Fused Dibenzo[a,m]rubicene: A New Bowl-Shaped Subunit of C$_{70}$ Containing Two Pentagons

Junzhi Liu,[†] Silvio Osella,[‡,∥] Ji Ma,[†] Reinhard Berger,[†] David Beljonne,[‡] Dieter Schollmeyer,[§] Xinliang Feng,*,[†] and Klaus Müllen*,[⊥]

[†]Center for Advancing Electronics Dresden & Department of Chemistry and Food Chemistry, Technische Universität Dresden, 01062 Dresden, Germany
[‡]Laboratory for Chemistry of Novel Materials, University of Mons, B-7000 Mons, Belgium
[§]Institut für Organische Chemie, Universität Mainz, 55099, Mainz, Germany
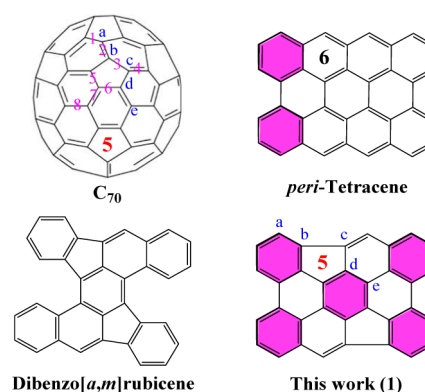[⊥]Max-Planck Institut für Polymerforschung, 55128, Mainz, Germany

Ⓢ *Supporting Information*

ABSTRACT: Total synthetic approaches of fullerenes are the holy grail for organic chemistry. So far, the main attempts have focused on the synthesis of the buckminsterfullerene C$_{60}$. In contrast, access to subunits of the homologue C$_{70}$ remains challenging. Here, we demonstrate an efficient bottom-up strategy toward a novel bowl-shaped polycyclic aromatic hydrocarbons (PAH) C34 with two pentagons. This PAH represents a subunit for C$_{70}$ and of other higher fullerenes. The bowl-shaped structure was unambiguously determined by X-ray crystallography. A bowl-to-bowl inversion for a C$_{70}$ fragment in solution was investigated by dynamic NMR analysis, showing a bowl-to-bowl inversion energy ($\Delta G^{\ddagger}$) of 16.7 kcal mol^{-1}, which is further corroborated by DFT calculations.

Scheme 1. Structure of a Fragment of C$_{70}$

owl-shaped polycyclic aromatic hydrocarbons, also named buckybowls, have attracted interest due to their unique chemical and physical properties,[1−4] such as bowl inversion,[5,6] supramolecular assembly,[7,8] electronic conductivity,[9,10] and chirality.[11,12] In the past decade, C_{3v}-symmetric sumanene[13,14] and C_{5v}-symmetric corannulene,[2,3] as the typical subunits of C$_{60}$, have been intensively investigated. These molecules can not only serve as precursors for the bottom-up synthesis of fullerene C$_{60}$ and carbon nanotubes[15−17] but also provide insight into the chemical and physical properties of corresponding fullerenes. Based on this groundwork, Scott and co-workers reported the first rational synthesis of C$_{60}$ by using the smaller buckybowl molecules.[15,18] In contrast to C$_{60}$, C$_{70}$ has a reduced symmetry of D_{5h}.[19,20] Moreover, C$_{70}$ contains five types of carbon atoms (a−e, blue) and features eight types of C−C bonds (1−8, purple) (Scheme 1).[21−23] Compared to C$_{60}$, which is a representative n-type semiconducting material, C$_{70}$ displays stronger light absorption and deeper HOMO and LUMO levels. Thus far, most studies on fullerene chemistry have focused on the synthesis of bowl-shaped molecules as subunits of fullerene C$_{60}$, and synthesis of fragments of C$_{70}$ remains elusive mostly due to a lack of proper synthetic protocols and accessibility in reasonable amounts.[24,25]

Here, we demonstrate the efficient synthesis of a novel fused dibenzo[a,m]rubicene, dinaphtho[1,2,3,4,5-ijklm:1′,2′,3′,4′,5′-uvwxa]rubicene (**1**), by Pd-catalyzed intramolecular cyclization of the prefused dibenzo[a,m]rubicene[26,27] derivative as the key reaction (Scheme 1). Compound **1**, with 34 carbon atoms, is a fragment for investigating C$_{70}$ because it contains all types of carbon atoms present in C$_{70}$ (Scheme 1). Furthermore, **1** also can serve as a fragment of other higher fullerenes, such as C$_{76}$, C$_{78}$, and C$_{84}$.[28−30] A number of unique structural and physical properties were disclosed for compound **1**, such as a bowl-to-bowl inversion at the room temperature.

