1c** which bear electron-withdrawing phenyl rings, while spectra of **1a** and **1d** exhibited broadening and bathochromic shifts of the lowest energy absorption bands. Fluorescence spectra (Figure 1b) exhibited broadening and reduction of the quantum yields for **1a** and **1d**, suggesting existence of an intramolecular charge transfer interaction. To evaluate

(7) Recent examples of supramolecular architectures with PBIs via hydrogen bonding interactions. (a) Görl, D.; Zhang, X.; Würthner, F. *Angew. Chem., Int. Ed.* **2012**, *51*, 6328. (b) Yagai, S.; Usui, M.; Seki, T.; Murayama, H.; Kikkawa, Y.; Uemura, S.; Karatsu, T.; Kitamura, A.; Asano, A.; Seki, S. *J. Am. Chem. Soc.* **2012**, *134*, 7983. (c) Seki, T.; Asano, A.; Seki, S.; Kikkawa, Y.; Murayama, H.; Karatsu, T.; Kitamura, A.; Yagai, S. *Chem.—Eur. J.* **2011**, *17*, 3598. (d) Yagai, S.; Seki, T.; Karatsu, T.; Kitamura, A.; Würthner, F. *Angew. Chem., Int. Ed.* **2008**, *47*, 3367. (e) Kaiser, T. E.; Wang, H.; Stepanenko, V.; Würthner, F. *Angew. Chem., Int. Ed.* **2007**, *46*, 5541.

(8) (a) Fan, L.; Xu, Y.; Tian, H. *Tetrahedron Lett.* **2005**, *46*, 4443. (b) Würthner, F.; Stepanenko, V.; Chen, Z.; Saha-Möller, C. R.; Kocher, N.; Stalke, D. *J. Org. Chem.* **2004**, *69*, 7933. (c) Huang, C.; Barlow, S.; Marder, S. R. *J. Org. Chem.* **2011**, *76*, 2386.

(9) (a) Eversloh, C. L.; Li, C.; Müllen, K. *Org. Lett.* **2011**, *13*, 4148. (b) Jiang, W.; Li, Y.; Yue, W.; Zhen, Y.; Qu, J.; Wang, Z. *Org. Lett.* **2010**, *12*, 228. (c) Yan, Q.; Cai, K.; Zhang, C.; Zhao, D. *Org. Lett.* **2012**, *14*, 4654. (d) Müller, S.; Müllen, K. *Chem. Commun.* **2005**, 4045. (e) Alibert-Fouet, S.; Seguy, I.; Bobo, J.-F.; Destruel, P.; Bock, H. *Chem.—Eur. J.* **2007**, *13*, 1746.

(10) One example of a π-extended PBI at 2,5,8,11-positions: Yao, J. H.; Chi, C.; Wu, J.; Loh, K.-P. *Chem.—Eur. J.* **2009**, *15*, 9299.

(11) (a) Nakazono, S.; Imazaki, Y.; Yoo, H.; Yang, J.; Sasamori, T.; Tokitoh, N.; Cédric, T.; Kageyama, H.; Kim, D.; Shinokubo, H.; Osuka, A. *Chem.—Eur. J.* **2009**, *15*, 7530. (b) Nakazono, S.; Easwaramoorthi, S.; Kim, D.; Shinokubo, H.; Osuka, A. *Org. Lett.* **2009**, *11*, 5426. (c) Teraoka, T.; Hiroto, S.; Shinokubo, H. *Org. Lett.* **2011**, *13*, 2532.

(12) Battagliarin, G.; Li, C.; Enkelmann, V.; Müllen, K. *Org. Lett.* **2011**, *13*, 3012.

(13) Battagliarin, G.; Zhao, Y.; Li, C.; Müllen, K. *Org. Lett.* **2011**, *13*, 3399.

(14) Würthner, F.; Thalacker, C.; Sautter, A.; Schärtl, W.; Ibach, W.; Hollricher, O. *Chem.—Eur. J.* **2000**, *6*, 3871.

