DOI: 10.1002/ange.201409389

Macrocycles

Thiophene-Based, Radial π-Conjugation: Synthesis, Structure, and Photophysical Properties of Cyclo-1,4-phenylene-2′,5′-thienylenes**

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Abstract: *The synthesis of cyclo-1,4-phenylene-2′,5′-thienylenes (CPTs) as the first example of a thiophene-based, radially π-conjugated system is described. X-ray crystal structures, UV-vis absorption and emission spectra, and theoretical studies revealed the unique structural and photophysical properties of CPTs. With all of these unique structural and photophysical properties, the radially π-conjugated CPTs are expected to open a door for the discovery and development of new functional organic materials.*

In organic-based materials science, thiophene-based π systems have been recognized as "privileged structures" for optoelectronic applications such as organic light-emitting diodes, organic field-effect transistors, organic solar cells, and many others.[1] Representative examples include oligothiophenes, polythiophenes, and thiophene-phenylene co-oligomers, where the shape, length, orientation, and self-assembling nature of π-conjugation are critically important factors in determining their properties. While the majority of reported thiophene-based materials form linear π-conjugation, cyclic π-conjugated compounds have recently received attention as new two-dimensional topological materials (Figure 1).[2] For example, cyclothiophenes,[3] cycloethynylenethienylenes,[4] thiaporphyrins,[5] and thiocirculenes[6] have been the subject of considerable research. Although many of their unique properties stem from their shape-persistent cyclic structures as well as infinite π-conjugation, their p orbitals are aligned perpendicular to the backbone structure as in the case of linear π-conjugated compounds. Thus, a new and alternative mode of π-conjugation is highly desirable in this area to explore new properties and opportunities in thiophene-based π materials.

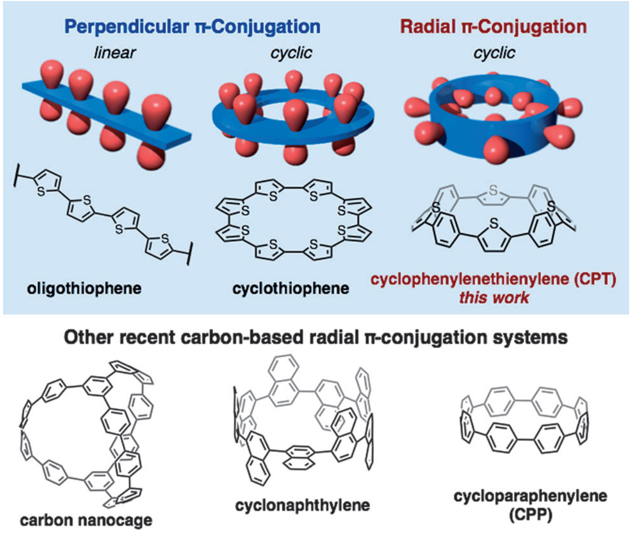

Figure 1. Perpendicular and radial π-conjugated systems bearing linear and cyclic structures.

In the area of carbon-based π materials, radially π-conjugated systems[7] have been in the limelight because of their unique structures and unprecedented photophysical properties. Fullerenes and carbon nanotubes represent highly popular compounds having radially oriented p orbitals,[7] but in addition to these, short segments of carbon nanotubes as exemplified by cycloparaphenylenes (CPPs), show remarkable and unique photophysical, electrochemical, and host–guest properties based on their radially π-conjugated systems.[8,9] Such molecules are unique in that they are characterized by both infinite π-conjugation and shape-persistent cyclic structures which can be used to control the direction of π-conjugation. Herein we report the synthesis of cyclo-1,4-phenylene-2′,5′-thienylenes ([*n*]CPT; $n = 4, 5, 6$; *n* represents the number of 1,4-phenylene-2′,5′-thienylene unit) as the first example of thiophene-based, radially π-conjugated systems (Figure 1). Interesting photophysical and structural properties of CPTs including characterization by X-ray crystallography and computational analysis are also described.

