JOURNAL OF THE AMERICAN CHEMICAL SOCIETY

COMMUNICATION

pubs.acs.org/JACS

One-Pot Synthesis of Stable NIR Tetracene Diimides via Double Cross-Coupling

Wan Yue,[†,‡] Jing Gao,[†,‡] Yan Li,[*,†] Wei Jiang,[†] Simone Di Motta,[§,∥] Fabrizia Negri,[*,§,∥] and Zhaohui Wang[*,†]

[†]Beijing National Laboratory for Molecular Science, Key Laboratory of Organic Solids, Institute of Chemistry, Chinese Academy of Science, Beijing 100190, China

[‡]Graduate School of the Chinese Academy of Sciences, Beijing 100190, China

[§]Dipartimento di Chimica 'G. Ciamician', Università di Bologna, Via F. Selmi, 2, 40126 Bologna, Italy

[∥]INSTM, UdR Bologna, Italy

S *Supporting Information*

ABSTRACT: Tetracene tetracarboxylic diimides have been synthesized based on direct double ring extension of electron-deficient naphthalene diimides involving metallacyclopentadienes. Atomic structure and electronic transitions responsible for their NIR absorption spectra are investigated with quantum-chemical calculations. In light of their unique structure and admirable photophysical and electronic properties, this new molecular skeleton is promising candidate for n-type semiconductors.

The design and synthesis of acenes have attracted considerable interests owing to their potential applications as p-type organic semiconductors in organic electronics, such as field-effect transistors, organic light-emitting diodes, and solar cells.[1] Typically, tetracene and pentacene derivatives have been the subject of intense study because of the unique electronic properties associated with their π-bond topology.[2] One efficient approach to optimize the performance of acenes is to integrate functional groups into the parent molecules to improve their stability and processability.[3] However, the systematic change of effective functional groups on acenes poses a great challenge since there are very few synthetic methodologies that can serve this purpose.

Compared with aryl, alkynyl-subsitituted, and other functionalized groups, introduction of strong electron-withdrawing substituent to acenes is believed to be very crucial to invert the majority carrier sign to achieve efficient electron transport.[4] Perylene tetracarboxylic diimides (PDIs) and naphthalene tetracarboxylic diimides (NDIs), which combine p-type perylene or naphthalene aromatic cores with strong electron-withdrawing tetracarboxylic diimides substituents, were used as promising building blocks for most extensively investigated n-type semiconductors.[5] Thus, a similar strategy is expected to create new series of acene tetracarboxylic diimides as new n-type building blocks.

Aromatic annulation by double cross-coupling reactions of organometallic reagents and electron-rich acenes with dihalides function groups is an efficient method for region- and stereospecific formation of C−C bonds, which would provide a straightforward and promising method for extension of polycyclic aromatic molecules.[6] However, the efficient synthetic approach based on electro-deficient acenes for big π-delocalized functional molecules are rarely reported. Herein, we present a new family of stable and NIR tetracene derivatives functionalized by tetracarboxylic diimides substituents in one pot under mild conditions.

Inspired by fused aromatic rings via intermolecular coupling of metallacyclopentadiene with dihalo aromatics,[7] we envisage that double cross-coupling of metallacyclopentadiene with electron-deficient tetrabrominated naphthalene tetracarboxylic diimides will provide the desired tetracene diimides. Accordingly, 2,3,6,7-tetrabromo-1,4,5,8-naphthalene tetracarboxylic diimides **1** (TBNDIs) are prepared according to a known procedure.[8] The coupling reaction of compound **1** and zirconacyclopentadiene **2** proceeds well in THF in the presence of copper chloride at 50 °C (Scheme 1) to give desired tetracene diimides (TDIs) derivative **5** in good yield.

