

Synthesis of Oligoparaphenylene-Derived Nanohoops Employing an Anthracene Photodimerization–Cycloreversion Strategy

Ze-Ao Huang,[†] Chen Chen,[†] Xiao-Di Yang,^{*,‡} Xiang-Bing Fan,[†] Wen Zhou,[§] Chen-Ho Tung,[†] Li-Zhu Wu,[†] and Huan Cong^{*,†}

[†]Key Laboratory of Photochemical Conversion and Optoelectronic Materials, Technical Institute of Physics and Chemistry & University of Chinese Academy of Sciences, Chinese Academy of Sciences, Beijing 100190, China

[‡]Laboratory of Advanced Materials, Fudan University, Shanghai 200438, China

[§]Beijing National Laboratory for Molecular Sciences (BNLMS), College of Chemistry and Molecular Engineering, Peking University, Beijing 100871, China

S Supporting Information

ABSTRACT: The century-old yet synthetically underexplored anthracene photodimerization–cycloreversion reactions have been employed as the key steps to access highly strained aromatic hydrocarbons. Herein we report the chemical syntheses of oligoparaphenylene-derived nanohoops in five steps or less featuring a rigid dianthracene synthon. The newly synthesized nanohoops display intriguing experimental and computational properties.

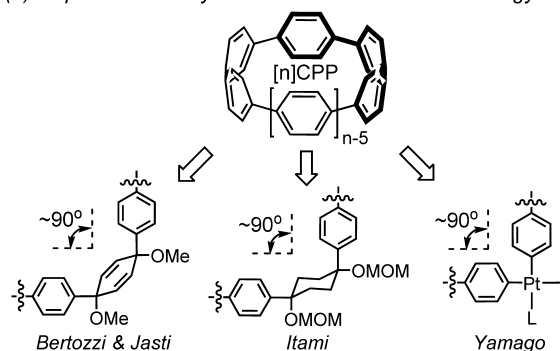
Highly strained, nonplanar aromatic hydrocarbons have been aggressively pursued synthetic targets for decades because of their unusual structures and distinct properties. The seemingly counterintuitive bond connections and forced geometries present considerable synthetic challenges that in turn have inspired creative molecular designs and impressive synthetic solutions.¹ In particular, significant progress has been reported recently on the syntheses of cycloparaphenylenes (CPPs) and related nonplanar oligoparaphenylenes.² To date, most successful synthetic approaches have employed three types of craftily designed L-shaped synthons³ in order to overcome these molecules' nontrivial strain energy (Scheme 1a).

We envisioned that the rigid yet reversible dianthracene scaffold,⁴ when appropriately functionalized, would serve as a new X-shaped building block toward strained aromatics such as nonplanar oligoparaphenylenes (Scheme 1b). In particular, this strategy would complement the aforementioned synthetic approaches by (1) establishing a dual-arched core structure with a bending angle of around 50° and (2) enabling late-stage ring expansion via photodimer cycloreversion. Although the century-old anthracene photodimerization has been extensively studied with versatile applications including polymers and molecular switches,⁵ the reaction's synthetic uses remain limited,⁶ largely because of a number of technical hurdles associated with the photodimers such as isomer separation and poor solubility.⁴ Here we disclose the preparation and crystal structure of a dianthracene-derived dual-curve oligoparaphenylene molecule, **1**, exhibiting attractive optoelectronic properties and synthetic utility toward nanohoop **2**.