Previously, we have synthesized a number of CPPs and related carbon nanorings and have uncovered their interesting properties.[8,10,11] In view of the significance of thiophene-containing π systems in materials science, we planned to

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[**] 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.). Dr. Keiko Kuwata (ITbM, Nagoya Univ) is acknowledged for HRMS measurements. Ms. Haruko Hirukawa (ITbM, Nagoya Univ) is acknowledged for the graphics. We thank Prof. Cathleen M. Crudden (ITbM, Nagoya Univ and Queen's Univ, Canada) for critical comments. Calculations were performed using the resources of the Research Center for Computational Science, Okazaki (Japan). H.I. was a recipient of JSPS research fellowship for young scientists. 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.201409389.

synthesize CPTs whose phenylene and thienylene units are alternately connected within the ring structure (Figure 1). CPT can be regarded as a well-defined hybrid of CPP and cyclothiophene, in some ways related to thiophene-phenylene co-oligomers, but with unique properties stemming from its perfectly alternating thiophene and benzene units, cyclic structure, and radial π-conjugation. Although the synthesis of cyclic compounds with higher phenylene/thienylene ratios might be achievable by simply employing thiophene diboronic acids analogously to our previous CPP synthetic methods, we chose a synthetic approach which would give perfectly alternating phenylene/thienylene groups within the macrocycle so as to more easily compare CPTs with cyclothiophenes and CPPs.

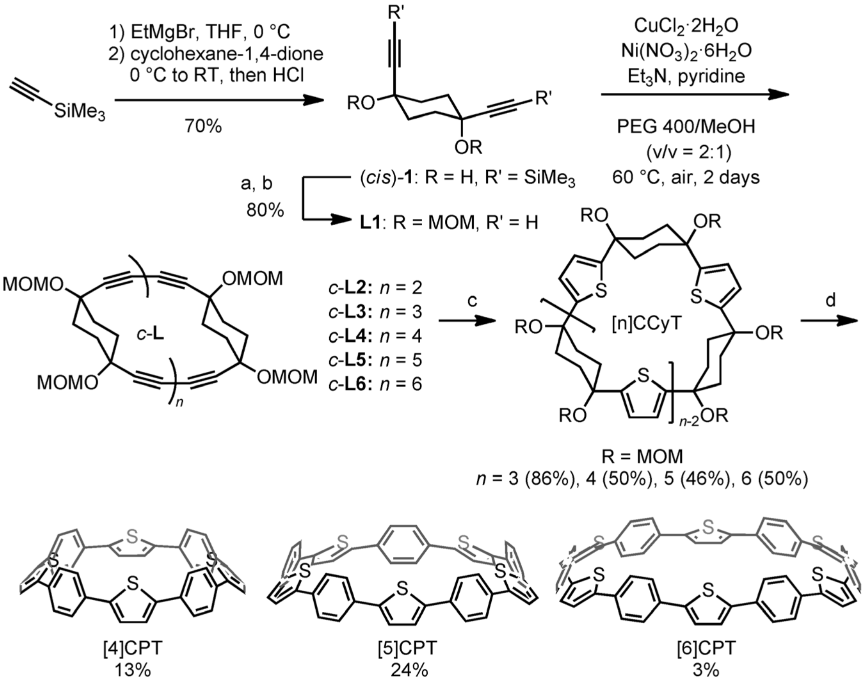
Radially π-extended CPTs are highly strained molecules unlike oligothiophenes and cyclothiophenes (see the Supporting Information for details). Therefore the synthetic route chosen must be able to attenuate the build-up of strain energy during the macrocyclization. We solved these issues by capitalizing on the ability of L-shaped *cis*-1,4-dialkoxycyclohexane-1,4-diyl[12] and 1,3-butadiyne-1,4-diyl to serve as precursors to benzene and thiophene rings, respectively. To accomplish this, we employed Glaser–Hay couplings (cyclo-oligomerizations) of L-shaped *cis*-1,4-diethynylcyclohexane units to prepare the key diyne-containing macrocycles, with the expectation that the thus-formed 1,3-butadiyne units could be transformed into thiophene rings by the action of Na_2S, followed by the final cyclohexane-to-benzene aromatization to achieve the synthesis of CPTs.