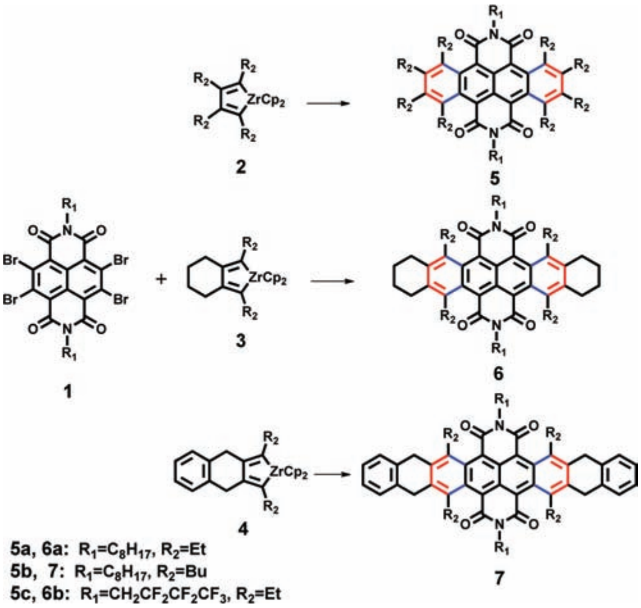
Encouraged by the success of such a facile double aromatic annulation, we used a range of zirconacyclopentadienes to check the scope of our procedure. By this method, different substituents can be conveniently introduced into the extended aromatic cores. Interestingly, the coupling of TBNDIs with zirconacyclopentadiene **3** or **4** prepared from 3,9-dodecadiyne or 1,2-di(hept-2-yn-1-yl)benzene provides octahydrotetracene **6** or tetrahydrotetracene **7** also in a moderate yield, which is expected to be further converted to higher acenes tetracarboxylic diimides. Notably, the introduction of semiperfluoroalkyl chain at the imides position of the TBNDIs also proceeded well. Incorporation of this semiperfluoroalkyl chain is known to have a strong influence not only on their self-assembled structures, but also on their transporting properties.[9]

Palladium-catalyzed double cross-coupling of 9-stannafluorene **9** with 1,2-dihaloarenes is known to serve as a new entry to aromatic annulation and provide a variety of triply annulated benzene derivatives.[10] As we expected, the cross-coupling reactions of 9-stannafluorene **9** with TBNDI **1** in the presence of $[Pd(P(t\text{-}Bu)_3)_2]$ and CsF in THF at 70 °C proceed well to afford tetrabenzotetracene diimides **11** (Scheme 2). Meanwhile, when we choose 1,1-dimethyl-2,3,4,5-tetraphenylstannole[11] as coupling reagent under the same conditions, surprisingly, we get the product **10**, which has extreme steric hindrance due to the eight phenyl groups in a moderate yield.

To determine the molecular structure of TDIs derivatives, crystal of **5c** suitable for single-crystal X-ray structure analysis was

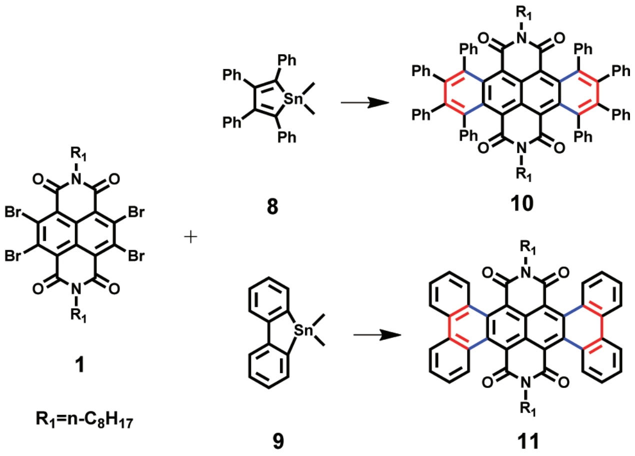
Received: August 12, 2011
Published: October 17, 2011

Scheme 1. The Synthetic Route towards TDIs[a]



[a] Conditions: TBNDIs, zirconacyclopentadiene, CuCl, THF, 50 °C, argon. The yields of compounds: **5a** (55%), **6a** (48%), **5b** (52%), **7** (48%), **5c** (44%), and **6b** (35%).

Scheme 2. Palladium-Catalyzed Annulation of TBNDI with Stannane Reagents[a]



[a] Conditions: TBNDIs, **8** or **9**, $[Pd(P(t\text{-}Bu)_3)_2]$, CsF, THF, 70 °C, argon. The yields of compounds: **10** (32%) and **11** (42%).

obtained by slow evaporation of a solution of dichloromethane and methanol at room temperature.[12] As can be seen from Figure 1, the molecule crystallizes in the monoclinic *Cc* space group, the crystal structure reveals that the molecule has crystallographically imposed inversion symmetry. Owing to the steric encumbrance effect between oxygen atoms and neighboring group, the tetracene core is found to be markedly nonplanar as well as the two imides rings with dihedral angles of 30−32°. The heliciform structure revealed by the crystal structure corresponds indeed to the lowest energy computed structure (B3LYP/6-31G*) of **5** and **11** (see Figures S2−S3 and Table S1).

