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Tridecacyclene: A Cyclic Tetramer of Acenaphthylene

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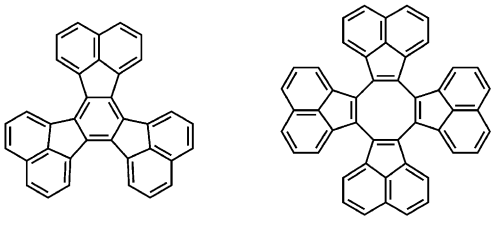
Abstract: In this manuscript, we describe the single-step preparation of a cyclic tetramer of acenaphthylene through a Lewis acid-catalyzed aldol cyclization of 1-acenaphthenone. The previously unexplored cyclic tetramer material differs from the better-known cyclic trimer, decacyclene, due to the presence of a central eight-membered ring. This ring not only forces the molecule to distort significantly from planarity, but is also responsible for its unique electronic properties, including a decrease in the reduction potential (by about 0.4 eV) and optical gap (by about 0.73 eV), compared to the more planar decacyclene. The synthesized compound crystallizes into a unique packing structure with significant π-stacking observed between adjacent molecules. Furthermore, due to its saddle-like shape, the cyclic tetramer is able to form shape-complementary interactions between its concave surface and the convex outer surface of buckminsterfullerene to generate cocrystalline supramolecular assemblies.

Decacyclene (**1**), a polycyclic aromatic hydrocarbon (PAH) exhibiting a three-fold symmetric propeller-like structure, was first reported by Dziewoński in 1903.[1] Over the past century, **1** has generated considerable interest and has found utility in a range of disciplines, including surface modification,[2] organometallic complexes,[3] and liquid crystals.[4] Furthermore, the ability of **1** to reversibly accept up to four electrons has provided motivation for its study as an n-type semiconductor,[5] its use in organic photovoltaics,[6] and investigations of its ferromagnetism.[7] Significant efforts have been made to develop functionalized derivatives of **1** that can be used as precursors for the synthesis of highly strained PAHs—the most notable being Scott's syntheses of both circumtrindene[8] and buckminsterfullerene (C_{60}).[9] Throughout these studies, obtaining the necessary precursors has relied heavily on the Lewis acid-catalyzed aldol cyclization of 1-acenaphthenone derivatives.[10] Although this reaction has been used almost exclusively for the synthesis of cyclic trimers, a number of groups have reported the presence of an analogous tetrameric species in mass spectra of crude reaction mixtures.[8b, 9a, 11] Surprisingly, despite the interesting structural and electronic properties that have recently been observed as a result of the incorporation of eight-membered rings into PAHs,[12] only a single report mentions the isolation of a cyclic tetramer from one of these reactions and the physical properties of these species have yet to be explored.[11a] Herein, we describe the synthesis and properties of 1.2;3.4;5.6;7.8-tetra[(1.8)-naphthylene]-1,3,5,7-cyclooctatetraene (**2**), which following the nomenclature used for decacyclene (ten cycles) we have appropriately named tridecacyclene (thirteen cycles).


decacyclene (**1**) tridecacyclene (**2**)

Although all reported cyclic tetramers have been derived from substituted 1-acenaphthenone derivatives, our investigations focused on unfunctionalized 1-acenaphthenone due to its availability, both commercially and synthetically, and the simplicity of the products that would be produced. To our surprise, subjecting 1-acenaphthenone to the most commonly used aldol cyclotrimerization conditions ($TiCl_4$ in 1,2-dichlorobenzene at 180 °C) produced two major products, which were distinguishable by thin layer chromatography (TLC)—a yellow fluorescent spot with spectroscopic data matching that of **1** (<1% yield) and a brown spot of similar polarity that we have identified as **2** (21% yield).

Compound **2** is a stable brown solid that unlike **1** readily dissolves in a range of organic solvents. The ^{1}H NMR spectrum of **2** in $CDCl_3$ gives three peaks of equal integration at $\delta = 7.87$, 7.67, and 7.56 ppm. Similarly, the ^{13}C NMR spectrum displays seven unique chemical environments for the 48 carbon atoms in the structure, indicating a high degree of symmetry. Furthermore, the ^{1}H NMR shifts provide a strong indication that **2** adopts a nonplanar topology. The ^{1}H NMR of **1** exhibits a downfield resonance at $\delta = 8.83$ ppm, which corresponds to the proton in the bay region of the molecule. The significant downfield shift is a result of the fact that each of these protons

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feels the ring current of both the aromatic rings that they are attached to as well as the adjacent aromatic ring, a direct result of the molecule being primarily planar in geometry. In **2**, the proton is found about 1 ppm further upfield, indicating much less of a contribution from the adjacent ring, and therefore, a strong indication that the compound is not planar.

