Donor–Acceptor Systems

International Edition: DOI: 10.1002/anie.201503397
German Edition: DOI: 10.1002/ange.201503397

Curved Oligophenylenes as Donors in Shape-Persistent Donor–Acceptor Macrocycles with Solvatofluorochromic Properties**

*Takuya Kuwabara, Jun Orii, Yasutomo Segawa, and Kenichiro Itami**

Abstract: *Many optoelectronic organic materials are based on donor–acceptor (D–A) systems with heteroatom-containing electron donors. Herein, we introduce a new molecular design for all-carbon curved oligoparaphenylenes as donors, which results in the generation of unique shape-persistent D–A macrocycles. Two types of acceptor-inserted cycloparaphenylenes were synthesized. These macrocycles display positive solvatofluorochromic properties owing to their D–A characteristics, which were confirmed by theoretical and electrochemical studies.*

Donor–acceptor (D–A) systems have been extensively investigated and applied in various ways, such as in artificial photosynthesis,[1] organic solar cells,[2] and fluorescent probes.[3] In most D–A systems, electron-rich heterocycles or aromatic rings bearing alkylamino, arylamino, or alkoxy groups are employed as the donor moiety (Figure 1a). The use of heteroatom-containing donors is thus common practice in D–A-based organic materials. While unsubstituted all-carbon oligophenylenes would be able to function as unique donors with a number of advantages, such as resistance to oxidative conditions, which would result in higher stability, they are rarely used as donors because of their extremely low solubility in common organic solvents and relatively low-lying HOMOs.[4] Therefore, it is necessary to improve the solubility and raise the HOMO energy of oligophenylenes to enhance their suitability as donors. Although the introduction of long alkyl chains is a conventional way to improve the solubility of π-conjugated molecules, bending π-electron systems has recently been recognized as a new strategy to increase both the solubility and HOMO energy.

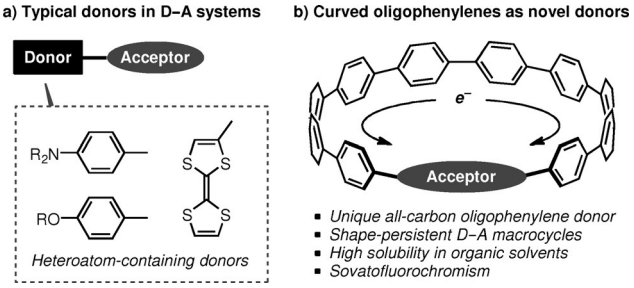


Figure 1. a) Typical donors in D–A systems. b) Curved oligophenylenes as novel donors (this work).