Synthesis of a buckybowl **1** embedding two pentagons is depicted in Scheme 2. First, compound 2-((4-(*tert*-butyl)phenyl)ethynyl)-4′-(2-((4-(*tert*-butyl)phenyl)ethynyl)phenyl)-2″-chloro-5′-(2-chlorophenyl)-1,1′:2′,1″-terphenyl (**3**) was prepared by two-fold Suzuki coupling of 2′,5′-dibromo-2,2″-dichloro-1,1′:4′,1″-terphenyl (**2**) with (2-((4-(*tert*-butyl)phenyl)ethynyl)phenyl)boronic acid in 63% yield. ICl-induced cyclization was subsequently performed to provide 6,13-bis(4-(*tert*-butyl)phenyl)-7,14-bis(2-chlorophenyl)-5,12-diiodobenzo[k]tetraphene (**4**) in 85% yield. Next, the iodo substituents were removed by using *n*-BuLi to afford **5** in 58% yield. A Scholl reaction of **5** was carried out with 2,3-dichloro-5,6-dicyano-1,4-benzoquinone (DDQ) and trifluoromethanesulfonic acid in dry dichloromethane (DCM) at 0 °C, affording 5,14-bis(4-(*tert*-

Scheme 2. Synthesis of Buckybowl 1[a]
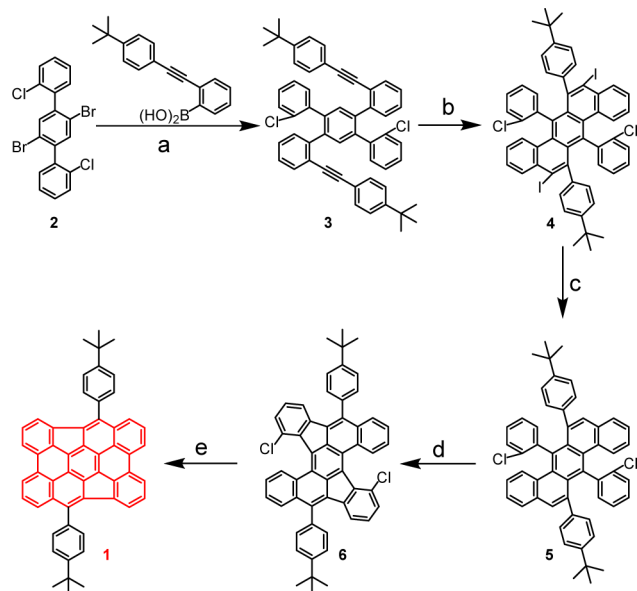
[a]Reagents and conditions: (a) Pd(PPh$_3$)$_4$, K$_2$CO$_3$, dioxane/H$_2$O, 90 °C, 36 h, 63%; (b) ICl (1 M in DCM), −78 °C, 3 h, 85%; (c) n-BuLi, THF, MeOH, 1 h, 58%; (d) DDQ/CF$_3$SO$_3$H, DCM, 0 °C, 1 h, 45%; (e) PdCl$_2$(PCy$_3$)$_2$, DBU, DMF, 160 °C, 6 h, microwave, 34%.

butyl)phenyl)-9,18-dichlorodibenzo[a,m]rubicene (**6**) in 45% yield including a highly selective 1,2-shift of aryl groups.[26] Finally, intramolecular cyclization of **6** was performed in the presence of [Pd-(PCy$_3$)$_2$Cl$_2$] and a stoichiometric amount of 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU) in N,N-dimethylformamide (DMF), providing compound **1** in 34% yield.[4] The chemical identity of **1** was first confirmed by MALDI-TOF MS analysis, as depicted in Figure S1. There is only one dominant peak in the mass spectra of **1**, revealing its defined molecular composition. The isotopic distribution pattern of the mass peak is in good agreement with the calculated one.