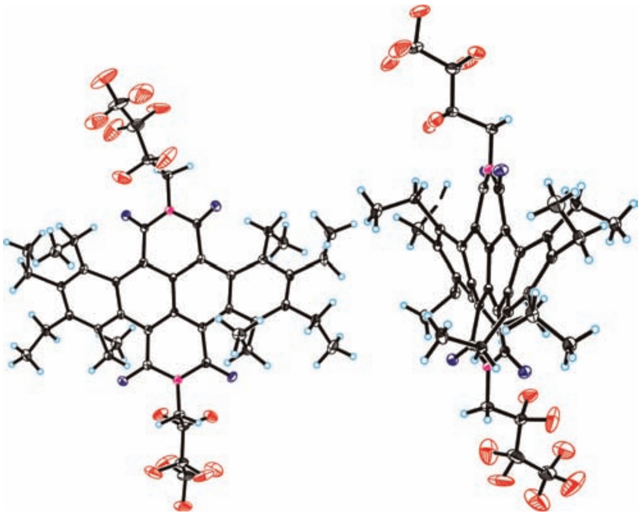


Figure 1. Molecular structure of **5c**, the X-ray structure along the crystallographic *b* axis (right), the X-ray structure along the crystallographic *c* axis (left).

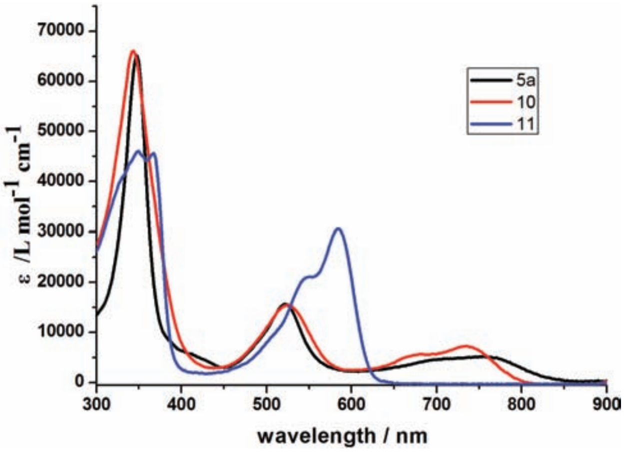


Figure 2. UV−vis-NIR absorption spectra of **5a** (black), **10** (red), and **11** (blue) in chloroform.

The absorption spectra of the representative TDIs in chloroform are shown in Figure 2, showing broad absorption which covers the whole visible and NIR region, rendering them as "full-absorption dyes" and therefore potential objects in solar cells. Compared with their all-carbon parent, tetracene (474 nm),[13] those TDIs display broad and significantly red-shifted spectra and have higher molar extinction coefficient in the visble-NIR region. The remarkable difference between TDIs and tetracene in their absorption peaks and intensities reflect the substantial electronic effect of the attachment of strong electron-withdrawing diimides groups. Furthermore, in contrast with NDI (380 nm),[14] which show absorption only in the UV region, the fusion of two additional aromatic rings also leads to much more red shift in absorption as a reflection of a larger extensive conjugation over the electronic system (see below).

The absorption spectra of **11** lead to a remarkable change. The purple-red solution of compound **11** exhibits a major absorption band at 584 nm with a blue shift of 176 nm relative to **10** (λ_{max} = 740 nm), as a reflection of the interruption of

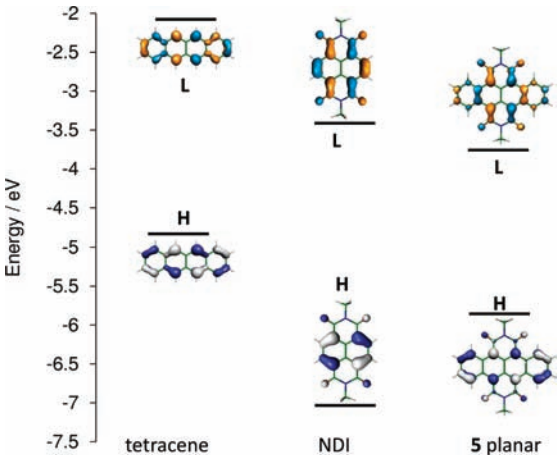


Figure 3. Energies and shapes of B3LYP/6-31G* frontier orbitals (HOMO and LUMO) of tetracene, NDI, and a planar model of **5**.

tetrabenzo-units to the effective conjugation along the cores of the TDIs.