Dark brown crystals of **2**·1,2-DCE, grown from the slow diffusion of hexane into 1,2-dichloroethane, were used to validate the structure through single-crystal x-ray diffraction (SC-XRD) studies.[13] The solid-state structure (Figure 1 A) matches that predicted from density functional theory (DFT) calculations,[14] and unlike **1**, the structure distorts significantly from planarity (with the average atom in the eight-membered ring deviating from the mean plane of the ring by 0.37 Å), producing an alternating up-down-up-down arrangement of the acenaphthylene units.

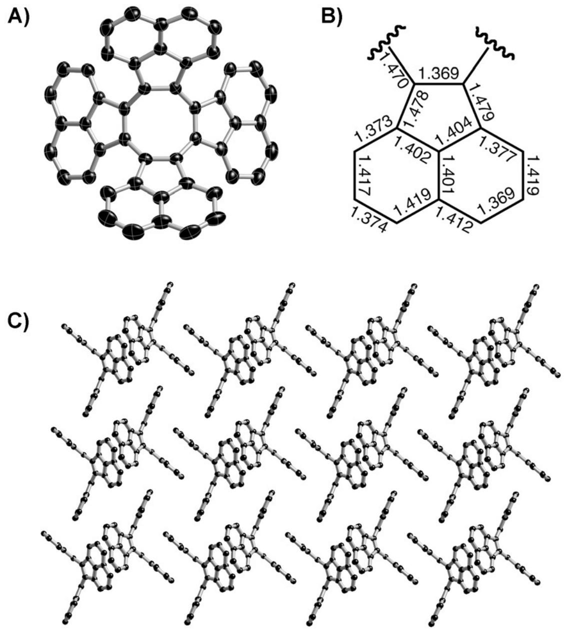

Figure 1. A) The solid-state structure of **2**; hydrogen atoms have been omitted for clarity and the ellipsoids are shown at 80 % probability. B) Representative bond lengths (Å) calculated from the solid-state structure of **2**; a full list of bond lengths is provided in the Supporting Information. C) Crystal packing of **2**, illustrating the π-stacking interactions that exist between adjacent molecules.

The bond lengths obtained from the x-ray structure (Figure 1 B) of **2** are consistent with those of acenaphthylene as substantial bond alternation is observed in the naphthalene subunits and significant double-bond character exists in the bond shared by the five- and eight-membered ring. Bond alternation is also observed in the central ring, with the bonds connecting the acenaphthylene units displaying significantly more single-bond character than those within the five-membered rings. This is in contrast to what has been observed for **1**, in which the bond alternation places the shorter bonds between the acenaphthylene units. The solid-state packing of **2** (Figure 1 C) is unique, with two orthogonal naphthalene subunits of each molecule forming π-stacking interactions (about 3.4 Å apart) with two adjacent molecules, resulting in a zigzag pattern throughout the crystal. The structure is further stabilized by an abundance of intermolecular C–H/π-interactions.

The aromaticity of each of the rings of **2** was calculated using the harmonic oscillator model of aromaticity (HOMA),[15] and the results were found to be consistent to those of **1**. In each case, the six-membered rings of the naphthylene units are highly aromatic (HOMA values of 0.89 and 0.90 for **1** and 0.84 and 0.90 for **2**) and the five-membered rings are predominantly non-aromatic (HOMA values of 0.11 and −0.07 for **1** and **2**, respectively), although a small degree of antiaromaticity is present in **1**.

