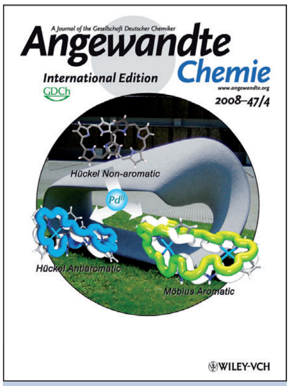
Angewandte
Author Profile

Angewandte Chemie
International Edition

A. Osuka

The author presented here has recently published more than ***50 articles*** *since 2000 in Angewandte Chemie, most recently:*
"Effective meso Fabrications of Subporphyrins": M. Kitano, S. Hayashi, T. Tanaka, H. Yorimitsu, N. Aratani, A. Osuka, *Angew. Chem.* **2012**, *124*, 5691–5695; *Angew. Chem. Int. Ed.* **2012**, *51*, 5593–5597.



The work of A. Osuka has been featured on the inside cover of Angewandte Chemie:
"Metalation of Expanded Porphyrins: A Chemical Trigger Used To Produce Molecular Twisting and Möbius Aromaticity": Y. Tanaka, S. Saito, S. Mori, N. Aratani, H. Shinokubo, N. Shibata, Y. Higuchi, Z. S. Yoon, K. S. Kim, S. B. Noh, J. K. Park, D. Kim, A. Osuka, *Angew. Chem.* **2008**, *120*, 693–696; *Angew. Chem. Int. Ed.* **2008**, *47*, 681–684.

Atsuhiro Osuka

Date of birth:	October 16, 1954
Position:	Professor of Organic Chemistry, Department of Chemistry, Graduate School of Science, Kyoto University (Japan)
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Education:	1973–1978 Undergraduate degree in chemistry, Kyoto University 1978–1979 Master's degree in chemistry, Kyoto University 1982 PhD in Chemistry with Prof. K. Maruyama, Kyoto University
Awards:	**1988** The Chemical Society of Japan Award for Young Chemists; **1999** The Japanese Photochemistry Association Award; **2009** NOZOE Memorial Lectureship at the 13th International Symposium of Novel Aromatic Compounds (ISNA-13) Luxemburg; **2010** The Chemical Society of Japan Award
Current research interests:	After the serendipitious discovery of meso–meso coupled porphyrin arrays and meso-aryl expanded porphyrins, the exploration of novel porphyrinoid molecules has become the primary focus of my research. We have synthesized extremely long porphyrin arrays, extensively π-conjugated porphyrin tapes, large porphyrin wheels, an antiaromatic porphyrin sheet, porphyrin belts, and porphyrin barrels. Meso-aryl expanded porphyrins are fascinating molecules that undergo intriguing metalations, transannular reactions, and splitting reactions. In addition, meso-aryl expanded porphyrins are a nice platform to realize twisted Möbius aromatic and antiaromatic systems. Subporphyrins are smaller congeners of porphyrins but display highly tunable optical properties beyond porphyrins. Porphyrin pincer complexes are also our favorite molecules and are now studied extensively.
Hobbies:	Reading, watching professional Igo (Go) and Shogi (Japanese chess) games

If I were not a scientist, I would be … a painter.

The most significant scientific advance of the last 100 years has been … the Haber–Bosch process for ammonia synthesis.

What I look for first in a publication is … the author's name.

My favorite place on earth is … my hometown Miya, which is a small fishing port surrounded by mountains in the Aichi Prefecture.

My greatest achievement has been … mentoring many talented young students.

The best advice I have ever been given is … to see myself as a young flower capable of blossoming at any time.

I can never resist … looking for nice new restaurants in the city.

When I'm frustrated I … take a walk around the hill near the university or old temples in the city.

My favorite food is … Japanese-modified Italian food in my favorite restaurants.

What originally triggered your interest in porphyrin analogues?

My research on porphyrins started in the field of artificial photosynthesis by making light-harvesting and charge-separation model systems. In these studies, I had been fully responsible for the molecular design and continuously requested my students to synthesize the target molecules by following my designs. In the course of the research on the energy-gap dependence of electron-transfer reactions in collaboration with Prof. N. Mataga of Osaka University, we needed strongly electron-deficient porphyrins. I arbitrarily chose meso-nitroporphyrin and tetrakis(pentafluorophenyl)porphyrin. This collaboration allowed us to find both meso–meso coupled porphyrin oligomers and meso-aryl expanded porphyrins quite accidentally. After that, I changed my research style to look for unexpected compounds or reactions.

Where do you get the inspiration for the design of new macrocycles?

Most of our important molecules were found or made by my students without my inspiration. Thus I have been so fortunate to enjoy chemistry with these talented students. The best way, at least for me, is to keep my students as free as possible so as to think by themselves and not to miss unexpected but important byproducts. Unexpected gifts, which I always want to receive, from the God of Science are very difficult to predict. I really want to know the best way to realize this.

What has been the most gratifying discovery of your career?

The best one is how we came across Möbius aromatic expanded porphyrins. After finding a series of meso-aryl expanded porphyrins, it was strange for me that many students tried to insert various metal ions into the expanded porphyrins without any specific purpose. As a result, many metal complexes accumulated and were left for some time, including Möbius aromatic metal complexes. Regrettably, we published several papers on some complexes without noting Möbius aromaticity. One day, my student Y. Tanaka realized that his complex had distinct Möbius aromaticity.