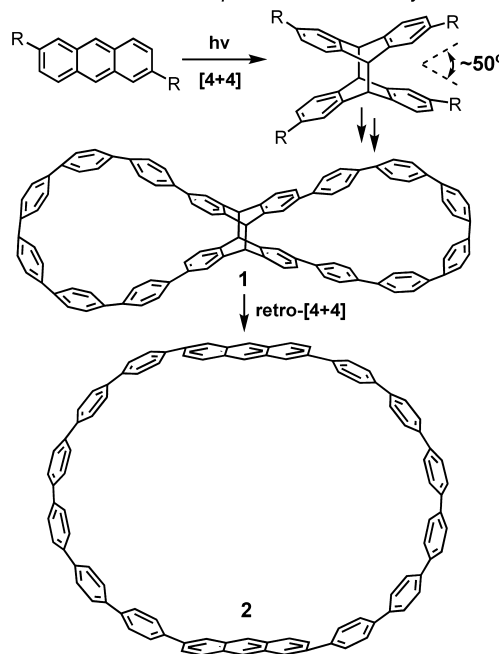
Our study commenced with the [4 + 4] photodimerization of 2,6-dibromoanthracene (**3**) (Scheme 2). The reaction cleanly

Scheme 1. Synthetic Design

(a) Representative synthons to overcome strain energy

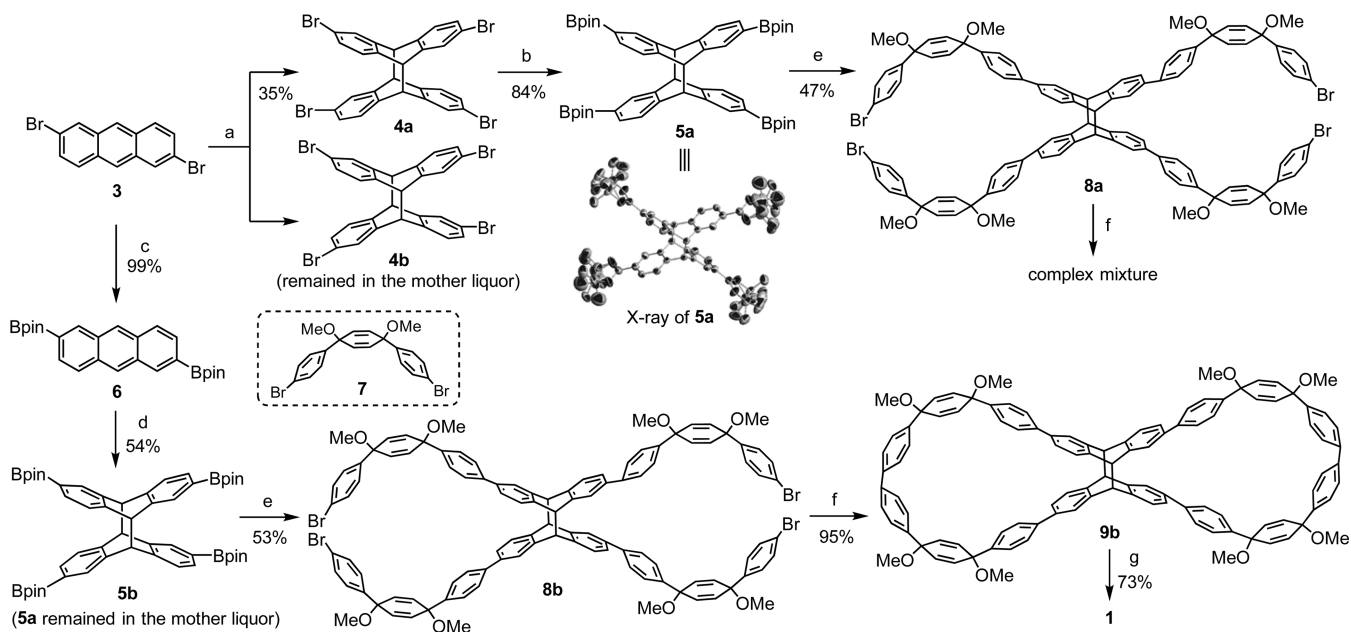


(b) This work - anthracene photodimerization-cycloreversion



Received: July 25, 2016

Published: August 19, 2016

Scheme 2. Synthesis of **1** Employing a Dianthracene-Derived Key Synthons^a

^aReagents and conditions: (a) benzene, xenon lamp, 80 °C, 24 h (**4a:4b** = 65:35), then recrystallization in CHCl₃; (b) Pd(OAc)₂, S-Phos, B₂pin₂, K₃PO₄, 1,4-dioxane, 70 °C, 24 h; (c) Pd(OAc)₂, S-Phos, B₂pin₂, K₃PO₄, 1,4-dioxane, 80 °C, 20 h; (d) benzene, xenon lamp, 30 °C, 12 h (**5a:5b** = 20:80), then recrystallization in EtOAc; (e) **7**, Pd(OAc)₂, dppf, K₂CO₃, Ag₂O, PhMe/H₂O, 80 °C, 24 h; (f) Ni(cod)₂, 2,2'-bipyridyl, THF, 65 °C, 24 h; (g) sodium naphthalenide, THF, -78 °C, 1 h, then quenching with I₂.

generated a mixture of two barely soluble stereoisomers under irradiation with a xenon lamp. Refluxing benzene was found to be optimal for best dissolving the starting material and the products, and one of the photodimers was more soluble in hot chloroform than the other one. Thus, the less soluble isomer **4a** was isolated by recrystallization in 35% yield. Palladium-catalyzed Miyaura borylation⁷ of **4a** smoothly afforded tetraborate **5a** (84% yield), the stereochemistry of which was unambiguously confirmed to be head-to-head (H–H) by X-ray crystallography.⁸ The head-to-tail (H–T) dimer **5b** could be obtained from **3** by reversing the order of the photodimerization and borylation steps. The quantitative dimer formation from bis-borylated anthracene **6** favored the less hindered **5b** over **5a**, likely because of increased sterics, and recrystallization with ethyl acetate thus allowed isolation of the H–T isomer **5b** in 54% yield.