The synthesis of CPTs using this strategy is outlined in Scheme 1. The L-shaped *cis*-1,4-diethynylcyclohexane unit **L1** was synthesized by 1) the double carbonyl addition of 2-trimethylsilylethynylmagnesium bromide to cyclohexane-1,4-dione, 2) the protection of hydroxy groups on (*cis*)-**1** as methoxymethoxy groups, and 3) desilylation. Next, the key cyclo-oligomerization of **L1** by Glaser–Hay coupling was investigated. After extensive examination, we found that the phase-separation method reported by Collins[13] allowed us to conduct the cyclo-oligomerization of **L1** on a gram scale. For example, the treatment of **L1** (20 mmol) with $CuCl_2{\cdot}2H_2O$ (1 equiv), $Ni(NO_3)_2{\cdot}6H_2O$ (1 equiv), triethylamine (3 equiv), and pyridine (5 equiv) in PEG 400 (400 mL) and MeOH (200 mL) at 60 °C and open to air afforded the corresponding cyclic dimer *c*-**L2** (32 %), trimer *c*-**L3** (31 %), tetramer *c*-**L4** (15 %), and pentamer *c*-**L5** (6 %) in 84 % combined yield (see Table S1 in the Supporting Information). Notably, each cyclic product was easily separable by chromatography. The structures of *c*-**L2**, *c*-**L3**, and *c*-**L4** were confirmed by X-ray crystallography (see the Supporting Information).[14] To obtain cyclic hexamer *c*-**L6**, the volumes of solvents were reduced such that the concentration increased fourfold and gave *c*-**L6** in 3 % yield, albeit with a marked decrease in total yield.

We next tried to transform the diyne components of *c*-**L3**–**L6** to thiophene rings in the presence of $Na_2S{\cdot}9H_2O$ (Scheme 1). Under microwave irradiation, *c*-**L3**–**L6** were easily converted into the corresponding cyclic 1,4-cyclohexylene-2′,5′-thienylenes ([3]CCyT, [4]CCyT, [5]CCyT, and [6]CCyT) in moderate to high yields (Scheme 1). The structure of [3]CCyT was confirmed by X-ray crystallography (see the Supporting Information).[14] The final cyclohexane-to-benzene aromatization[8] of [*n*]CCyT using $NaHSO_4$ in *m*-xylene/DMSO at 150 °C open to air furnished [4]CPT, [5]CPT, and [6]CPT in 13, 24, and 3 % yields, respectively, upon isolation. The reaction of [3]CCyT did not give [3]CPT, probably because of the lower thermal stability of more highly strained [3]CPT. The CPTs thus obtained are yellow solids which are soluble in typical organic solvents such as $CHCl_3$, Et_2O, EtOAc, and DMSO.

The ^1H NMR spectra of [4]-[6]CPT in CD_2Cl_2 or $[D_6]$DMSO at room temperature were simple. For example, in the spectrum of [4]CPT singlets at $\delta =$ 7.08 and 7.32 ppm are assigned to the equivalent protons on phenylene and thienylene moieties, thus clearly indicating that [4]CPT–[6]CPT have highly symmetric time-averaged structures consistent with the dynamic free rotations of phenylene and thienylene groups at room temperature. Indeed, we found that the rotation barriers of these CPTs are about 4 kcal mol^{-1} by DFT calculation (see the Supporting Information).

We conducted the X-ray crystallographic analysis of a needle-shaped single crystal of [4]CPT·2cyclohexane obtained by recrystallization from THF/cyclohexane.[14] As depicted in



Scheme 1. Synthesis of [4]CPT, [5]CPT, and [6]CPT. Reaction conditions: a) iPr_2NEt, CH_3OCH_2Cl, CH_2Cl_2, RT. b) K_2CO_3, MeOH, RT. c) $Na_2S{\cdot}9H_2O$, 160 °C, microwave. d) $NaHSO_4{\cdot}H_2O$, DMSO/*m*-xylene, 150 °C, 2–3 days. DMSO = dimethylsulfoxide, MOM = methoxylmethyl.