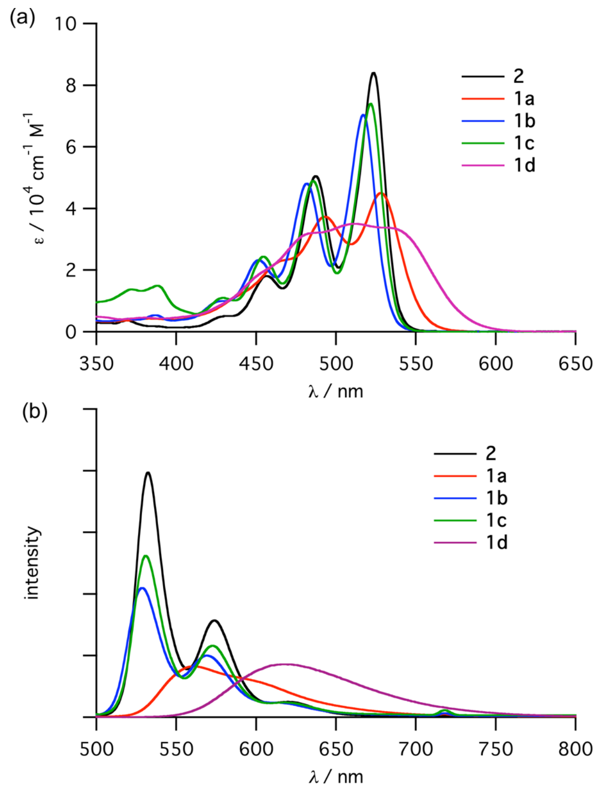
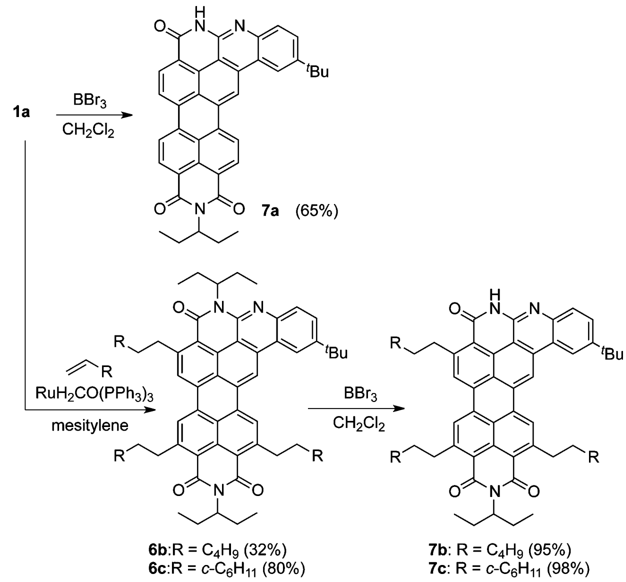


Figure 1. (a) UV/vis absorption and (b) fluorescence spectra of **2**, **1a**, **1b**, **1c**, and **1d** in CH_2Cl_2.

the charge-transfer character of **1d**, the solvent effect on optical properties was examined. Positive solvatochromic behavior was observed for both UV/vis absorption and emission spectra. A linear correlation with a positive slope was confirmed between Stokes shifts and orientation polarizabilities of solvents (Figure S29). These results indicate that the change of the dipole moment upon excitation is dependent on solvent polarity. In addition, fluorescence quenching occurred in polar media such as acetone and ethyl acetate. We calculated the molecular orbitals of **1c** and **1d** by the DFT method at the B3LYP/6-31G(d) level (Figure S35). Both the HOMO and LUMO of **1c** mainly spread over the perylene core and there were small MO coefficients on the fused rings. On the other hand, the HOMO of **1d** was mainly located on the fused rings, while the LUMO was localized on the perylene part, indicating the substantial charge-transfer interaction from the benzene ring to the perylene core.