With pure isomers **5a** and **5b** in hand, Suzuki cross-coupling⁹ with Jasti's cyclohexadiene-derived synthon **7**¹⁰ stitched four new C–C bonds in a single step with good efficiency. In both reactions, greater than 80% yield per bond formation was achieved.

The macrocycle-closing step was expected to be the most challenging and crucial, since molecular strain builds up significantly. Similar steps employing coupling strategies were reported in the syntheses of CPPs and related compounds, albeit with low to moderate yields.^{2a} It turned out that subjecting tetraborides **8a** and **8b** to nickel-mediated Yamamoto coupling conditions¹¹ led to contrasting results. Although a trace signal of the desired mass could be observed by MALDI-TOF analysis of the complex crude reaction mixture from the H–H isomer **8a**, isolation of either mono- or bicyclic products was unsuccessful. In sharp contrast, treatment of the H–T isomer **8b** with Ni(cod)₂/2,2'-bipyridyl furnished exclusively the desired double cyclization with a 95% yield of **9b** (>97% yield per bond formation!). To the best of our knowledge,

this result represents the highest yield among similar strained macrocycle formations, still less in the case of forming two highly strained rings in a single step. Final reduction of **9b** with freshly made sodium naphthalenide^{3a} effectively afforded the target molecule **1** as a yellow solid.

X-ray crystallographic analysis of a single crystal of **1**⁸ confirmed the propeller-like dual-curve structure, which deviated somewhat from C₂ symmetry (Figure 1). With four bridgehead sp³

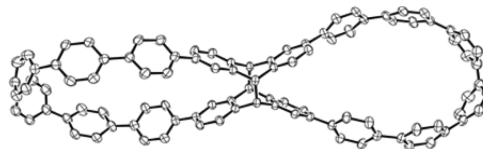
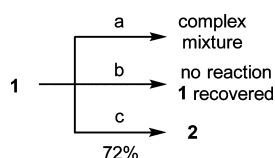


Figure 1. ORTEP drawing of **1** with the thermal ellipsoids shown at 50% probability.