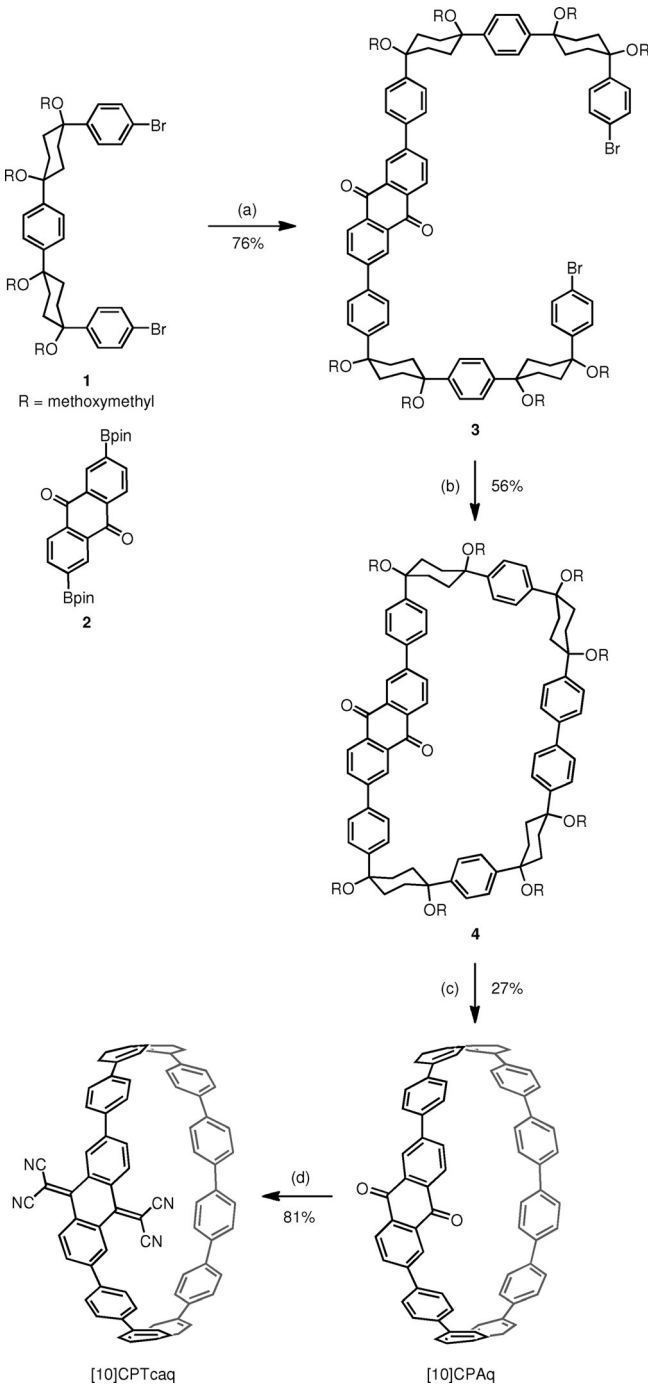
After the successful synthesis of [*n*]cycloparaphenylenes ([*n*]CPPs) by the groups of Bertozzi, Jasti, Itami, and Yamago,[5–7] various unique properties of CPPs have been uncovered.[8] For example, owing to their curved structure, no intermolecular π–π stacking occurs in CPPs, which leads to much higher solubility in common organic solvents compared to linear oligoparaphenylenes.[9] Moreover, because of the curved structure and cyclic conjugation, the energy of the HOMOs of [*n*]CPPs becomes higher than that in linear [*n*]paraphenylenes ($n \leq 20$).[7a,8b] These results led us to propose a new molecular design for using curved oligoparaphenylenes as donors in D–A systems, which results in the generation of unique shape-persistent D–A macrocycles (Figure 1b). Herein, we report the synthesis and photophysical properties of CPP derivatives with an anthraquinone (AQ) or a tetracyanoanthraquinodimethane (TCAQ) moiety inserted into the ring as an acceptor. The effects of the inserted acceptors on the electronic structures of the D–A macrocycles are addressed through theoretical and electrochemical studies.

The synthetic approach to the CPP-based novel D–A macrocycles is illustrated in Scheme 1.[10] The palladium-catalyzed Suzuki–Miyaura coupling reaction between U-shaped unit **1**[6g] and 2,6-diborylanthraquinone (**2**)[10] provided C-shaped unit **3** in 76% yield. The nickel-mediated cyclization reaction of C-shaped dibromide **3** afforded cyclohexane-inserted macrocycle **4** in 56% yield. With this new macrocycle in hand, the aromatization reaction was examined. In a method we previously reported,[6] *m*-xylene and DMSO were used as solvents for the aromatization of cyclohexane units. For the aromatization of **4**, we tried DMSO-free conditions to avoid the unpleasant smell caused by the decomposition of DMSO. After extensive optimization of this particular aromatization step, it was found that the treatment

[*] Dr. T. Kuwabara, Prof. Dr. Y. Segawa, Prof. Dr. K. Itami
JST-ERATO, Itami Molecular Nanocarbon Project
Chikusa, Nagoya, 464-8602 (Japan)
E-mail: itami@chem.nagoya-u.ac.jp
Dr. T. Kuwabara, J. Orii, Prof. Dr. Y. Segawa, Prof. Dr. K. Itami
Graduate School of Science
Nagoya University, Chikusa, Nagoya 464-8602 (Japan)
Dr. T. Kuwabara, Prof. Dr. K. Itami
Institute of Transformative Bio-Molecules (WPI-ITbM)
Nagoya University, Chikusa, Nagoya, 464-8602 (Japan)

[**] This work was supported by the ERATO program from JST (K.I.) and the Funding Program for Next Generation World-Leading Researchers from JSPS (220GR049 to K.I.). T.K. acknowledges JSPS for a Research Fellowship for Young Scientists. We thank Akiko Gocho, Kakishi Uno, Dr. Taishi Nishihara, and Dr. Kin-ichi Oyama (Nagoya Univ.) for support with measurements and analysis. Calculations were performed using the resources of the Research Center for Computational Science, Okazaki (Japan). ITbM is supported by the World Premier International Research Center (WPI) Initiative (Japan).