Despite the fact that similar bonding patterns exist in **1** and **2**, the optoelectronic properties of the two are considerably different. In the UV/Vis spectra (Figure 2 A), we observe that the λ_{max} undergoes a hypsochromic shift when converting from **1** (377 nm) to **2** (360 nm) with a slight reduction in molar absorptivity, likely as a result of more efficient orbital overlap for the more planar structure. Surprisingly, the solution-based optical gaps display the opposite trend, as judged by the absorption onsets, with the optical gap of **2** being considerably lower in energy than that of **1**. The cyclic voltammograms (Figure 2 B) support this observation because **2** is considerably easier to reduce than **1** (by about 0.4 eV), primarily as a result of a significant decrease in the energy of the lowest unoccupied molecular orbital (LUMO). This observation is directly related to the presence of the eight-membered cyclooctatetraene core, because aromaticity is known to develop in such

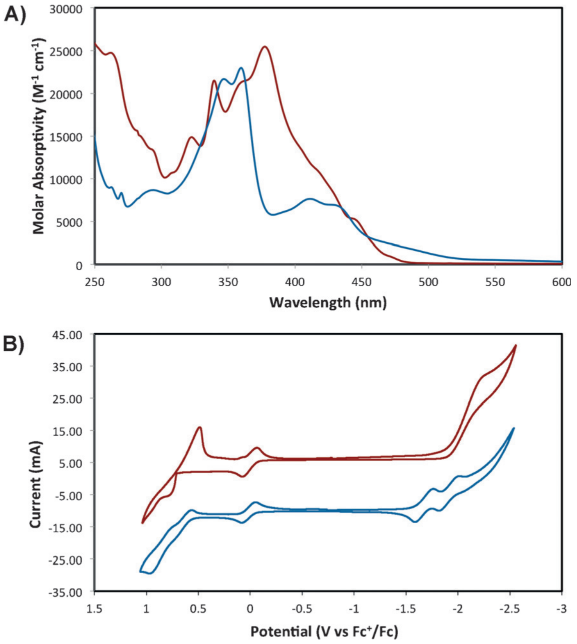

Figure 2. A) Absorption spectra of **1** (red) and **2** (blue) in CH_2Cl_2. B) Cyclic voltammetry of **1** (red) and **2** (blue) in 0.05 м tetrabutylammonium hexafluorophosphate in MeCN with a Pt working electrode, Pt counter electrode, and Ag/AgCl reference electrode. Scan rate: 50 mV s^{-1}. Ferrocene was added as an internal standard and referenced to 0 V.

rings through two-electron reduction processes.[16] Interestingly, this occurs through two one-electron processes rather than a single two-electron process, indicating that the radical anion generated from the first reduction is a stable species under the experimental conditions. The highest occupied molecular orbital (HOMO) energies are similar between the two compounds with the HOMO of **2** being 0.16 eV higher in energy than that of **1** (Table 1).

Table 1. Summary of optoelectronic properties of **1** and **2**.[a]

	1	**2**
$E_{ox/onset}$	0.73	0.57
$E_{red/onset}$	−1.90	−1.54
HOMO [eV]	−5.53	−5.37
LUMO [eV]	−2.90	−3.26
E-chem gap [eV]	2.63	2.11
λ_{max} [nm]	377	360
optical gap [eV]	2.57	1.84

[a] Measurements taken at sample concentrations of 0.2 mM and potentials measured relative to a ferrocenium/ferrocene redox couple used as an internal standard (Figure 2B). $E_{ox/onset}$ is the onset of the oxidation potential and $E_{red/onset}$ is the onset of the reduction potential. HOMO and LUMO values were calculated on the basis of the oxidation of the ferrocene reference in vacuum (4.8 eV).

In view of the concave surfaces of **2**, we were interested to see if the compound would form supramolecular interactions with the convex surface of buckminsterfullerene (C_{60}). Although such interactions are prevalent in the literature,[17] the ability to complex a fullerene on two opposing concave surfaces is quite unique and such assemblies have only been reported in the literature on two occasions.[18] Such complexes are inherently applicable to the area of photovoltaics due to their potential to act as p–n junctions. It is important to note, however, that in the two previous examples of such complexes, the host molecules were more difficult to prepare than **2**.