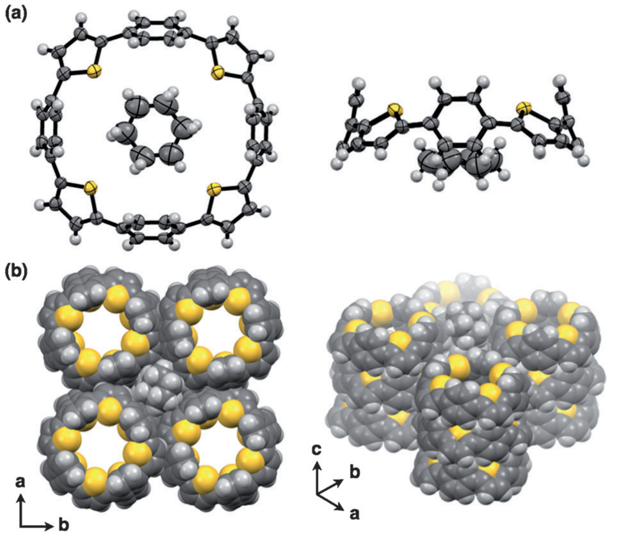


Figure 2. X-ray crystal structures of [4]CPT·2cyclohexane.[14] a) ORTEP drawings of [4]CPT (cyclohexane between [4]CPT molecules is omitted for clarity). Thermal ellipsoids shown at 50% probability. b) The tubular packing structures of [4]CPT (cyclohexane inside a [4]CPT ring is omitted for clarity).

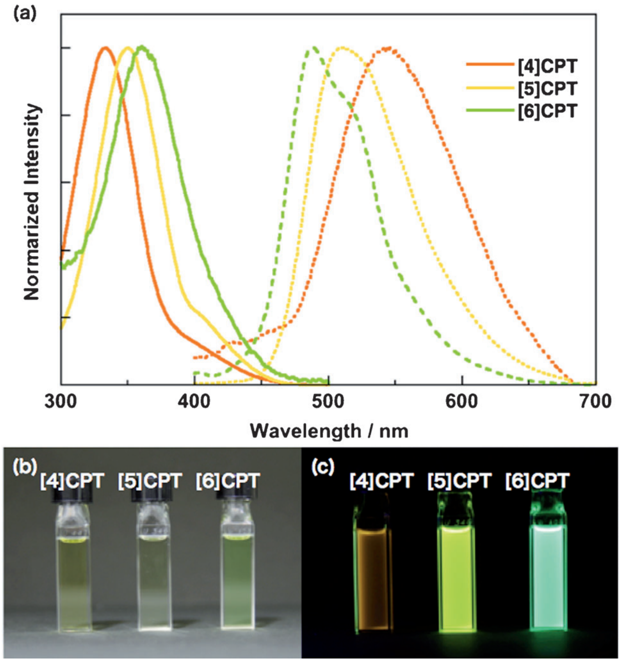


Figure 3. a) UV-Vis absorption (broken line) and fluorescence spectra (solid line) of [4]CPT, [5]CPT, and [6]CPT in cyclohexane (absorption and fluorescence spectra were normalized). b) Pictures of [4]CPT, [5]CPT, and [6]CPT in cyclohexane under b) ambient light and c) UV irradiation at $\lambda = 365$ nm.

Figure 2, the four thiophene rings of [4]CPT point in the same direction in the solid state, thus forming a C_{4v}-symmetric truncated cone shape. Moreover, tubular stacking along the c-axis was observed with all [4]CPT molecules oriented in the same direction. Furthermore, a high dipole moment value (2.7 D) was obtained by DFT calculations on one [4]CPT molecule extracted from the X-ray crystallographic structure. Given that almost all CPPs adopt a herringbone structure in crystal packing,[8,9] the ability of cone-shaped [4]CPT to easily stack in a tubular fashion is noteworthy. These striking structural features speak well for the potentially unique behavior of CPTs in various solid-state applications. We also evaluated the structural features of [4]CPT–[6]CPT, such as ring diameters and ring strain, in their most stable cone-shaped structures. Details including bend angles and torsion angles are provided in Tables S3, S4, and S5 and Figures S6 and S7 in the Supporting Information.