Single crystals of **1** were grown by slow evaporation from solutions in hexane/dichloromethane; the bowl-shaped structure of **1** was elucidated by X-ray diffraction (Figure 1). Five-membered rings embedded in a hexagonal lattice impart geodesic curvature, as in fullerenes. The bowl depth, which is defined as

Figure 1. Structural features of buckybowl **1**. (a) Top view of **6** in the single crystal. (b) Top view of **1**. (c) Side view of **1**. (d) Packing mode of **1** in the crystal. (e) Bond lengths of **1** from single crystal analysis. (f) HOMA values and resonance structure of **1**.

the distance between the mean plane that consists of four carbons at the edge and the centroid of the six member ring, is 1.68 Å. This value is higher than that of corannulene (0.86 Å). X-ray diffraction data also disclose the detailed bonding parameters of **1** (Figure 1e). The C−C bonds at the five-membered rings of **1** (red one in Figure 1e) are obviously longer (1.56 Å) than other bonds, which suggests their single bond character. On the basis of the crystal structures, the local aromaticity of individual rings was analyzed using the harmonic oscillator model of aromaticity (HOMA).[31,32] As shown in Figure 1f, ring A in **1** has the highest HOMA value (0.999) followed by rings B and C with HOMA values greater than 0.83 while rings D and E have significantly lower HOMA values (0.409 and 0.406). Thereby, there are five Clar's aromatic sextets in **1** in the ground state, while peri-tetracene has only two Clar's aromatic sextets (Scheme 1). According to the Clar sextet rule, the compound with more aromatic sextets is more stable as a result of gaining the aromatic stabilization energies, which suggests that the pentagon-embedding peri-tetracene **1** has enhanced stability compared to the conventional peri-tetracene that consists solely of six-membered rings.

Compound **1** was further investigated by variable-temperature ^{1}H NMR spectra. The bowl-to-bowl inversion of **1** was detected at room temperature using dynamic NMR analysis (Figure 2).
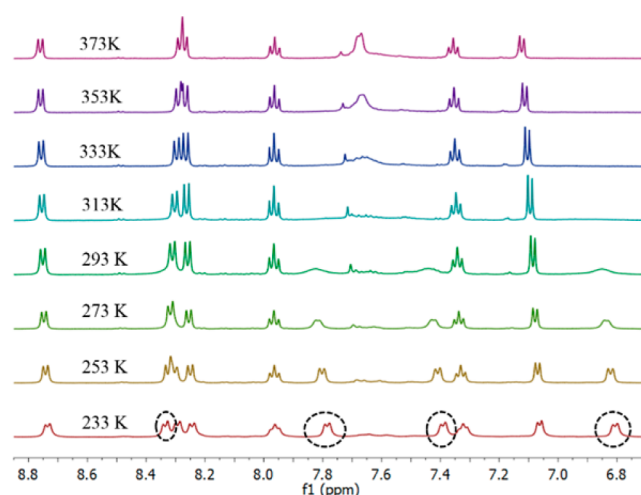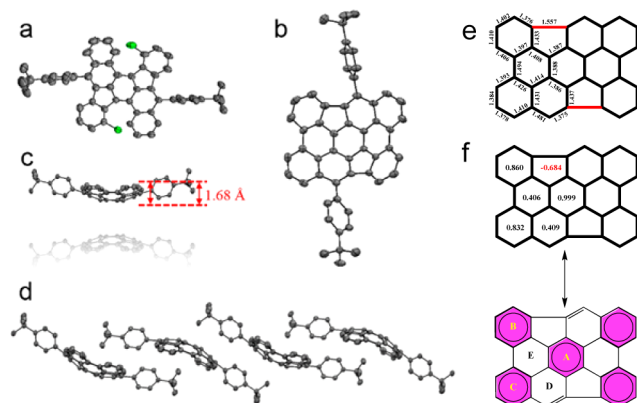

Figure 2. Variable-temperature ^{1}H NMR spectra of buckybowl **1** (500 MHz, C$_2$D$_2$Cl$_4$).