When saturated chlorobenzene solutions of **2** and C_{60} were combined, crystals of the supramolecular assembly (Figure 3) suitable for SC-XRD were produced.[12] The crystal is composed of C_{60}, **2**, and chlorobenzene (asymmetric unit ratio of 2:1:3, respectively), wherein **2** and C_{60} form a repeating zigzag pattern throughout the solid-state structure. As predicted, each molecule of **2** interacts ("interaction" here means atom–atom contacts less than the sum of their van der Waals radii) with two symmetry-related C_{60} molecules, one on each of its opposing concave faces. On the other hand, the two C_{60} molecules occupy two distinctly different environments. One C_{60} unit (blue) interacts with half of two molecules of **2** in one hemisphere, whereas the other hemisphere interacts with the second C_{60} unit. The other C_{60} unit (green) interacts with one acenaphthylene moiety of two different molecules of **2**, three molecules of the first C_{60} unit, and two molecules of chlorobenzene. The complexes between **2** and C_{60} exhibit strong π–π interactions, wherein the shortest distance from an atom of C_{60} to the plane of an interacting naphthalene moiety is 3.00 Å. This distance is nearly identical to those observed in the previously reported systems.

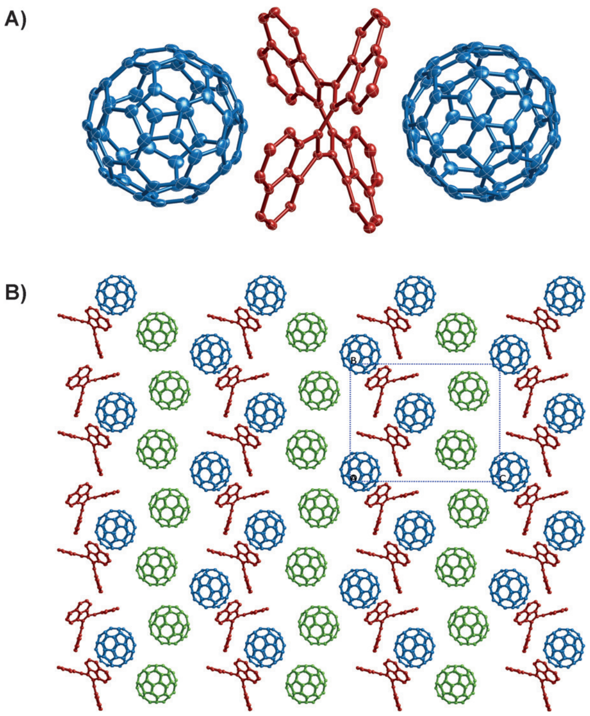

Figure 3. A) The solid-state cocrystalline supramolecular assembly of **2** (red) and C_{60} (blue). Hydrogen atoms and solvent molecules have been omitted for clarity and the ellipsoids are shown at 80% probability. The C_{60} molecule on the left is related to the C_{60} molecule on the right by the symmetry operation ($-x+1/2$, $y+1/2$, $-z+1/2$). B) The crystal packing of **2** and two separate units of C_{60} (blue and green), illustrating the zigzag arrangement of components as well as the π-stacking interactions that exist between **2** and one of the C_{60} units (blue) and the C–H/π-interactions that exist between adjacent molecules of **2**. The unit cell is indicated with a doted blue line.

In conclusion, we have isolated a saddle-shaped cyclic tetramer of acenaphthylene as the major product from a single-step reaction that has historically been used extensively for cyclic trimer formation. This compound exhibits a range of beneficial properties when compared to its trimeric analog, including increased solubility, a significant decrease in reduction potential (and a decrease in the corresponding optically and electrochemically measured HOMO-LUMO gap), and the ability to form supramolecular assemblies with fullerenes. Further tuning of such properties for a host of applications is currently ongoing in our laboratory.

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Keywords: arenes · buckminsterfullerene · Lewis acids · polycyclic aromatic hydrocarbons · supramolecular chemistry

[1] K. Dziewoński, *Chem. Ber.* **1903**, *36*, 962 – 971.

[2] a) M. Schunack, L. Petersen, A. Kühnle, E. Lægsgaard, I. Stensgaard, I. Johannsen, F. Besenbacher, *Phys. Rev. Lett.* **2001**, *86*, 456 – 459; b) M. Schunack, E. Lñgsgaard, I. Stensgaard, I. Johannsen, F. Besenbacher, *Angew. Chem. Int. Ed.* **2001**, *40*, 2623 – 2626; *Angew. Chem.* **2001**, *113*, 2693 – 2696.