The UV-vis absorption and fluorescence spectra were measured to elucidate the photophysical properties of [*n*]CPTs (Figure 3). Absorption maxima of each [4]CPT–[6]CPT appeared at $\lambda = 333$, 350, and 362 nm, respectively. This tendency to red-shift upon increasing the number of aromatic units is similar to that found in common π-conjugated compounds. Shoulder peaks were also observed around $\lambda = 370$ to 480 nm. Interestingly, in the fluorescence spectra, emission maxima were blue-shifted as the ring size of CPT increases ([4]CPT: $\lambda = 546$ nm, [5]CPT: $\lambda = 510$ nm, [6]CPT: $\lambda = 488$ nm), showing orange, yellow, and green fluorescence (Figure 3c). In particular, a much larger Stokes shift was observed in [4]CPT. We assume that this derives from a more significant structural relaxation which can occur at the excited state in the case of smaller and more strained [4]CPT.

Next we conducted TD-DFT calculations on C_{nv}-symmetric cone-shaped [*n*]CPT at the B3LYP/6-31G(d) level of theory. Six frontier molecular orbitals and the energy diagrams of representative [4]CPT are depicted in Figure 4. The HOMO and LUMO are delocalized over the entire ring, thus indicating the formation of intriguing cone-shaped radial π-conjugation. In contrast, HOMO-1/HOMO-2 and LUMO+1/LUMO+2 are each degenerate and slightly localized to two opposite sides. These tendencies, which are

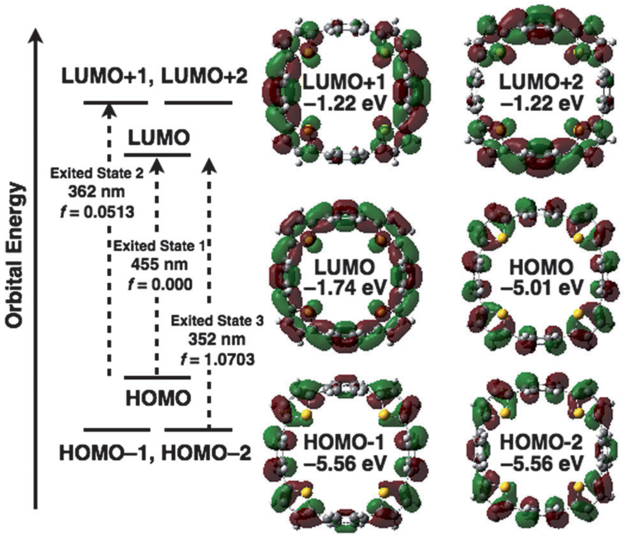


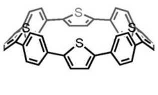
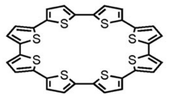
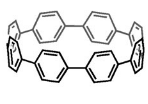
Figure 4. Energy diagram and pictorial representation of six frontier molecular orbitals of [4]CPT, calculated at the B3LYP/6-31G(d) level of theory.

similar to those of CPP, most likely stem from the high symmetry of CPT. Furthermore, three energetically low-lying characteristic transitions arise from the set of six orbitals: 1) a symmetry-forbidden HOMO→LUMO transition with the oscillator strength (f) of 0.00 (excited state 1), 2) a degenerate transition in which both HOMO→LUMO + 1 and LUMO + 2 excitations mix with a low f value of 0.05 (excited state 2), and 3) a degenerate transition in which both HOMO-1 and HOMO-2→LUMO excitations mix with a high f value of 1.07 (excited state 3). Taking these into consideration, a shoulder peak ($\lambda = 370$–450 nm) in the UV-vis absorption spectrum of [4]CPT likely originates from the forbidden HOMO→LUMO excitation 1. The λ_{max} of 333 nm can be mainly attributed to excitation 3, while the solvent effect in cyclohexane is expected to induce a blue shift of the absorption from the calculated value of $\lambda = 352$ nm.