Supporting information for this article is available on the WWW under http://dx.doi.org/10.1002/anie.201503397.



Scheme 1. Synthesis of [10]CPAq and [10]CPTcaq. Reaction conditions: a) $Pd(PPh_3)_4$, Na_2CO_3, nBu_4NBr, THF, reflux, 41 h. b) $Ni(cod)_2$, 2,2′-bipyridyl, THF, reflux, 25 h. c) $NaHSO_4{\cdot}H_2O$, *o*-chloranil, *m*-xylene, water, 150 °C, 75 h. d) malononitrile, $TiCl_4$, pyridine, CH_2Cl_2, 0 °C to RT, 26 h. Bpin = 4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl, THF = tetrahydrofuran, cod = 1,5-cyclooctadiene.

of **4** with $NaHSO_4{\cdot}H_2O$ in *m*-xylene/water at 150 °C induced aromatization to produce the target anthraquinone-containing macrocycle, cyclo[10]paraphenylene-9,10-anthraquinon-2,6-ylene ([10]CPAq), in 10% yield as a yellowish orange powder. The yield of [10]CPAq was improved to 27% by further adding *o*-chloranil to the reaction. The AQ moiety in [10]CPAq can easily be converted into a TCAQ unit, which is a stronger acceptor than AQ.[11] The reaction of [10]CPAq with malononitrile in the presence of $TiCl_4$ and pyridine afforded cyclo[10]paraphenylene-2,6-tetracyanoanthraquinodimethanylene ([10]CPTcaq) as a red powder in 81% yield.

Next, the UV/Vis absorption and fluorescence properties of [10]CPAq and [10]CPTcaq were studied (Table 1 and Figure 2). The effect of the acceptor moieties (AQ and TCAQ) on the electronic structures and properties of the D–A macrocycles was estimated by using the photophysical data for [12]CPP, which has a ring size similar to those of [10]CPAq and [10]CPTcaq. The absorption maxima of [10]CPAq (332 nm) and [10]CPTcaq (335 nm) were almost the same as that of [12]CPP (338 nm).[6] However, a new broad shoulder peak appeared on the spectrum of [10]CPAq. Peak separation led to the detection of three absorption maxima at 331, 379, and 429 nm (see Figure S1 in the Supporting Information). By contrast, a broad peak ranging from 400 to 650 nm was observed for [10]CPTcaq. The assignments of these broad absorption bands are explained later by using theoretical calculations.

Table 1: UV/Vis absorption and fluorescence data for [10]CPAq and [10]CPTcaq.

	λ_{abs}[a] [nm]	λ_{em}[b] [nm] (solvent)	Φ_F[c]
[10]CPAq	332, 379, 429	496 (CCl_4)	0.08
		523 (C_6H_6)	0.15
		531 (Et_2O)	0.30
		591 (C_6H_5Cl)	0.18
[10]CPTcaq	335, 450	611 (CCl_4)	0.02
		642 (C_6H_6)	0.05

[a] In chloroform. [b] Emission maxima upon excitation at 420 nm and 480 nm for [10]CPAq and [10]CPTcaq, respectively. [c] Absolute fluorescence quantum yields determined by a calibrated integrating sphere system within ±3% errors.