The ^{1}H NMR spectrum of **1** in 1,1,2,2-tetrachloroethane-d_2 at −40 °C exhibited four doublet peaks for phenyl protons of tert-butylphenyl groups at δ = 8.24, 7.78, 7.39, and 6.81 ppm. This nonsymmetric feature indicates that there is no bowl-to-bowl inversion for compound **1** at such low temperature. However, when the temperature is increased, the phenyl proton signals of tert-butylphenyl groups gradually broaden (Figure 2), and these signals coalesce at 333 K. Accordingly, the bowl-to-bowl inversion energy ($\Delta G^{\ddagger}$) was calculated by two-dimensional exchange spectroscopy (2D EXSY) experiments. At 333 K, $\Delta G^{\ddagger}$ was determined to be 16.7 (±0.2) kcal mol^{-1}.[33] This value is higher than that of the parent corannulene (10.2 ± 0.2 kcal mol^{-1}).[34] Experimentally determined bowl inversion energy of **1** is further corroborated by theoretical calculation. DFT calculations at the B3LYP/cc-pVDZ level of theory (using the Gaussian09 suite of programs[35]) show that compound **1** undergoes a bowl-to-bowl conversion through a flat transition

state (Figure 3), with free activation energy of $\Delta G^{\ddagger} = 14.4$ kcal mol^{-1}. The computed inversion barrier is in reasonable
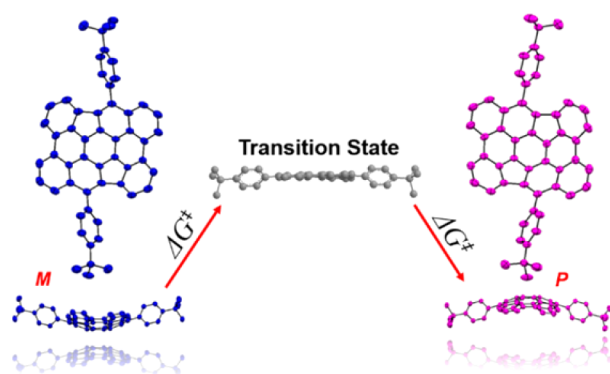

Figure 3. Inversion dynamics of the M and P conformers of buckybowl **1**.

agreement with experiment and much higher than that of corannulene (9.1 kcal mol^{-1})[33] calculated at the same level of theory. Two different conformations of **1** were found in the same crystal, that is, conformers M and P coexist in a 1:1 ratio in the crystal (Figure 3).[36]

Compound **1** has good solubility in common organic solvents such as DCM, THF, toluene, and hexane. The UV−vis absorption spectra of precursor **6** and final product **1** in DCM solutions are compared in Figure 4a. Compound **1** shows a
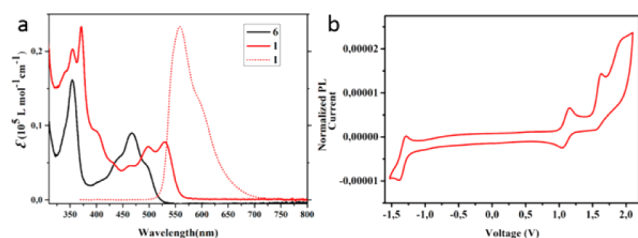

Figure 4. Physical properties of buckybowl **1**. (a) UV−vis absorption spectra (solid) and fluorescence spectra (dot) of **6** and **1** (for all spectra: 10^{-5} M in DCM). (b) Cyclic voltammetry of **1** (0.1 M nBu$_4$NPF$_6$ in DCM) at a scan rate of 50 mV s^{-1}.

significant absorption maximum red-shifted by 36 nm relative to that of **6**, with an absorption maximum at 529 nm and two other shoulder peaks at 499 and 461 nm. This reflects the extended conjugation in **1**. Thus, the optical band gaps of **6** and **1** are determined from the onsets of their UV−vis absorption spectra, which are 2.40 and 2.21 eV, respectively. Compound **1** shows fluorescence in DCM solution with a maximum at 559 nm and a quantum yield of 12% (fluorescein as the reference, $\Phi_F = 90\%$ in 0.1 M NaOH aqueous solution),[37] as shown in Figure 4a. Time-dependent DFT calculations on **1** yield optical transitions that well match the experimental spectrum, with a low-energy HOMO-to-LUMO transition at 526 nm and two higher-energy shoulders at 441 and 403 nm involving deeper occupied molecular orbitals (see Supporting Information).