Through these extensive investigations, we are now in the position to compare the basic properties of CPTs with those of related cyclothiophenes and CPPs of similar ring size (Table 1). In general, both linear and planar π-conjugated compounds including cyclothiophenes show an increase in HOMO energy level and a decrease of LUMO energy level as the π-conjugation length is extended. In contrast, as we and others already reported,[8–10] CPPs behave in quite the opposite way with regards to HOMO/LUMO energy. While LUMOs of CPTs follow the general tendency to decrease the LUMO energy level with the extension of π-conjugation length, the energy levels of HOMOs of CPTs do not change significantly regardless of the ring size. This can be rationalized by the assumption that the HOMO of CPT has the nature of both cyclothiophene and CPP, thus resulting in the cancellation of stabilizing/destabilizing effects at the HOMO. When comparing absorption spectra, CPT shows a red-shift upon increasing ring size, like cyclothiophene, which corresponds to a decrease in the HOMO/LUMO gap. In contrast, fluorescence spectra of CPTs are blue-shifted with increasing the ring size. This observation is unusual but quite similar to those of CPPs. Previously we and others found that the fluorescence spectra of CPPs are abnormally blue-shifted with increasing ring size.[9,10b] We also clarified that these unique properties are derived from the radial, cyclic π-conjugation of CPP.[10] Judging from the results of the DFT calculations and photophysical property analyses, we conclude that CPT assumes the character of both planar (usual) and radial (unusual) π-conjugation. The usual red-shift of absorption found in the larger CPT derivatives is clearly consistent with the behavior of planar π-conjugated materials such as cyclothiophenes and thiophene-phenylene co-oligomers.

Table 1: Comparison of photophysical properties and ring sizes of CPT, cyclothiophene, and CPP.

as the ring size becomes larger

	 CPT[a]	 cyclothiophene[b]	 CPP[c]
LUMO (eV)[d]	⇩	⇩	⬆
HOMO (eV)[d]	—	⬆	⇩
λ_{abs} (nm)[e]	⬆	⬆	⇩
λ_{em} (nm)[f]	⇩	⬆	⇩

[a] Data of [4]CPT–[6]CPT were used. [b] Data of syn-cyclo[*n*]thiophenes from Ref. [3]. [c] Data of [5]CPP–[16]CPP from Ref. [8] and [9]. [d] Calculated at B3LYP/6-31G(d) level of theory. [e] Shoulder-like absorption band at longer wavelength region. [f] Maximum emission wavelength.

In summary, we have achieved the synthesis of cyclo-1,4-phenylene-2′,5′-thienylenes (CPTs) as the first example of a thiophene-based, radially π-conjugated system. We also succeeded in obtaining an X-ray crystal structure of [4]CPT, which revealed that the four thiophene rings of [4]CPT point in the same direction in the solid state, thus forming a C_{4v}-symmetric truncated cone shape. Moreover, tubular stacking along the c-axis was observed with all [4]CPT molecules oriented in the same direction. These striking structural features speak well for the potentially unique behavior of CPTs in various solid-state applications. The measurement of absorption and fluorescence spectra and theoretical calculations revealed the unique structural and photophysical properties of CPTs. Upon increasing the ring size of CPT, the LUMO energy levels decrease while the energy levels of the HOMO are almost unchanged. Reflecting the decrease of the HOMO/LUMO gap with increasing ring size, the red-shift of absorption maxima is observed in CPT. However, we observed a significant blue-shift in the fluorescence maxima. With all of these unique structural and photophysical properties, we believe that radially π-conjugated CPTs will open a door for the discovery and development of new functionalized organic materials.

Received: September 23, 2014

Keywords: conjugation · cyclooligomerization · cycloparaphenylenes · macrocycles · oligothiophenes

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[1] a) A. Mishra, C.-Q. Ma, P. Bäuerle, *Chem. Rev.* **2009**, *109*, 1141; b) *Handbook of Thiophene-Based Materials: Applications in Organic Electronics and Photonics* (Eds.: I. F. Perepichka, D. F. Perepichka), Wiley-VCH, Weinheim, **2009**; c) T. Otsubo, Y. Aso, K. Takimiya, *Bull. Chem. Soc. Jpn.* **2001**, *74*, 1789; d) D. T. McQuade, A. E. Pullen, T. M. Swager, *Chem. Rev.* **2000**, *100*, 2537.