[10]CPAq and [10]CPTcaq exhibited green and red fluorescence, respectively, in CCl_4. These long-wavelength emissions are clearly different from the blue fluorescence of [12]CPP. Interestingly, solutions of [10]CPAq were observed to undergo a remarkable change in fluorescence color, from green in CCl_4 to orange in chlorobenzene. The higher the polarity of the solvent, the more pronounced the red-shift of the emission maxima (Table 1 and Table S1 in the Supporting Information). A plot of the wavenumber against the solvent parameter $E_T(30)$[12] fits to a linear line (Figure S2), thus clearly indicating the positive solvatofluorochromic behavior of [10]CPAq. While solutions of [10]CPTcaq in polar solvents are nonfluorescent, the emission spectra of this compound in nonpolar solvents showed a similar bathochromic shift (Table 1 and Figure 2). It should be noted that such solvatochromism has never been reported for CPP derivatives. Since solvatofluorochromism is often observed in D–A molecules capable of intramolecular charge transfer,[13] [10]CPAq and [10]CPTcaq can be regarded as unique macrocyclic D–A systems.

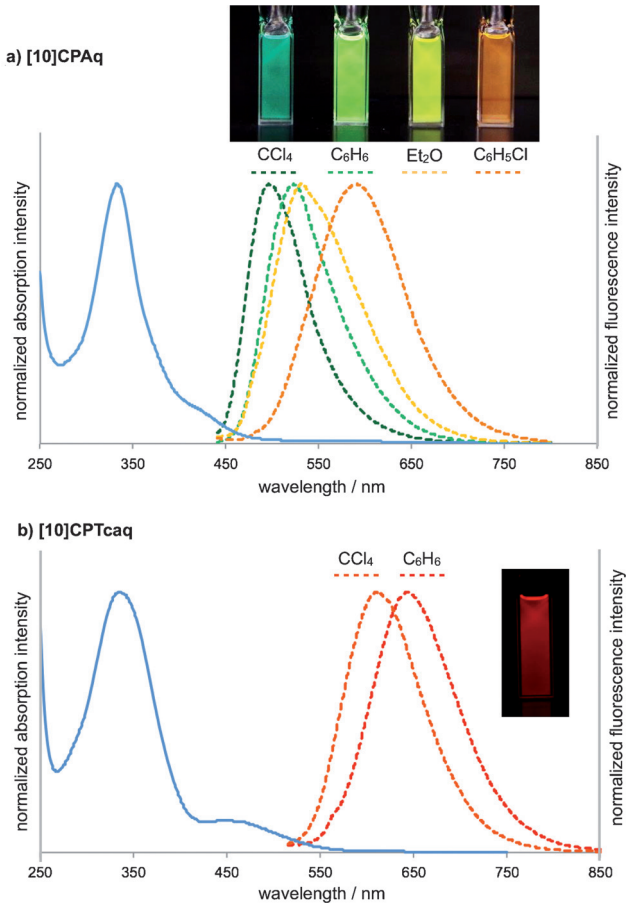


Figure 2. (a) UV/Vis absorption (in $CHCl_3$; solid line) and fluorescence (excited at 420 nm in various solvents; broken lines) spectra of [10]CPAq. Photographs show the emission colors of [10]CPAq in various solvents. (b) UV/Vis absorption (in $CHCl_3$; solid line) and fluorescence (excited at 480 nm in various solvents; broken lines) spectra of [10]CPTcaq. A photograph shows the emission color of [10]CPTcaq in CCl_4.

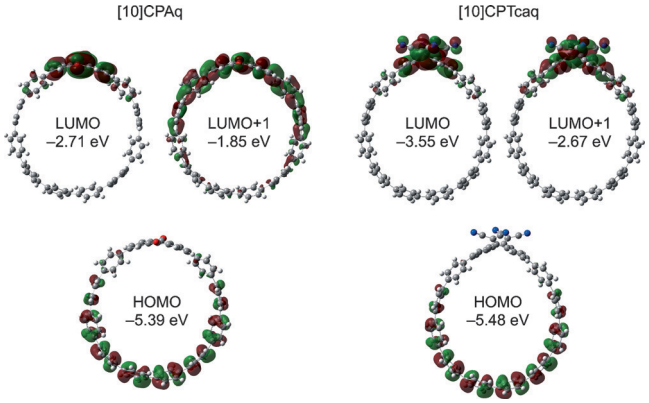


Figure 3. Frontier MOs of [10]CPAq (left) and [10]CPTcaq (right) calculated at the B3LYP/6-31G(d) level (isovalue = 0.02). C Gray, H white, O red, N blue.