carbons connecting a total of 16 benzene rings on both sides, the furthest *ipso*-carbons within a single **1** molecule are 2.8 nm apart, and the width of one macrocycle was measured as 0.85 nm. In comparison, the diameters of [6]- and [7]CPPs are 0.79 and 0.95 nm, respectively.¹² The oligoparaphenylene subunits are heavily yet unevenly bent, with torsional angles between adjacent benzene rings broadly ranging from 7.2° to 43.6° (24.8° on average). Notably, the two “propeller blades” are almost orthogonal to each other, exhibiting a dihedral angle of 75° between the two furthest C(*ipso*)–C(*ipso*) bonds. The average bond lengths for C(sp²)–C(sp²) within a benzene unit and C(*ipso*)–C(*ipso*) are 1.39 and 1.48 Å, respectively, which are in accordance with the CPPs.¹² In the crystalline state, a unit cell of racemic **1** contains a pair of opposite enantiomers that alternatively pack on top of each other with good alignment (Figure S11).

Next, the synthetic utility of **1** was explored by inducing cycloreversion of its dianthracene core (Scheme 3). The concurrent

Scheme 3. Synthesis of **2** via Cycloreversion^a



^aReagents and conditions: (a) 8 W 254 nm UV lamp, CH₂Cl₂, 25 °C, 3 h; (b) toluene, 110 °C, 12 h; (c) *o*-dichlorobenzene, 175 °C, in the dark, 18 h.

ring expansion should afford the anthracene-incorporated aromatic macrocycle **2**, a new nano hoop potentially applicable for bottom-up syntheses of carbon nanotubes (CNTs).¹³ The challenging aspect for the ring expansion is that neither **1** nor **2** has polar functional groups, and therefore, excessive byproduct formation or incomplete starting material conversion would complicate product purification. The photoinduced cycloreversion^{6b} of **1** under 254 nm UV light led to decomposition into a complex mixture. This result was echoed by the absence of the characteristic UV–vis absorption of the dianthracene unit in **1** (cf. Figure 3), likely due to its extended conjugated structure. We then investigated thermally induced conditions,^{4c,6a} and **1** was found intact after hours in refluxing toluene. After an extensive survey of solvents with higher boiling points, we established that heating **1** in *o*-dichlorobenzene at 175 °C for 18 h in the dark cleanly produced the desired product **2** in 72% isolated yield.

Compound **2** was characterized by NMR and mass spectrometry, showing only simple ¹H and ¹³C NMR spectra.¹⁴ With the incorporation of two 2,6-disubstituted anthracene units, the nano hoop **2** was expected to generate stereoisomers as a result of rotation of the anthracene units.¹⁵ In order to gain

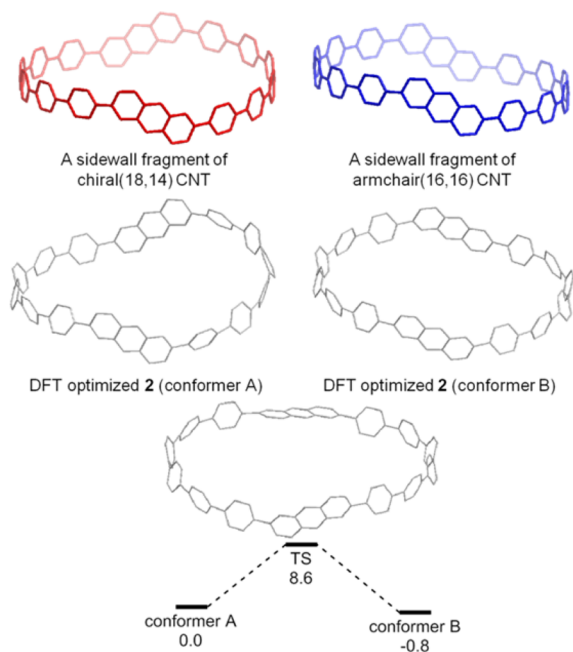
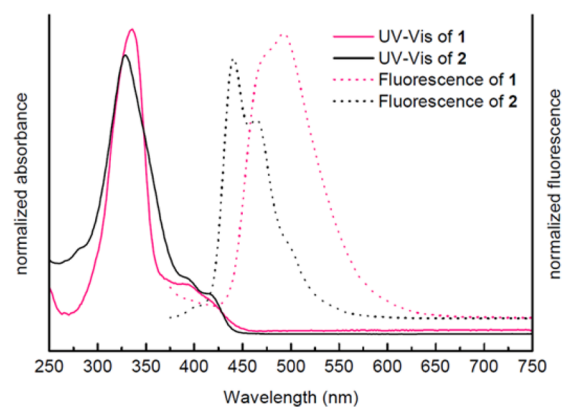