[2] a) M. Iyoda, J. Yamakawa, M. J. Rahman, *Angew. Chem. Int. Ed.* **2011**, *50*, 10522; *Angew. Chem.* **2011**, *123*, 10708; b) S. Höger, *J. Polym. Sci. Part A* **1999**, *37*, 2685.

[3] a) J. Krömer, I. Rios-Carreras, G. Fuhrmann, C. Musch, M. Wunderlin, T. Debaerdemacker, E. Mena-Osteritz, P. Bäuerle, *Angew. Chem. Int. Ed.* **2000**, *39*, 3481; *Angew. Chem.* **2000**, *112*, 3623; b) G. Fuhrmann, J. Krömer, P. Bäurele, *Synth. Met.* **2001**, *119*, 125; c) E. Mena-Osteritz, *Adv. Mater.* **2002**, *14*, 609; d) E. Mena-Osteritz, P. Bäuerle, *Adv. Mater.* **2006**, *18*, 447; e) A. Bhaskar, G. Ramakrishna, K. Hagedorn, O. Varnavski, E. Mena-Osteritz, P. Bäuerle, T. Goodson III, *J. Phys. Chem. B* **2007**, *111*, 946; f) F. Zhang, G. Götz, H. D. F. Winkler, C. A. Schalley, P.

Bäuerle, *Angew. Chem. Int. Ed.* **2009**, *48*, 6632; *Angew. Chem.* **2009**, *121*, 6758; g) F. Zhang, G. Götz, E. Mena-Osteritz, M. Weil, B. Sarkar, W. Kaim, P. Bäuerle, *Chem. Sci.* **2011**, *2*, 781.

[4] a) K. Nakao, M. Nishimura, T. Tamachi, Y. Kuwatani, H. Miyasaka, T. Nishinaga, M. Iyoda, *J. Am. Chem. Soc.* **2006**, *128*, 16740; b) M. Iyoda, K. Tanaka, H. Shimizu, M. Hasegawa, T. Nishinaga, T. Nishiuchi, Y. Kunugi, T. Ishida, H. Ohtani, H. Sato, K. Inukai, K. Tahara, Y. Tobe, *J. Am. Chem. Soc.* **2014**, *136*, 2389; c) Y. Tobe, N. Utsumi, A. Nagano, M. Sonoda, K. Naemura, *Tetrahedron* **2001**, *57*, 8075.

[5] Reviews: a) J. L. Sessler, D. Seidel, *Angew. Chem. Int. Ed.* **2003**, *42*, 5134; *Angew. Chem.* **2003**, *115*, 5292; b) S. Saito, A. Osuka, *Angew. Chem. Int. Ed.* **2011**, *50*, 4342; *Angew. Chem.* **2011**, *123*, 4432.

[6] a) K. Y. Chernichenko, V. V. Sumerin, R. V. Shpanchenko, E. S. Balenkova, V. G. Nenajdenko, *Angew. Chem. Int. Ed.* **2006**, *45*, 7367; *Angew. Chem.* **2006**, *118*, 7527; b) T. Fujimoto, M. M. Matsushita, H. Yoshikawa, K. Awaga, *J. Am. Chem. Soc.* **2008**, *130*, 15790.

[7] a) *Fragments of Fullerenes and Carbon Nanotube: Designed Synthesis Unusual Reactions, and Coordination Chemistry* (Eds.: M. A. Petrukhina, L. T. Scott), Wiley-VCH, Weinheim, **2012**; b) B. D. Steinberg, L. T. Scott, *Angew. Chem. Int. Ed.* **2009**, *48*, 5400; *Angew. Chem.* **2009**, *121*, 5504; c) U. H. F. Bunz, S. Menning, N. Martín, *Angew. Chem. Int. Ed.* **2012**, *51*, 7094; *Angew. Chem.* **2012**, *124*, 7202; d) H. W. Kroto, J. R. Heath, S. C. O'Brien, R. F. Curl, R. E. Smalley, *Nature* **1985**, *318*, 162; e) N. Martin, L. Sanchez, B. Illescas, I. Perez, *Chem. Rev.* **1998**, *98*, 2527.