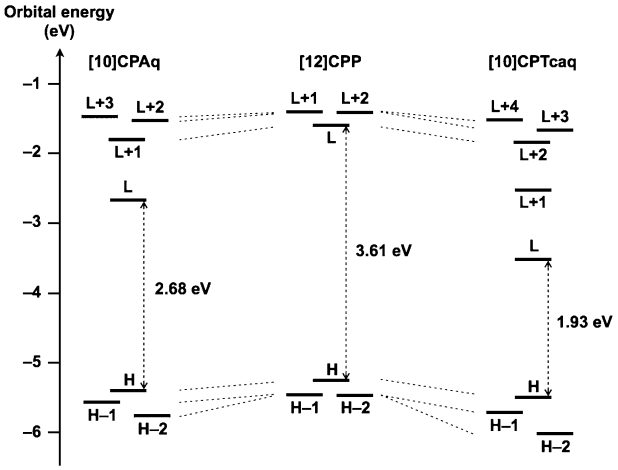


Figure 4. Energy diagrams for MOs of [10]CPAq (left), [12]CPP (center), and [10]CPTcaq (right). Two-way arrows represent HOMO–LUMO gaps. H = HOMO, L = LUMO.

To understand the electronic structures of [10]CPAq and [10]CPTcaq, DFT and time-dependent DFT (TD-DFT) calculations were performed using Gaussian 09 at the B3LYP/6-31G(d) level. The frontier molecular orbitals (MOs) of [10]CPAq and [10]CPTcaq are depicted in Figure 3. In both cases, the HOMOs are localized on the paraphenylene moieties, whereas the LUMOs are localized on the acceptors (AQ and TCAQ). Localization of the LUMO on AQ is commonly observed in solvatochromic compounds bearing AQ as an acceptor.[14] The LUMO in [10]CPAq and LUMO and LUMO + 1 in [10]CPTcaq correspond to those in AQ and TCAQ (Figure S3 and S4). Because of the effective HOMO–LUMO separation, the excited states of these acceptor-inserted CPPs are polarized, which appears to be the cause of their solvatofluorochromism. A comparison of the energy diagrams of [12]CPP to those of [10]CPAq and [10]CPTcaq is shown in Figure 4. In contrast to the similar HOMO energies of [10]CPAq, [10]CPTcaq, and [12]CPP (−5.39 eV, −5.48 eV, and −5.25 eV,[8a] respectively), the LUMO energies of the acceptor-inserted CPPs were calculated to be much lower in energy than that of [12]CPP (−2.71 eV ([10]CPAq) and −3.55 eV ([10]CPTcaq) vs. −1.64 eV ([12]CPP)),[8a] which resulted in smaller HOMO–LUMO gaps in the acceptor-inserted CPPs. Unlike [12]CPP, degeneration was not found in the frontier MOs of the acceptor-inserted CPPs because of their low symmetry (see Figures S3 and S4 for depictions of these MOs). TD-DFT calculations enabled us to assign the origin of their UV/Vis absorption bands (Tables S3 and S4). In the absorption spectrum of [10]CPAq, the shoulder peak at 429 nm is mainly derived from the HOMO−2→LUMO transition, whereas the peak at 379 nm originates from the HOMO→LUMO + 3 and HOMO−1→LUMO + 1 transitions. The strongest absorption peak is assigned to several transitions, such as HOMO→LUMO + 2, + 3, and HOMO−2→LUMO. The transitions responsible for the peaks at 379 and 331 nm correspond to HOMO→LUMO + 1, + 2, and HOMO−1, −2→LUMO transitions in [12]CPP.[8a] For [10]CPTcaq, the broad absorption from 400 to 650 nm originates from HOMO, HOMO−1, −2→LUMO and HOMO−1→LUMO + 1 transitions, thus revealing that the TCAQ moiety functions as an acceptor.