An analysis in terms of the orbital nature of the TD-B3LYP/6-31G* computed electronic transitions of **5** and other TDI derivatives (see Tables S1−S3 and Figures S4−S5 for a comparison between computed and observed spectra) sheds more light on the nature of the lowest energy transitions (and specifically the NIR transitions of TDIs). The computed excitation energies show that the lower energy portion of the absorption spectra of **5** (and other TDI derivatives) and **11** is dominated by two low lying transitions, the first of which is weaker than the second one, considerably more intense (see also Tables S1−S3). The lowest energy and weaker transition (responsible for the NIR absorption of TDIs) corresponds always to the HOMO → LUMO excitation.

The HOMO orbital of all the TDI derivatives is dominated by the tetracenic HOMO nature, while the LUMO orbital shows the typical character of diimide derivatives (see Figure 3, Figure S6 and Table S2). Therefore, the low energy transition of TDI derivatives is a new transition reflecting the peculiar frontier orbital nature. While for **5** the $S_0 \rightarrow S_1$ transition is well separated in energy from the next, higher intensity transition, the two excitations are almost degenerate for **11** (see Table S1). Interestingly, the second (more intense) transition of TDIs is also dominated by a $\pi \rightarrow \pi^*$ electronic excitation from an occupied orbital of tetracenic nature to the LUMO (see Figure S7 and Table S3).

The redox properties of these TDIs were studied by cyclic voltammetry in dichloromethane (in V vs Ag/AgCl). The half-wave reduction potentials of the representative compounds are −0.63, −1.11 V for NDI; −0.40, −0.73 V for **5a**; and −0.32, −0.64 V for **11**. The first reduction potentials of these TDIs are much less negative than those of parent NDI (Table 1), thus, revealing the extremely strong electron-accepting abilities, and the first reduction potential of **5c** is less negative by about 0.1 V than the other alkyl substituted TDIs, which is probably due to the introduction of semiperfluoroalkyl chains.

The optical band gaps and LUMO energy levels of these compounds were calculated based on UV−vis-NIR absorption data and the onset potential of the first reduction wave. It is worth mentioning that the band gap of these TDIs are much smaller than the gap of NDI (λ_{max} = 380 nm, optical gap = 3.12 eV), which could be related to the increasing conjugation length, and the LUMO fall into −4.0 to −4.2 eV indicating that all of them could be served as candidates for air-stable n-type semiconductors. Notably, the value of the gaps are comparable to the HOMO−LUMO gap of heptacene,[15] which means that the introduction of electron-withdrawing tetracarboxylic diimides can reduce the gaps more efficiently than the fusion of rings.

Table 1. Opto-Electronic Properties of TDIs and Energy Levels of Representative Compounds

	λ_1 [nm]^a	E_{1r} [V]^b	LUMO [eV]^c	HOMO (eV)^d	E_g [eV]^e
NDI^f	380	−0.63	−3.90	−7.02	3.12
5a	756	−0.40	−4.06	−5.54	1.48
6a	780	−0.40	−4.06	−5.50	1.44
5c	774	−0.29	−4.17	−5.50	1.43
10	737	−0.35	−4.12	−5.68	1.56
11	584	−0.32	−4.14	−6.13	1.99

[a] λ_1 as peak of the visible-NIR regions [b] V vs Ag/AgCl. Half wave redox potential (in V vs Ag/AgCl) measured in CH_2Cl_2 with a scan rate of 0.1 V/s. [c] Calculated by measuring the onset potential of the first reduction wave. [d] Estimated from LUMO levels and E_g. [e] Obtained from the edge of the absorption spectra. [f] NDI: *N*,*N*′-di (*n*-octyl)-naphthalene-1,2:6,7-tetracarboxylic bisimide.