[3] a) M. Munakata, L. P. Wu, G. L. Ning, T. Kuroda-Sowa, M. Maekawa, Y. Suenaga, N. Maeno, *J. Am. Chem. Soc.* **1999**, *121*, 4968 – 4976; b) J. J. Schneider, D. Spickermann, C. W. Lehmann, J. Magull, H.-J. Krüger, J. Ensling, P. Gütlich, *Chem. Eur. J.* **2006**, *12*, 1427 – 1435.

[4] a) E. Keinan, S. Kurnar, R. Moshenberg, R. Ghirlando, E. J. Wachtel, *Adv. Mater.* **1991**, *3*, 251 – 254; b) K. Hirota, K. Tajima, K. Hashimoto, *Synth. Met.* **2007**, *157*, 290 – 296.

[5] T. Saji, S. Aoyagui, *J. Electroanal. Chem.* **1979**, *102*, 139 – 141.

[6] G. M. Su, T. V. Pho, N. D. Eisenmenger, C. Wang, F. Wudl, E. J. Kramer, M. L. Chabinyc, *J. Mater. Chem. A* **2014**, *2*, 1781 – 1789.

[7] J. B. Torrance, P. S. Bagus, I. Johannsen, A. I. Nazzal, S. S. P. Parkin, *J. Appl. Phys.* **1988**, *63*, 2962 – 2965.

[8] a) L. T. Scott, M. S. Bratcher, S. Hagen, *J. Am. Chem. Soc.* **1996**, *118*, 8743 – 8744; b) R. B. M. Ansems, L. T. Scott, *J. Am. Chem. Soc.* **2000**, *122*, 2719 – 2724.

[9] a) M. M. Boorum, Y. V. Vasil'ev, T. Drewello, L. T. Scott, *Science* **2001**, *294*, 828 – 831; b) L. T. Scott, M. M. Boorum, B. J. McMahon, S. Hagen, J. Mack, J. Blank, H. Wegner, A. de Meijere, *Science* **2002**, *295*, 1500 – 1503.

[10] a) D. Astruc, *Modern Arene Chemistry*, Wiley, New York, **2002**; b) A. Amick, L. T. Scott, *J. Org. Chem.* **2007**, *72*, 3412 – 3418.

[11] a) W. Zhang, X.-Y. Cao, H. Zi, J. Pei, *Org. Lett.* **2005**, *7*, 959 – 962; b) T. J. Hill, R. K. Hughes, L. T. Scott, *Tetrahedron* **2008**, *64*, 11360 – 11369; c) M. A. Kabdulov, K. Y. Amsharov, M. Jansen, *Tetrahedron* **2010**, *66*, 8587 – 8593; d) A. Mueller, K. Yu, *Eur. J. Org. Chem.* **2015**, 3053 – 3056.

[12] a) K. Y. Chernichenko, V. V. Sumerin, R. V. Shpanchenko, E. S. Balenkova, V. G. Nenajdenko, *Angew. Chem. Int. Ed.* **2006**, *45*, 7367 – 7370; *Angew. Chem.* **2006**, *118*, 7527 – 7530; b) C.-N. Feng, M.-Y. Kuo, Y.-T. Wu, *Angew. Chem. Int. Ed.* **2013**, *52*, 7791 – 7794; *Angew. Chem.* **2013**, *125*, 7945 – 7948; c) Y. Sakamoto, T. Suzuki, *J. Am. Chem. Soc.* **2013**, *135*, 14074 – 14077; d) R. W. Miller, A. K. Duncan, S. T. Schneebeli, D. L. Gray, A. C. Whalley, *Chem. Eur. J.* **2014**, *20*, 3705 – 3711; e) X.-D. Xiong, C.-L. Deng, X.-S. Peng, Q. Miao, H. N. C. Wong, *Org. Lett.* **2014**, *16*, 3252 – 3255; f) S. Nobusue, H. Miyoshi, A. Shimizu, I. Hisaki, K. Fukuda, M. Nakano, Y. Tobe, *Angew. Chem. Int. Ed.* **2015**, *54*, 2090 – 2094; *Angew. Chem.* **2015**, *127*, 2118 – 2122.