The results of the cyclic voltammetry measurements of [10]CPAq and [10]CPTcaq also support their electron-accepting character (Figure S5). Two reversible reduction waves ($E_{1/2} = -1.45$ V, -1.90 V vs ferrocene/ferrocenium) were observed for [10]CPAq, while a quasi-reversible reduction wave ($E_{pc} = -1.85$ V, $E_{pa} = -1.32$ V) was observed for [10]CPTcaq. Interestingly, the reduction potentials of [10]CPAq were found to be similar to those of cyclohexane-inserted macrocycle **4** ($E_{1/2} = -1.47$ V, -1.95 V; Figure S5), which indicates that the elongated π conjugation has little effect on the electron-accepting properties. It should be mentioned that the reduction wave was not observed for [12]CPP under otherwise identical conditions. These results clearly indicate that the observed reduction waves of [10]CPAq and [10]CPTcaq are derived from the acceptor moieties, and are in good agreement with the LUMOs obtained from the theoretical calculations. All of these newly discovered D–A characteristics of [10]CPAq and [10]CPTcaq, together with their unique shape-persistent ring structures, suggest potential applications for these macrocycles in a range of optoelectronic applications.

In summary, we have synthesized the first donor–acceptor macrocycles with curved oligoparaphenylene as the donor. Notably, the fluorescence color of [10]CPAq in solution changes from green to orange depending on the solvent polarity. Theoretical calculations and cyclic voltammetry results elucidated the electron-donor and electron-acceptor behavior of the oligoparaphenylene and acceptor moieties, respectively. These findings provide a new molecular design strategy for D–A systems that makes use of curved π-electron ring systems.

Keywords: anthraquinone · cycloparaphenylenes · donor–acceptor systems · macrocycles · solvatofluorochromism

How to cite: *Angew. Chem. Int. Ed.* **2015**, *54*, 9646–9649
Angew. Chem. **2015**, *127*, 9782–9785