Electrochemical properties of **1** were investigated by cyclic voltammetry (CV) in DCM solutions (Figure 4b). Notably, compound **1** displays one reversible and two irreversible oxidations with first, second, and third oxidation potentials of $E_{ox1} = +1.01$ V, $E_{ox2} = +1.47$ V, and $E_{ox3} = +1.50$ V vs the ferrocene/ferrocenium couple (Fc/Fc$^+$). In the negative potential region, one reversible reduction wave was observed at

$E_{red} = -1.17$ V (vs Fc/Fc$^+$). Compared to the corannulene or C$_{60}$, which are reduced easily (up to four- and six-electron reductions, respectively), they are slightly difficult to oxidize due to the electron-accepting ability of the five-membered rings.[38−41] In contrast, **1** can be oxidized easily and reduced. The HOMO and LUMO energy levels are estimated from the onsets of the first reversible oxidation and reduction peaks to be −5.81 and −3.63 eV, respectively. Thus, the energy gap of **1** is about 2.18 eV calculated based on the CV measurement, which is consistent with the optical band gap.

In summary, we have demonstrated an efficient synthetic approach toward an unprecedented fragment of the fullerene C$_{70}$ containing two five-membered rings. The geometric and optoelectronic nature of the resulting buckybowl is comprehensively investigated by single-crystal X-ray, dynamic NMR, UV−vis absorption, and CV analysis. For the first time, we were able to investigate the bowl-to-bowl inversion behavior of a C$_{70}$ subunit and determine the activation energy to be 16.7 kcal mol^{-1}. This synthetic investigation can help to provide an in-depth insight into the chemistry of fullerene C$_{70}$ and other higher fullerene analogues. They also pave the way toward stable *peri*-acene-like molecules, possibly incorporating five-, seven-, and/or eight-membered rings.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/jacs.6b04426.

> Experimental details, synthesis, characterizations, computational studies, and NMR spectra (PDF)
> X-ray data for **6** (CIF)
> X-ray data for **1** (CIF)

■ AUTHOR INFORMATION

Corresponding Authors

*xinliang.feng@tu-dresden.de
*muellen@mpip-mainz.mpg.de

Present Address

∥Division of Theoretical Chemistry and Biology, KTH Royal Institute of Technology, Roslagstullsbacken 15, S-10691 Stockholm, Sweden.

Notes

The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

■ REFERENCES

(1) Scott, L. T. *Pure Appl. Chem.* **1996**, *68*, 291−300.
(2) Tsefrikas, V. M.; Scott, L. T. *Chem. Rev.* **2006**, *106*, 4868−4884.
(3) Wu, Y.-T.; Siegel, J. S. *Chem. Rev.* **2006**, *106*, 4843−4867.
(4) Wu, Y.-T.; Wu, T.-C.; Chen, M.-K.; Hsin, H.-J. *Pure Appl. Chem.* **2014**, *86*, 539−544.
(5) Tan, Q.; Higashibayashi, S.; Karanjit, S.; Sakurai, H. *Nat. Commun.* **2012**, *3*, 891.

(6) Juríček, M.; Strutt, N. L.; Barnes, J. C.; Butterfield, A. M.; Dale, E. J.; Baldridge, K. K.; Stoddart, J. F.; Siegel, J. S. *Nat. Chem.* **2014**, *6*, 222−228.

(7) Xiao, W.; Passerone, D.; Ruffieux, P.; Aït-Mansour, K.; Gröning, O.; Tosatti, E.; Siegel, J. S.; Fasel, R. *J. Am. Chem. Soc.* **2008**, *130*, 4767−4771.