Figure 2. DFT-calculated conformers and rotation barriers (in kcal/mol) of **2**.



	absorbance (nm)	fluorescence (nm)	quantum yield	singlet lifetime (ns)	HOMO/LUMO gap (eV)
[8]CPP	340 ^a	553 ^a	0.10 ^a	17.6 ^a	3.41 ^c
1	336, 396	494	0.59	2.4	3.41
[16]CPP	339 ^b	415, 438 ^b	0.88 ^b	– ^b	3.67 ^c
2	329, 395, 418	441, 464	0.68	1.9	3.17 ^d

Figure 3. Photophysical data and DFT-calculated HOMO–LUMO gaps. Notes: ^afrom ref 12; ^bfrom ref 18; ^cfrom ref 19; ^daverage gap calculated on the basis of optimized conformers A and B of **2** (see the Supporting Information).

further structural information on **2**, we performed preliminary density functional theory (DFT) calculations with Gaussian 09¹⁶ (Figure 2), which showed two thermodynamically favored conformers corresponding to the sidewall fragments of chiral(18,14) and armchair(16,16) CNTs. The two conformers exhibited a minimal energy difference (0.8 kcal/mol) based on their computationally optimized geometries. Notably, the calculated energy barriers for interconversion between the two conformers were less than 10 kcal/mol. This result indicated rapid rotations of the anthracene units at ambient temperature and thus was consistent with the observed NMR spectra of **2**.

Molecules **1** and **2** exhibited intriguing photophysical properties compared with structurally related CPPs (Figure 3). The octaparaphenylene-containing **1** was paired with [8]CPP, highlighting the effect of interrupted versus cyclic conjugated aromatic loops. **1** showed an absorption maximum at 336 nm, consistent with the CPPs' common λ_{max} between 336 and 340 nm.¹² A shoulder peak was observed spanning from 350 to 450 nm, which can be assigned to transitions including HOMO → LUMO and HOMO–1 → LUMO/HOMO → LUMO+1 (Table S12).¹⁴ The fluorescence emission of **1** was blue-shifted with a much higher quantum yield of 0.59 and a much shorter singlet lifetime of 2.4 ns.¹⁷

The anthracene-incorporated nano hoop **2** was compared to [16]CPP on the basis of their similar diameters, thus showcasing the effect of anthracene as a photophysically functional moiety.¹⁸ The absorption maximum of **2** was slightly blue-shifted to 329 nm, with shoulder peaks at 395 and 418 nm that corresponded to DFT-calculated transitions involving the HOMO, LUMO, and adjacent molecular orbitals (Tables S13 and S14).¹⁴ **2** showed red-shifted dual maxima at 441 and 464 nm, consistent with a smaller calculated HOMO–LUMO gap.¹⁹ The lower quantum yield of **2** may be related to nonradiative decay pathways of the photoexcited state due to rotation of the anthracene units (cf. Figure 2).

In conclusion, chemical syntheses of highly strained oligoparaphenylene molecules **1** and **2** have been achieved in 27% yield over four steps and 20% yield over five steps, respectively.

Key synthetic features include a rigid anthracene photodimer synthon, late-stage ring expansion through cycloreversion, and high-yielding macrocycle formation via Yamamoto coupling. Both **1** and **2** display attractive properties experimentally and theoretically, suggesting their potential utility as organic optoelectronic materials and building blocks for bottom-up carbon nanotube synthesis. Further synthetic applications of the anthracene photodimerization–cycloreversion strategy are under investigation and will be reported in due course.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: [10.1021/jacs.6b07673](https://doi.org/10.1021/jacs.6b07673).