All the TDIs derivatives show good solubility in common organic solvents such as dichloromethane, chloroform, toluene, and tetrahydrofuran. Their structures are unambiguously identified by ^{1}H NMR, ^{13}C NMR spectroscopy, and MALDI-TOF. They exhibited very good stability on exposure to light and air condition, whereas the tetracene is air and light sensitive materials, that is, the introduction of strong electron-withdrawing imides groups into the tetracene improved their photo-oxidative resistances significantly and make them to be stable n-type semiconductors and NIR dyes (Supporting Information).[16]

In conclusion, a new family of stable low band gap tetracene tetracarboxylic diimides derivatives has been designed and synthesized for the first time from readily available TBNDIs. In light of their unique structure and admirable photophysical and electro-optical properties, this new molecular skeleton is promising candidate for air stable n-type semiconductors and solar cell materials. We believe that this straightforward route, based on direct double ring extension involving organometallic reagents, opens a new way to access elusive stable and higher acenes tetracarboxylic diimides in the near future.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information. Experimental details and characterization data of all new compounds, computational details, optimized structures of **5** and **11**, computed absorption spectra, room-temperature UV−vis-NIR spectral measurements. This material is available free of charge via the Internet at http://pubs.acs.org.

■ AUTHOR INFORMATION

Corresponding Authors

wangzhaohui@iccas.ac.cn; fabrizia.negri@unibo.it; yanli@iccas.ac.cn

■ ACKNOWLEDGMENT

For financial support of this research, we thank the National Natural Science Foundation of China (91027043), 973 Program

(2011CB932301), NSFC-DFG joint project TRR61, Solvay, the Chinese Academy of Sciences, and Italian PRIN 2008, project JKBBK4.

■ REFERENCES

(1) (a) Kelley, T. W.; Baude, P. F.; Gerlach, C.; Ender, D. E.; Muyres, D.; Haase, M. A.; Vogel, D. E.; Theiss, S. D. *Chem. Mater.* **2004**, *16*, 4413. (b) Jang, B.-B.; Lee, S. H.; Kafafi, Z. H. *Chem. Mater.* **2006**, *18*, 449. (c) Murphy, A. R.; Fréchet., J. M. J. *Chem. Rev.* **2007**, *107*, 1066.

(2) (a) Anthony, J. E. *Angew. Chem., Int. Ed.* **2008**, *47*, 452. (b) Moon, H.; Zeis, R.; Borkent, E.-J.; Besnard, C.; Lovinger, A. J.; Siegrist, T.; Kloc, C.; Bao, Z. *J. Am. Chem. Soc.* **2004**, *126*, 15322. (c) Bendikov, M.; Wudl, F.; Perepichka, D. F. *Chem. Rev.* **2004**, *104*, 4891.

(3) (a) Anthony, J. E. *Chem. Rev.* **2006**, *106*, 5028. (b) Chen, Z.; Müller, P.; Swager, T. M. *Org. Lett.* **2006**, *8*, 273.

(4) For recent review: (a) Usta, H.; Facchetti, A.; Marks, T. J. *Acc. Chem. Res.* **2011**, *44*, 501. (b) Würthner, F.; Stolte, M. *Chem. Commun.* **2011**, *47*, 5109. For recent example:Katsuta, S.; Tanaka, K.; Maruya, Y.; Mori, S.; Masuo, S.; Okujima, T.; Uno, H.; Nakayma, K.; Yamada, H. *Chem. Commun.* **2011**, *47*, 10112.

(5) (a) Katz, H. E.; Lovinger, A. J.; Johnson, J.; Kloc, C.; Slegrist, T.; Li, W.; Lin, Y.-Y.; Dodabalapur, A. *Nature* **2000**, *404*, 478. (b) Gao, X.; Di, C.; Hu, Y.; Yang, X.; Fan, H.; Zhang, F.; Liu, Y.; Li, H.; Zhu, D. *J. Am. Chem. Soc.* **2010**, *132*, 3697. (c) Gsänger, M.; Oh, J. H.; Könemann, M.; Hoffken, H. W.; Krause, A. M.; Bao, Z.; Würthner, F. *Angew. Chem., Int. Ed.* **2010**, *49*, 740. (d) Schmidt, R.; Oh, J. H.; Sun, Y.; Deppisch, M.; Krause, A. M.; Radacki, K.; Braunschweig, H.; Konemann, M.; Erk, P.; Bao, Z.; Würthner, F. *J. Am. Chem. Soc.* **2009**, *131*, 6215. (e) Guo, X.; Watson, M. D. *Org. Lett.* **2008**, *10*, 5333. (f) Lu, X.; Zhu, W.; Xie, Y.; Li, X.; Gao, Y.; Li, F.; Tian, H. *Chem.—Eur. J.* **2010**, *16*, 8355.