(8) Stöckl, Q.; Bandera, D.; Kaplan, C. S.; Ernst, K.-H; Siegel, J. S. *J. Am. Chem. Soc.* **2014**, *136*, 606−609.

(9) Amaya, T.; Seki, S.; Moriuchi, T.; Nakamoto, K.; Nakata, T.; Sakane, H.; Saeki, A.; Tagawa, S.; Hirao, T. *J. Am. Chem. Soc.* **2009**, *131*, 408−409.

(10) Schmidt, B. M.; Seki, S.; Topolinski, B.; Ohkubo, K.; Fukuzumi, S.; Sakurai, H.; Lentz, D. *Angew. Chem., Int. Ed.* **2012**, *51*, 11385−11388.

(11) Higashibayashi, S.; Sakurai, H. *J. Am. Chem. Soc.* **2008**, *130*, 8592−8593.

(12) Bandera, D.; Baldridge, K. K.; Linden, A.; Dorta, R.; Siegel, J. S. *Angew. Chem., Int. Ed.* **2011**, *50*, 865−867.

(13) Sakurai, H.; Daiko, T.; Hirao, T. *Science* **2003**, *301*, 1878.

(14) Sakurai, H.; Daiko, T.; Sakane, H.; Amaya, T.; Hirao, T. *J. Am. Chem. Soc.* **2005**, *127*, 11580−11581.

(15) Scott, L. T.; Boorum, M. M.; McMahon, B. J.; Hagen, S.; Mack, J.; Blank, J.; Wegner, H.; de Meijere, A. *Science* **2002**, *295*, 1500−1503.

(16) Scott, L. T.; Jackson, E. A.; Zhang, Q.; Steinberg, B. D.; Bancu, M.; Li, B. *J. Am. Chem. Soc.* **2012**, *134*, 107−110.

(17) Sanchez-Valencia, J. R.; Dienel, T.; Gröning, O.; Shorubalko, I.; Mueller, A.; Jansen, M.; Amsharov, K.; Ruffieux, P.; Fasel, R. *Nature* **2014**, *512*, 61−64.

(18) Boorum, M. M.; Vasil'ev, Y. V.; Drewello, T.; Scott, L. T. *Science* **2001**, *294*, 828−831.

(19) McKenzie, D. R.; Davis, C. A.; Cockayne, D. J. H.; Muller, D. A.; Vassallo, A. M. *Nature* **1992**, *355*, 622−624.

(20) Hedberg, K.; Hedberg, L.; Bühl, M.; Bethune, D. S.; Brown, C. A.; Johnson, R. D. *J. Am. Chem. Soc.* **1997**, *119*, 5314−5320.

(21) Croucher, P. D.; Marshall, J. M. E.; Nichols, P. J.; Raston, C. L. *Chem. Commun.* **1999**, 193−194.

(22) Pham, D.; Ceron-Bertran, J.; Olmstead, M. M.; Mascal, M.; Balch, A. L. *Cryst. Growth Des.* **2007**, *7*, 75−82.

(23) Nikolaev, A. V.; Dennis, T. J. S.; Prassides, K.; Soper, A. K. *Chem. Phys. Lett.* **1994**, *223*, 143−148.

(24) Wegner, H. A.; Reisch, H.; Rauch, K.; Demeter, A.; Zachariasse, K. A.; de Meijere, A.; Scott, L. T. *J. Org. Chem.* **2006**, *71*, 9080−9087.

(25) Wu, T.-C.; Chen, M.-K.; Lee, Y.-W.; Kuo, M.-Y.; Wu, Y.-T. *Angew. Chem., Int. Ed.* **2013**, *52*, 1289−1293.

(26) Liu, J.; Narita, A.; Osella, S.; Zhang, W.; Schollmeyer, D.; Beljonne, D.; Feng, X.; Müllen, K. *J. Am. Chem. Soc.* **2016**, *138*, 2602−2608.

(27) Gu, X.; Xu, X.; Li, H.; Liu, Z.; Miao, Q. *J. Am. Chem. Soc.* **2015**, *137*, 16203−16208.