Experimental, spectral, and computational details and complete ref **16** (PDF)

Crystallographic data for **1** (CIF)

Crystallographic data for **5a** (CIF)

■ AUTHOR INFORMATION

Corresponding Authors

*yangxiaodi@fudan.edu.cn

*hcong@mail.ipc.ac.cn

Notes

The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

Financial support from the “Thousand Youth Talents Plan”, the TIPC Director’s Fund, the NSFC (21672227), and the CAS Strategic Priority Research Program (Grant XDB17030200) is gratefully acknowledged. We thank Professors Zhenfeng Xi (Peking University) and Congyang Wang (ICCAS) for helpful discussions and Mr. Xu-Zhe Wang (TIPC) for assistance with electrochemical measurements.

■ REFERENCES

- (1) (a) Scott, L. T. *Angew. Chem., Int. Ed.* **2004**, *43*, 4994. (b) Pascal, R. A., Jr. *Chem. Rev.* **2006**, *106*, 4809. (c) Tahara, K.; Tobe, Y. *Chem. Rev.* **2006**, *106*, 5274. (d) Merner, B. L.; Dawe, L. N.; Bodwell, G. J. *Angew. Chem., Int. Ed.* **2009**, *48*, 5487. (e) Eisenberg, D.; Shenhar, R.; Rabinovitz, M. *Chem. Soc. Rev.* **2010**, *39*, 2879. (f) Gingras, M. *Chem. Soc. Rev.* **2013**, *42*, 968. (g) Golder, M. R.; Jasti, R. *Acc. Chem. Res.* **2015**, *48*, 557. (h) Narita, A.; Wang, X.-Y.; Feng, X.; Müllen, K. *Chem. Soc. Rev.* **2015**, *44*, 6616. (i) Yamago, S.; Kayahara, E.; Hashimoto, S. *Cycloparaphenylenes and Carbon Nanorings*. In *Polycyclic Arenes and Heteroarenes: Synthesis, Properties, and Applications*; Qian, M., Ed.; John Wiley & Sons: Chichester, U.K., 2015; pp 143–162. (j) Hammer, B. A. G.; Müllen, K. *Chem. Rev.* **2016**, *116*, 2103. (k) Segawa, Y.; Ito, H.; Itami, K. *Nat. Rev. Mater.* **2016**, *1*, 15002. (l) Segawa, Y.; Yagi, A.; Matsui, K.; Itami, K. *Angew. Chem., Int. Ed.* **2016**, *55*, 5136.
- (2) (a) For a recent comprehensive summary, see: Lewis, S. E. *Chem. Soc. Rev.* **2015**, *44*, 2221. (b) Kayahara, E.; Patel, V. K.; Mercier, A.; Kündig, E. P.; Yamago, S. *Angew. Chem., Int. Ed.* **2016**, *55*, 302. (c) Kayahara, E.; Kouyama, T.; Kato, T.; Yamago, S. *J. Am. Chem. Soc.* **2016**, *138*, 338. (d) Sisto, T. J.; Zakharov, L. N.; White, B. M.; Jasti, R. *Chem. Sci.* **2016**, *7*, 3681. (e) Golder, M. R.; Colwell, C. E.; Wong, B. M.; Zakharov, L. N.; Zhen, J.; Jasti, R. *J. Am. Chem. Soc.* **2016**, *138*, 6577. (f) Sakamoto, H.; Fujimori, T.; Li, X.; Kaneko, K.; Kan, K.; Ozaki, N.; Hijikata, Y.; Irle, S.; Itami, K. *Chem. Sci.* **2016**, *7*, 4204. (g) Lu, D.; Wu, H.; Dai, Y.; Shi, H.; Shao, X.; Yang, S.; Yang, J.; Du, P. *Chem. Commun.* **2016**, *52*, 7164. (h) Sun, Z.; Suenaga, T.; Sarkar, P.; Sato, S.; Kotani, M.; Isobe, H. *Proc. Natl. Acad. Sci. U. S. A.* **2016**, *113*, 8109.
- (3) (a) Jasti, R.; Bhattacharjee, J.; Neaton, J. B.; Bertozzi, C. R. *J. Am. Chem. Soc.* **2008**, *130*, 17646. (b) Takaba, H.; Omachi, H.; Yamamoto,