We then attempted selective dealkylation of one of the *N*-alkyl groups to create a hydrogen bonding site.[7b] Treatment of **1a** with BBr_3 at room temperature afforded dealkylated product **7a** in 65% yield (Scheme 3).[15] Unfortunately, however, **7a** was not very soluble in common organic solvents. To enhance the solubility, alkyl chains were introduced. The reaction of **1a** with 1-hexene or vinylcyclohexane in the presence of a $RuH_2CO(PPh_3)_3$ catalyst furnished trialkylated PBI **6b** and **6c** in 32 and 80% yields, respectively.[11a] During the reaction, no overalkylated products were detected. The addition of BBr_3 into a dichloromethane solution of **6b** and **6c** provided dealkylated product **7b** and **7c** in 95 and 98% yields, respectively. Interestingly, dealkylation occurred exclusively on nitrogen adjacent to the pyridine ring due to the directing effect of the pyridine nitrogen. Both **7b** and **7c** were soluble enough in various organic solvents.

Scheme 3. Regioselective Dealkylation and Alkylation of **1a**



We then investigated the association behavior of **7c** with carboxylic acids. An amidine moiety has been well-known to associate with carboxylic acid guests through formation of a strong amidinium–carboxylate complex.[16] The well-defined structure of the amidinium–carboxylate complex and strong hydrogen bonding would be useful for the construction of supramolecular assemblies.[17] An addition of benzoic acid into a dichloromethane solution of **7c** induced no noticeable change on the UV/vis absorption spectrum. In contrast, titration with $C_6F_5CO_2H$ (pK_a = 1.6) caused an enhancement of the absorbance and a red shift of the peak around 520 nm (Figure 2a). In addition, an increase of the fluorescence intensity was observed. The fluorescence quantum yield was enhanced from Φ_f = 0.35 to 0.61. The enhancement of the emission can be detected

(15) BBr_3-mediated dealkylation was facilitated by a pyridine ring. Palikov, E.; Strekowski, L. *Tetrahedron Lett*. **2004**, *45*, 4093.

(16) Kraft, A.; Peters, L.; Powell, H. R. *Tetrahedron* **2002**, *58*, 3499.

(17) Recent examples of supramolecular assemblies with amidinium–carboxylate bridges. (a) Yamada, H.; Wu, Z.-Q.; Furusho, Y.; Yashima, E. *J. Am. Chem. Soc*. **2012**, *134*, 9506. (b) Ito, H.; Ikeda, M.; Hasegawa, T.; Furusho, Y.; Yashima, E. *J. Am. Chem. Soc*. **2011**, *133*, 3419. (c) Yamada, H.; Furusho, Y.; Ito, H.; Yashima, E. *Chem. Commun*. **2010**, *46*, 3487. (d) Young, E. R.; Rosenthal, J.; Hodgkiss, J. M.; Nocera, D. G. *J. Am. Chem. Soc*. **2009**, *131*, 7678. (e) Ito, H.; Furusho, Y.; Hasegawa, T.; Yashima, E. *J. Am. Chem. Soc*. **2008**, *42*, 14008. (f) Maeda, T.; Furusho, Y.; Sakurai, S.-I.; Kumaki, J.; Okoshi, K.; Yashima, E. *J. Am. Chem. Soc*. **2008**, *130*, 7938. (g) Otsuki, J.; Kanazawa, Y.; Kaito, A.; Islam, D.-M.-S.; Araki, Y.; Ito, O. *Chem.—Eur. J*. **2008**, *14*, 3776.