(28) Thilgen, C.; Herrmann, A.; Diederich, F. *Angew. Chem., Int. Ed. Engl.* **1997**, *36*, 2268−2280.

(29) Epple, L.; Amsharov, K.; Simeonov, K.; Dix, I.; Jansen, M. *Chem. Commun.* **2008**, 5610−5162.

(30) Liu, J.; Ravat, P.; Wagner, M.; Baumgarten, M.; Feng, X.; Müllen, K. *Angew. Chem., Int. Ed.* **2015**, *54*, 12442−12446.

(31) Kruszewski, J.; Krygowski, T. M. *Tetrahedron Lett.* **1972**, *13*, 3839−3842.

(32) Krygowski, T. M. *J. Chem. Inf. Model.* **1993**, *33*, 70−78.

(33) Yokoi, H.; Hiraoka, Y.; Hiroto, S.; Sakamaki, D.; Seki, S.; Shinokubo, H. *Nat. Commun.* **2015**, *6*, 8215.

(34) Biedermann, P. U.; Pogodin, S.; Agranat, I. *J. Org. Chem.* **1999**, *64*, 3655−3662.

(35) Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Scalmani, G.; Barone, V.; Mennucci, B.; Petersson, G. A.; Nakatsuji, H.; Caricato, M.; Li, X.; Hratchian, H. P.; Izmaylov, A. F.; Bloino, J.; Zheng, G.; Sonnenberg, J. L.; Hada, M.; Ehara, M.; Toyota, K.; Fukuda, R.; Hasegawa, J.; Ishida, M.; Nakajima, T.; Honda, Y.; Kitao, O.; Nakai, H.; Vreven, T.; Montgomery, J. A., Jr.; Peralta, J. E.; Ogliaro, F.; Bearpark, M.; Heyd, J. J.; Brothers, E.; Kudin, K. N.; Staroverov, V. N.; Kobayashi, R.; Normand, J.; Raghavachari, K.; Rendell, A.; Burant, J. C.; Iyengar, S. S.; Tomasi, J.; Cossi, M.; Rega, N.; Millam, J. M.; Klene, M.; Knox, J. E.; Cross, J. B.; Bakken, V.; Adamo, C.; Jaramillo, J.; Gomperts, R.; Stratmann, R. E.; Yazyev, O.; Austin, A. J.; Cammi, R.; Pomelli, C.; Ochterski, J. W.; Martin, R. L.; Morokuma, K.; Zakrzewski, V. G.; Voth, G. A.; Salvador, P.; Dannenberg, J. J.; Dapprich, S.; Daniels, A. D.; Farkas, O.; Foresman, J. B.; Ortiz, J. V.; Cioslowski, J.; Fox, D. J. *Gaussian 09*, revision A.1; Gaussian, Inc.: Wallingford, CT, 2009.

(36) Petrukhina, M. A.; Andreini, K. W.; Peng, L.; Scott, L. T. *Angew. Chem., Int. Ed.* **2004**, *43*, 5477−5481.

(37) Crosby, G. A.; Demas, J. N. *J. Phys. Chem.* **1971**, *75*, 991−1024.

(38) Janata, J.; Gendell, J.; Ling, C.-Y.; Barth, W. E.; Backes, L.; Mark, H. B.; Lawton, R. G. *J. Am. Chem. Soc.* **1967**, *89*, 3056−3058.

(39) Bruno, C.; Benassi, R.; Passalacqua, A.; Paolucci, F.; Fontanesi, C.; Marcaccio, M.; Jackson, E. A.; Scott, L. T. *J. Phys. Chem. B* **2009**, *113*, 1954−1962.

(40) Yang, Y.; Arias, F.; Echegoyen, L.; Chibante, L. P. F.; Flanagan, S.; Robertson, A.; Wilson, L. J. *J. Am. Chem. Soc.* **1995**, *117*, 7801−7804.

(41) Yang, Y.; Arias, F.; Echegoyen, L.; Chibante, L. P. F.; Flanagan, S.; Robertson, A.; Wilson, L. J. *J. Am. Chem. Soc.* **1995**, *117*, 7801−7804.