[13] CCDC 1440430 (**2**) and 1440429 (**2·2(C_{60})·3(C_6H_5Cl)**) contain the supplementary crystallographic data for this paper. These data are provided free of charge by The Cambridge Crystallographic Data Centre. Crystallographic data: **2**: triclinic, $C_{48}H_{24}$, $M_r = 600.67$, $a = 11.361(3)$, $b = 11.595(3)$, $c = 15.309(4)$ Å, $V = 1822.1(8)$ Å^3, $T = 100$ K, space group *P-1*, $Z = 4$, $\lambda = 0.71073$ Å, $\rho = 1.095$ g cm^{-3}, $\mu = 0.062$ mm^{-1}, $R_1 = 0.0540$, $wR_2 = 0.1582$ for $I > 2\sigma(I)$. **C_{60} Complex (2·2(C_{60})·3(C_6H_5Cl))**: monoclinic, $C_{186}H_{39}Cl_3$, $M_r = 2379.52$, $a = 17.600(4)$, $b = 21.050(4)$, $c = 26.780(5)$ Å, $V = 9919(3)$ Å^3, $T = 100$ K, space group $P12_1/n1$, $Z = 4$, $\rho = 1.593$ g cm^{-3}, $\mu = 0.122$ mm^{-1}, $R_1 = 0.0607$, $wR_2 = 0.1716$ for $I > 2\sigma(I)$. See the Supporting Information for more details.

[14] DFT calculations (B3LYP/6 – 31G**) were performed using the Jaguar (see Jaguar: Version 8.3, Maestro: Version 9.8, Schrödinger, LLC, New York, USA, **2014**) software package.

[15] T. M. Krygowski, K. Ejsmont, B. T. Stepień, M. K. Cyrański, J. Poater, M. Solà, *J. Org. Chem.* **2004**, *69*, 6634 – 6640.

[16] a) T. J. Katz, H. L. Strauss, *J. Chem. Phys.* **1960**, *32*, 1873 – 1875; b) T. J. Katz, *J. Am. Chem. Soc.* **1960**, *82*, 3784 – 3785; c) W. J. Evans, D. J. Wink, A. L. Wayda, D. A. Little, *J. Org. Chem.* **1981**, *46*, 3925 – 3928; d) K. Komatsu, T. Nishinaga, S. Aonuma, C. Hirosawa, K. Takeuchi, H. J. Lindner, J. Richter, *Tetrahedron Lett.* **1991**, *32*, 6767 – 6770; e) P. Poremba, H.-G. Schmidt, M. Noltemeyer, F. T. Edelmann, *Organometallics* **1998**, *17*, 986 – 988; f) A. Y. Sokolov, D. B. Magers, J. I. Wu, W. D. Allen, P. v. R. Schleyer, H. F. Schaefer, III, *J. Chem. Theory Comput.* **2013**, *9*, 4436 – 4443.

[17] a) O. Ermer, *Helv. Chim. Acta* **1991**, *74*, 1339 – 1351; b) J. W. Steed, P. C. Junk, J. L. Atwood, *J. Am. Chem. Soc.* **1994**, *116*, 10346 – 10347; c) S. Kang, T. Umeyama, M. Ueda, Y. Matano, H. Hotta, K. Yoshida, S. Isoda, M. Shiro, H. Imahori, *Adv. Mater.* **2006**, *18*, 2549 – 2552; d) A. Sygula, F. R. Fronczek, R. Sygula, P. W. Rabideau, M. M. Olmstead, *J. Am. Chem. Soc.* **2007**, *129*, 3842 – 3843; e) H. Yokoi, Y. Hiraoka, S. Hiroto, D. Sakamaki, S. Seki, H. Shinokubo, *Nat. Commun.* **2015**, *6*, 8215.

[18] a) Z. Wang, F. Dötz, V. Enkelmann, K. Müllen, *Angew. Chem. Int. Ed.* **2005**, *44*, 1247 – 1250; *Angew. Chem.* **2005**, *117*, 1273 – 1276; b) N. J. Tremblay, A. A. Gorodetsky, M. P. Cox, T. Schiros, B. Kim, R. Steiner, Z. Bullard, A. Satler, W.-Y. So, Y. Itoh, M. F. Toney, H. Ogasawara, A. P. Ramirez, I. Kymissis, M. L. Steigerwald, C. Nuckolls, *ChemPhysChem* **2010**, *11*, 799 – 803.

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