[1] M. R. Wasielewski, *Chem. Rev.* **1992**, *92*, 435–461.
[2] a) P. Peumans, A. Yakimov, S. R. Forrest, *J. Appl. Phys.* **2003**, *93*, 3693–3723; b) Y. Wu, W. Zhu, *Chem. Soc. Rev.* **2013**, *42*, 2039–2058.
[3] a) K. E. Sapsford, L. Berti, I. L. Medintz, *Angew. Chem. Int. Ed.* **2006**, *45*, 4562–4589; *Angew. Chem.* **2006**, *118*, 4676–4704; b) L. Yuan, W. Lin, K. Zheng, S. Zhu, *Acc. Chem. Res.* **2013**, *46*, 1462–1473.
[4] a) G. L. Closs, J. R. Miller, *Science* **1988**, *240*, 440–447; b) T. N. Das, K. I. Priyadarshini, *J. Chem. Soc. Faraday Trans.* **1994**, *90*, 963–968.
[5] Reports from Bertozzi and Jasti's groups: a) R. Jasti, J. Bhattacharjec, J. B. Neaton, C. R. Bertozzi, *J. Am. Chem. Soc.* **2008**, *130*, 17646–17647; b) T. J. Sisto, M. R. Golder, E. S. Hirst, R. Jasti, *J. Am. Chem. Soc.* **2011**, *133*, 15800–15802; c) J. Xia, R. Jasti, *Angew. Chem. Int. Ed.* **2012**, *51*, 2474–2476; *Angew. Chem.* **2012**, *124*, 2524–2526; d) J. Xia, J. W. Bacon, R. Jasti, *Chem. Sci.* **2012**, *3*, 3018–3021; e) E. R. Darzi, T. J. Sisto, R. Jasti, *J. Org. Chem.* **2012**, *77*, 6624–6628; f) P. J. Evans, E. R. Darzi, R. Jasti, *Nat. Chem.* **2014**, *6*, 404–408.
[6] Reports from Itami's group: a) H. Takaba, H. Omachi, Y. Yamamoto, J. Bouffard, K. Itami, *Angew. Chem. Int. Ed.* **2009**, *48*, 6112–6116; *Angew. Chem.* **2009**, *121*, 6228–6232; b) H. Omachi, S. Matsuura, Y. Segawa, K. Itami, *Angew. Chem. Int. Ed.* **2010**, *49*, 10202–10205; *Angew. Chem.* **2010**, *122*, 10400–10403; c) Y. Segawa, S. Miyamoto, H. Omachi, S. Matsuura, P. Šenel, T. Sasamori, N. Tokitoh, K. Itami, *Angew. Chem. Int. Ed.* **2011**, *50*, 3244–3248; *Angew. Chem.* **2011**, *123*, 3302–3306; d) Y. Segawa, P. Šenel, S. Matsuura, H. Omachi, K. Itami, *Chem. Lett.* **2011**, *40*, 423–425; e) Y. Ishii, Y. Nakanishi, H. Omachi, S. Matsuura, K. Matsui, H. Shinohara, Y. Segawa, K. Itami, *Chem. Sci.* **2012**, *3*, 2340–2345; f) F. Sibbel, K. Matsui, Y. Segawa, A. Studer, K. Itami, *Chem. Commun.* **2014**, *50*, 954–956; g) Y. Segawa, T. Kuwabara, K. Matsui, S. Kawai, K. Itami, *Tetrahedron* **2015**, *71*, 4500–4503.
[7] Reports from Yamago's group: a) S. Yamago, Y. Watanabe, T. Iwamoto, *Angew. Chem. Int. Ed.* **2010**, *49*, 757–759; *Angew. Chem.* **2010**, *122*, 769–771; b) T. Iwamoto, Y. Watanabe, Y. Sakamoto, T. Suzuki, S. Yamago, *J. Am. Chem. Soc.* **2011**, *133*, 8354–8361; c) E. Kayahara, Y. Sakamoto, T. Suzuki, S. Yamago, *Org. Lett.* **2012**, *14*, 3284–3287; d) E. Kayahara, T. Iwamoto, T. Suzuki, S. Yamago, *Chem. Lett.* **2013**, *42*, 621–623; e) E. Kayahara, V. K. Patel, S. Yamago, *J. Am. Chem. Soc.* **2014**, *136*, 2284–2287; f) V. K. Patel, E. Kayahara, S. Yamago, *Chem. Eur. J.* **2015**, *21*, 5742–5749.
[8] a) Y. Segawa, A. Fukazawa, S. Matsuura, H. Omachi, S. Yamaguchi, S. Irle, K. Itami, *Org. Biomol. Chem.* **2012**, *10*, 5979–5984; b) L. Adamska, I. Nayyar, H. Chen, A. K. Swan, N. Oldani, S. Fernandez-Alberti, M. R. Golder, R. Jasti, S. K. Doorn, S. Tretiak, *Nano Lett.* **2014**, *14*, 6539–6546.
[9] a) H. Omachi, Y. Segawa, K. Itami, *Acc. Chem. Res.* **2012**, *45*, 1378–1389; b) M. R. Golder, R. Jasti, *Acc. Chem. Res.* **2015**, *48*, 557–566.
[10] For details, see the Supporting Information.
[11] F. Bureš, W. B. Schweizer, C. Boudon, J. P. Gisselbrecht, M. Gross, F. Diederich, *Eur. J. Org. Chem.* **2008**, *6*, 994–1004.
[12] C. Reichardt, *Chem. Rev.* **1994**, *94*, 2319–2358.
[13] a) E. M. Kosower, *Acc. Chem. Res.* **1982**, *15*, 259–266; b) Z. R. Grabowski, K. Rotkiewicz, *Chem. Rev.* **2003**, *103*, 3899–4032.
[14] a) J. Yang, A. Dass, A.-M. M. Rawashdeh, C. Sotiriou-Leventis, M. J. Panzner, D. S. Tyson, J. D. Kinder, N. Leventis, *Chem. Mater.* **2004**, *16*, 3457–3468; b) W.-W. Zhang, W.-L. Mao, Y.-X. Hu, Z.-Q. Tian, Z.-L. Wang, Q.-J. Meng, *J. Phys. Chem. A* **2009**, *113*, 9997–10003; c) Q. Zhang, H. Kuwabara, W. J. Potscavage, Jr., S. Huang, Y. Hatae, T. Shibata, C. Adachi, *J. Am. Chem. Soc.* **2014**, *136*, 18070–18081.

Received: April 15, 2015
Published online: July 3, 2015