- Y.; Bouffard, J.; Itami, K. *Angew. Chem., Int. Ed.* **2009**, *48*, 6112. (c) Yamago, S.; Watanabe, Y.; Iwamoto, T. *Angew. Chem., Int. Ed.* **2010**, *49*, 757. Recent effective methods for nanohoop syntheses include but are not limited to: (d) Tran-Van, A.-F.; Huxol, E.; Basler, J. M.; Neuburger, M.; Adjizian, J.-J.; Ewels, C. P.; Wegner, H. A. *Org. Lett.* **2014**, *16*, 1594. (e) Thakellapalli, H.; Farajidizaji, B.; Butcher, T. W.; Akhmedov, N. G.; Popp, B. V.; Petersen, J. L.; Wang, K. K. *Org. Lett.* **2015**, *17*, 3470. (f) Mitra, N. K.; Meudom, R.; Corzo, H. H.; Gorden, J. D.; Merner, B. L. *J. Am. Chem. Soc.* **2016**, *138*, 3235.
- (4) (a) Becker, H.-D. *Chem. Rev.* **1993**, *93*, 145. (b) Bouas-Laurent, H.; Castellan, A.; Desvergne, J.-P.; Lapouyade, R. *Chem. Soc. Rev.* **2000**, *29*, 43. (c) Bouas-Laurent, H.; Castellan, A.; Desvergne, J.-P.; Lapouyade, R. *Chem. Soc. Rev.* **2001**, *30*, 248.
- (5) (a) Tung, C.-H.; Wu, L.-Z.; Zhang, L.-P.; Chen, B. *Acc. Chem. Res.* **2003**, *36*, 39. (b) Bringmann, S.; Brodbeck, R.; Hartmann, R.; Schäfer, C.; Mattay, J. *Org. Biomol. Chem.* **2011**, *9*, 7491. (c) Zhu, L.; Al-Kaysi, R. O.; Bardeen, C. J. *J. Am. Chem. Soc.* **2011**, *133*, 12569. (d) Kory, M. J.; Worle, M.; Weber, T.; Payamyar, P.; van de Poll, S. W.; Dshemuchadse, J.; Trapp, N.; Schluter, A. D. *Nat. Chem.* **2014**, *6*, 779. (e) Murray, D. J.; Patterson, D. D.; Payamyar, P.; Bhola, R.; Song, W.; Lackingner, M.; Schluter, A. D.; King, B. T. *J. Am. Chem. Soc.* **2015**, *137*, 3450.
- (6) (a) Takaguchi, Y.; Tajima, T.; Ohta, K.; Motoyoshiya, J.; Aoyama, H. *Chem. Lett.* **2000**, *29*, 1388. (b) Cao, D.; Meier, H. *Angew. Chem., Int. Ed.* **2001**, *40*, 186. (c) Benard, C. P.; Geng, Z.; Heuft, M. A.; VanCrey, K.; Fallis, A. G. *J. Org. Chem.* **2007**, *72*, 7229. (d) Liang, C.-K.; Desvergne, J.-P.; Bassani, D. M. *Photochem. Photobiol. Sci.* **2014**, *13*, 316. (e) Fukuhara, G.; Iida, K.; Kawanami, Y.; Tanaka, H.; Mori, T.; Inoue, Y. *J. Am. Chem. Soc.* **2015**, *137*, 15007. (f) Li, P.; Wong, B. M.; Zakharov, L. N.; Jasti, R. *Org. Lett.* **2016**, *18*, 1574.
- (7) Billingsley, K. L.; Barder, T. E.; Buchwald, S. L. *Angew. Chem., Int. Ed.* **2007**, *46*, 5359.
- (8) CCDC 1492176 (for **5a**) and 1492177 (for **1**) contain the supplementary crystallographic data for this paper. The data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/structures.