(6) For selected examples: (a) Shimizu, M.; Nagao, I.; Tomioka, Y.; Hiyama, T. *Angew. Chem., Int. Ed.* **2008**, *120*, 8216. (b) Lu, J.; Mao, G.; Zhang, W.; Xi, Z. *Chem. Commun.* **2005**, 4848. (c) Fang, H.; Li, G.; Mao, G.; Xi, Z. *Chem.—Eur. J.* **2004**, *10*, 3444. (d) Zhang, W.; Zhang, S.; Sun, X.; Nishiura, M.; Hou, Z.; Xi, Z. *Angew. Chem., Int. Ed.* **2009**, *48*, 7227.

(7) (a) Negishi, E.; Swanson, D. R.; Cederbaum, S.; Takahashi, T. *Tetrahedron. Lett.* **1986**, *27*, 2829. (b) Takahashi, T.; Hara, R.; Nishihara, Y.; Kotora, M. *J. Am. Chem. Soc.* **1996**, *118*, 5154. (c) Takahashi, T.; Li, Y.; Stepnicka, P.; Kitamura, M.; Liu, Y.; Nakajima, K.; Kotora, M. *J. Am. Chem. Soc.* **2002**, *124*, 576. (d) Takahashi, T.; Li, S.; Huang, W.; Kong, F.; Nakajima, K.; Shen, B.; Ohe, T.; Kanno, K.-I. *J. Org. Chem.* **2006**, *71*, 7967.

(8) Gao, X.; Qiu, W; Yang, X.; Liu, Y.; Wang, Y.; Zhang, H.; Qi, T.; Liu, Y.; Lu, K.; Du, C.; Shuai, Z.; Yu, G.; Zhu, D. *Org. Lett.* **2007**, *9*, 3917.

(9) (a) See, K. C.; Landis, C.; Sarjeant, A.; Katz, H. E. *Chem. Mater.* **2008**, *20*, 3609. (b) Krüger, H.; Janietz, S.; Sainova, D.; Dobreva, D.; Koch, N.; Vollmer, A. *Adv. Funct. Mater.* **2007**, *17*, 3715.

(10) Nagao, I.; Shimizu, M.; Hiyama., T. *Angew. Chem., Int. Ed.* **2009**, *48*, 7573.

(11) Freedman, H. H. *J. Org. Chem.* **1962**, *27*, 2298.

(12) CCDC 809110 (3d) contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via http://www.ccdc.cam.ac.uk/data_request/cif. Crystal data for **3d**: single crystals suitable for X-ray diffraction were obtained by slowly evaporating a solution of **3d** in solution of dichloromethane and methanol at room temperature. $C_{46}H_{44}F_{14}N_2O_4$, M = 954.83, monoclinic space group *Cc*, a = 27.048(6), b = 14.838(3), c = 11.731(3)_, α = 90.00°, β = 101.587(3) °, γ = 90.00°. V = 4611.9(18), Z = 4, black crystal.

(13) Odom, S. A.; Parkin, S. R.; Anthony, J. E. *Org. Lett.* **2003**, *5*, 4245.

(14) Thalacker, C.; Röger, C.; Würthner, F. *J. Org. Chem.* **2006**, *71*, 8098.

(15) (a) Chun, D.; Cheng, Y.; Wudl, F. *Angew. Chem., Int. Ed.* **2008**, *47*, 8380. (b) Kaur, I.; Stein, N. N.; Kopreski, R. P.; Miller., G. P. *J. Am. Chem. Soc.* **2009**, *131*, 3424.

(16) For recent example of NIR dyes:Zhu, X.; Tsuji, H.; Nakabayashi, K.; Ohkoshi, S.; Nakamura, E. *J. Am. Chem. Soc.* **2011**, *133*, 16342.