[8] Selected contributions from our group: a) H. Omachi, Y. Segawa, K. Itami, *Acc. Chem. Res.* **2012**, *45*, 1378; b) H. Takaba, H. Omachi, Y. Yamamoto, J. Bouffard, K. Itami, *Angew. Chem. Int. Ed.* **2009**, *48*, 6112; *Angew. Chem.* **2009**, *121*, 6228; c) H. Omachi, S. Matsuura, Y. Segawa, K. Itami, *Angew. Chem. Int. Ed.* **2010**, *49*, 10202; *Angew. Chem.* **2010**, *122*, 10400; d) Y. Segawa, S. Miyamoto, H. Omachi, S. Matsuura, P. Šenel, T. Sasamori, N. Tokitoh, K. Itami, *Angew. Chem. Int. Ed.* **2011**, *50*, 3244; *Angew. Chem.* **2011**, *123*, 3302; e) A. Yagi, Y. Segawa, K. Itami, *J. Am. Chem. Soc.* **2012**, *134*, 2962; f) K. Matsui, Y. Segawa, T. Namikawa, K. Kamada, K. Itami, *Chem. Sci.* **2013**, *4*, 84; g) Y. Nakanishi, H. Omachi, S. Matsuura, Y. Miyata, R. Kitaura, Y. Segawa, K. Itami, H. Shinohara, *Angew. Chem. Int. Ed.* **2014**, *53*, 3102; *Angew. Chem.* **2014**, *126*, 3166–3170.

[9] Selected contributions from other groups: a) R. Jasti, J. Bhattacharjee, J. B. Neaton, C. R. Bertozzi, *J. Am. Chem. Soc.* **2008**, *130*, 17646; b) S. Yamago, Y. Watanabe, T. Iwamoto, *Angew. Chem. Int. Ed.* **2010**, *49*, 757; *Angew. Chem.* **2010**, *122*, 769; c) S. Hitosugi, W. Nakanishi, T. Yamasaki, H. Isobe, *Nat. Commun.* **2011**, *2*, 492; d) P. J. Evans, E. R. Darzi, R. Jasti, *Nat. Chem.* **2014**, *6*, 404; e) F. E. Golling, M. Quernheim, M. Wagner, T. Nishiuchi, K. Müllen, *Angew. Chem. Int. Ed.* **2014**, *53*, 1525; f) K. Kayahara, V. K. Patel, S. Yamago, *J. Am. Chem. Soc.* **2014**, *136*, 2284.

[10] Theoretical studies on CPP: a) Y. Segawa, H. Omachi, K. Itami, *Org. Lett.* **2010**, *12*, 2262; b) Y. Segawa, A. Fukazawa, S. Matsuura, H. Omachi, S. Yamaguchi, S. Irle, K. Itami, *Org. Biomol. Chem.* **2012**, *10*, 5979; c) T. Nishihara, Y. Segawa, K. Itami, Y. Kanemitsu, *J. Phys. Chem. Lett.* **2012**, *3*, 3125; d) C. Camacho, T. A. Niehaus, K. Itami, S. Irle, *Chem. Sci.* **2013**, *4*, 187; e) T. Nishihara, Y. Segawa, K. Itami, Y. Kanemitsu, *Chem. Sci.* **2014**, *5*, 2293; f) M. Fujitsuka, D. W. Cho, T. Iwamoto, S. Yamago, T. Majima, *Phys. Chem. Chem. Phys.* **2012**, *14*, 14585; g) M. Fujitsuka, C. Lu, T. Iwamoto, E. Kayahara, S. Yamago, T. Majima, *J. Phys. Chem. A* **2014**, *118*, 4527.

[11] H. Omachi, T. Nakayama, E. Takahashi, Y. Segawa, K. Itami, *Nat. Chem.* **2013**, *5*, 572.

[12] M. Srinivasan, S. Sankararaman, H. Hopf, B. Varghese, *Eur. J. Org. Chem.* **2003**, 660.

[13] A.-C. Bédard, S. K. Collins, *J. Am. Chem. Soc.* **2011**, *133*, 19976.

[14] CCDC 1025378 (*c*-**L2**), 1025379 (*c*-**L3**), 1025380 (*c*-**L4**), 1025381 ([3]CCyT), and 1025382 ([4]CPT) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.