What was the biggest challenge you had to overcome in your PhD work?

In my PhD work, I studied the photochemistry of epoxy naphthoquinones. Upon photoillumination of an epoxy naphthoquinone in acetone, alkylidene phthalides that contained acetone were produced. But I had no idea about the reaction route to these photoproducts. I decided to monitor the reaction course by HPLC. After a month, I found a peak that rose very rapidly upon photoillumination. This initial cycloadduct was actually isolated in 95% yield by photoillumination for 5 min and its secondary photoreaction could explain the reaction routes to the phthalide products.

What are your thoughts on baseball?

I like to watch professional and high school baseball games. My favorite team in the professional Japanese league is the Chunichi Dragons at Nagoya, and I always cheer for high school baseball teams located in the Aichi Prefecture, since I was born there. I enjoy the super playing in professional games and the unbelievable enthusiasm in high school games. The game of baseball is like a story without a plot, and consists of many plays such as pitches, hits, runs, catches, and throws, among which one or two particular plays may be determinant. It is my hobby to identify such a play in the game.

The interview questions were provided by Daniel Seidel, Rutgers University (USA).

My 5 top papers:

1. "*meso,meso*-Linked Porphyrin Arrays": A. Osuka, H. Shimidzu, *Angew. Chem.* **1997**, *109*, 93–95; *Angew. Chem. Int. Ed. Engl.* **1997**, *36*, 135–137.
   We found this meso–meso coupling reaction accidentally during the preparation of meso-nitroporphyrin. This reaction has since been widely used for creation of various directly connected porphyrin arrays. Besides this, the reaction is important since it is the first demonstration that the oxidation of metalloporphyrins leads to the formation of directly linked porphyrin dimers and oligomers. On the basis of this reaction, my student N. Aratani synthesized a 1024-mer that has remained the longest discrete man-made molecule reported to date.
2. "Fully Conjugated Porphyrin Tapes with Electronic Absorption Bands That Reach into Infrared": A. Tsuda, A. Osuka, *Science* **2001**, *293*, 79–82.
   After the finding of meso–meso linked porphyrin oligomers, we dreamed of long meso–meso, β–β, β–β triply linked porphyrin oligomers (porphyrin tapes) because of their beautiful molecular shape and expected highly conjugated nature. In the meantime, my student A. Tsuda invented the oxidation with DDQ/Sc(OTf)$_3$, hence making our dream come true. The thus-prepared long porphyrin tapes indeed display remarkably red-shifted absorption bands that reach into the infrared.
3. "*meso*-Aryl-Substituted Expanded Porphyrins": J.-Y. Shin, H. Furuta, K. Yoza, S. Igarashi, A. Osuka, *J. Am. Chem. Soc.* **2001**, *123*, 7190–7191.
   In the synthesis of tetrakis(pentafluorophenyl)porphyrin by the Lindsey method, my student J.-Y. Shin found that when both reactants were at a concentration of 67 mM, 10 times the excess recommended for porphyrin synthesis, the reaction led to the formation of a series of meso-aryl expanded porphyrins. These compounds possess intriguing structures, reactivities, coordination behavior, and large two-photon absorption cross-sections.
4. "Tribenzosubporphines: Synthesis and Characterization": Y. Inokuma, J. H. Kwon, M.-C. Yoon, D. Kim, A. Osuka, *Angew. Chem.* **2006**, *118*, 975–978; *Angew. Chem. Int. Ed.* **2006**, *45*, 961–964.
   Subporphyrins are ring-contracted porphyrins consisting of three pyrrole rings and three methine carbon atoms. Despite their simple structures and important position in porphyrin chemistry, they were elusive until our first synthesis. My student Y. Inokuma independently explored the first synthesis of tribenzosubporphines, and confirmed their bowl-shaped structures, 14π-electronic aromaticity, and green fluorescence. This work was followed by the synthesis of meso-aryl-substituted subporphyrins that exhibit variable optical properties depending on the meso-aryl substituents.
5. "Metalation of Expanded Porphyrins: A Chemical Trigger Used to Produce Molecular Twisting and Möbius Aromaticity": Y. Tanaka, S. Saito, S. Mori, N. Aratani, H. Shinokubo, N. Shibata, Y. Higuchi, Z. S. Yoon, K. S. Kim, S. B. Noh, J. K. Park, D. Kim, A. Osuka, *Angew. Chem.* **2008**, *120*, 693–696; *Angew. Chem. Int. Ed.* **2008**, *47*, 681–684.
   Möbius aromaticity was predicted by Heilbronner almost 50 years ago, but its experimental verification had been thought very difficult, since the two conflicting structural elements, namely cyclic conjugation and twisted topology, have to be implemented within a single molecule. Meso-aryl expanded porphyrins have been demonstrated to be an ideal platform to realize Möbius aromatic and antiaromatic molecules. So far, we have synthesized more than 30 Möbius aromatic expanded porphyrins, thus showing that the formation of such porphyrins is not accidental but quite general.

DOI: 10.1002/anie.201203104