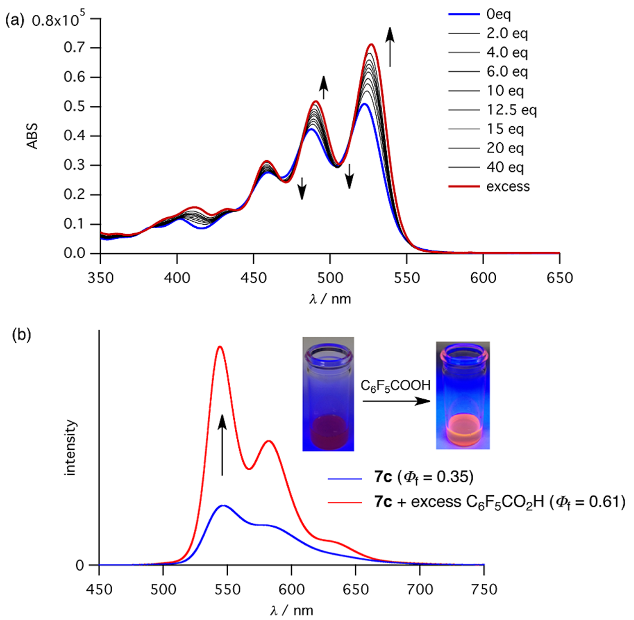


Figure 2. (a) Change of UV/vis absorption spectra of **7c** in CH_2Cl_2 (6.4×10^{-5} M) upon the addition of $C_6F_5CO_2H$. (b) Change of fluorescence spectra of **7c** in 1,2-dichloroethane. The blue lines show the spectra of **7c**, and the red lines show those of **7c** + excess $C_6F_5CO_2H$.

by the naked eye (Figure 2b). The binding constant was calculated to be 2640 M^{-1} in CH_2Cl_2. The addition of $C_6F_5CO_2H$ to **6c** resulted in no spectral change, excluding the possibility of simple protonation of the pyridine moiety. The binding structure was eventually determined by preliminary X-ray diffraction analysis (Figure S33). A pentafluorobenzoic acid molecule was aligned in the same plane of **7c**. The carboxylate moiety of $C_6F_5CO_2H$ faces the two nitrogen atoms of the amidine moiety.[18] These results elucidated the formation of the amidinium–carboxylate complex of **7c** with pentafluorobenzoic acid, which induced substantial changes in absorption and emission features because of the attenuation of intramolecular charge transfer. DFT calculations at the ωB97XD/6-31G(d) level revealed diminished MO coefficients around the fused rings in the HOMO of **7c** by binding with $C_6F_5CO_2H$ (Figure S36).

In summary, we have synthesized a series of pyridine-fused PBIs **1** in excellent total yields from borylated PBI **3**. The ring fusion with electron-withdrawing aryl groups does not significantly alter the optical properties from the parent PBI **2**, while fusion with the electron-donating ones causes an intramolecular charge-transfer interaction, resulting in broadening and bathochromic shifts of the electronic absorption spectrum and lowering of the fluorescence intensity. Furthermore, selective removal of one of the *N*-alkyl groups allows installation of an amidine moiety, which serves as a hydrogen binding site. In fact, the fused PBI **7c** strongly binds to pentafluorobenzoic acid, resulting in an enhancement of the fluorescence intensity. The present amidinium–carboxylate strategy would enable construction of rigid supramolecules on the basis of pyridine-fused PBIs.

(18) Interestingly, a columnar packing structure is constructed by a pair that includes one pentafluorobenzoic acid and one fused PBI in the crystal (Figure S34).

Acknowledgment. This work was supported by Grants-in-Aid for Scientific Research (Nos. 22750036 and 24350023) and Program for Leading Graduate Schools "Integrative Graduate Education and Research in Green Natural Sciences", MEXT, Japan. H.S. acknowledges Asahi Glass Foundation for financial support.

Supporting Information Available. General procedures, spectral data for compounds, absorption and fluorescence spectra. CIF file for the preliminary X-ray analysis of the complex of **7c** with $C_6F_5CO_2H$. This material is available free of charge via the Internet at http://pubs.acs.org.

The authors declare no competing financial interest.