- (9) (a) Martin, R.; Buchwald, S. L. *Acc. Chem. Res.* **2008**, *41*, 1461. (b) Fu, G. C. *Acc. Chem. Res.* **2008**, *41*, 1555.
- (10) Darzi, E. R.; Sisto, T. J.; Jasti, R. *J. Org. Chem.* **2012**, *77*, 6624.
- (11) (a) Nelson, T. D.; Crouch, R. D. *Org. React.* **2004**, *63*, 265. (b) Omachi, H.; Segawa, Y.; Itami, K. *Acc. Chem. Res.* **2012**, *45*, 1378. (c) Kayahara, E.; Patel, V. K.; Yamago, S. *J. Am. Chem. Soc.* **2014**, *136*, 2284. (d) Myśliwiec, D.; Kondratowicz, M.; Lis, T.; Chmielewski, P. J.; Stepień, M. *J. Am. Chem. Soc.* **2015**, *137*, 1643. (e) Yamamoto, T.; Wakabayashi, S.; Osakada, K. *J. Organomet. Chem.* **1992**, *428*, 223. (f) Ohlendorf, G.; Mahler, C. W.; Jester, S.-S.; Schnakenburg, G.; Grimme, S.; Höger, S. *Angew. Chem., Int. Ed.* **2013**, *52*, 12086.
- (12) Darzi, E. R.; Jasti, R. *Chem. Soc. Rev.* **2015**, *44*, 6401.
- (13) (a) Hitosugi, S.; Nakanishi, W.; Yamasaki, T.; Isobe, H. *Nat. Commun.* **2011**, *2*, 492. (b) Omachi, H.; Nakayama, T.; Takahashi, E.; Segawa, Y.; Itami, K. *Nat. Chem.* **2013**, *5*, 572. (c) Sanchez-Valencia, J. R.; Diemel, T.; Gröning, O.; Shorubalko, I.; Mueller, A.; Jansen, M.; Amsharov, K.; Ruffieux, P.; Fasel, R. *Nature* **2014**, *512*, 61. (d) Liu, C.; Cheng, H.-M. *J. Am. Chem. Soc.* **2016**, *138*, 6690.
- (14) See the [Supporting Information](#) for details.
- (15) (a) Omachi, H.; Segawa, Y.; Itami, K. *Org. Lett.* **2011**, *13*, 2480. (b) Hitosugi, S.; Nakanishi, W.; Isobe, H. *Chem. - Asian J.* **2012**, *7*, 1550. (c) Sun, Z.; Sarkar, P.; Suenaga, T.; Sato, S.; Isobe, H. *Angew. Chem., Int. Ed.* **2015**, *54*, 12800.
- (16) Frisch, M. J.; et al. *Gaussian 09*; Gaussian, Inc.: Wallingford, CT, 2009.
- (17) For a report on interrupted CPP molecules showing blue-shifted fluorescence and higher quantum yields than their parent CPPs, see: Li, P.; Sisto, T. J.; Darzi, E. R.; Jasti, R. *Org. Lett.* **2014**, *16*, 182.
- (18) (a) Segawa, Y.; Fukazawa, A.; Matsuura, S.; Omachi, H.; Yamaguchi, S.; Irle, S.; Itami, K. *Org. Biomol. Chem.* **2012**, *10*, 5979. (b) Yagi, A.; Venkataramana, G.; Segawa, Y.; Itami, K. *Chem. Commun.* **2014**, *50*, 957.
- (19) Iwamoto, T.; Watanabe, Y.; Sakamoto, Y.; Suzuki, T.; Yamago, S. *J. Am. Chem. Soc.* **2011**, *133*, 8354.