

Energy Outlook

International Institute for Carbon-Neutral Energy Research

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CCS Project in Japan to Enter Large-Scale Verification Testing Phase

~ The Current Tomakomai Project and Plans for its Future Development ~

Special Interview

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President, Japan CCS Co., Ltd.

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Lead Principal Investigator,
Associate Professor, CO₂ Storage Division,
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Verification tests for CCS (carbon dioxide capture and storage) in Japan will become fully operational in 2016. A test site was selected from 115 candidate sites nationwide. After various onsite investigations and national review sessions, Tomakomai in Hokkaido got the green light. In 2016, four years after the start of the project, injections of CO₂ into geological formations will begin. With the initial injections scheduled for less than a year away, I²CNER Principal Investigator Takeshi Tsuji sat down with Mr. Shoichi Ishii, the President of Japan CCS Co., Ltd., to find out the current status of the project, and the challenges and future prospects for CCS in Japan.



Shoichi Ishii

President, Japan CCS Co., Ltd.

Mr. Ishii graduated from the Faculty of Economics of Niigata University, and joined Japan Petroleum Exploration Co., Ltd. in 1973. After serving as the Manager of the Finance Department and the General Manager of the Planning Department, Mr. Ishii assumed the posts of Director in 2003, Managing Executive Officer in 2005, Managing Director in 2006, and Executive Vice President in 2014. At Japan CCS Co., Ltd., he has served as President since its establishment in 2008. He plays an active role in the Japanese energy industry, while also serving as President of the Japan Methane Hydrate Operating Co., Ltd. and Fukushima Gas Power Co., Ltd.

CO₂ Injections Are Right Around the Corner

Takeshi Tsuji: The CCS verification project in Tomakomai has entered the countdown phase for the CO₂ injection process, which will start in April 2016. What does this project mean for the future of Japan?

Shoichi Ishii: The 21st Session of the Conference of the Parties to the United Nations Framework Convention on Climate Change (COP21) will be held at the end of 2015 in Paris. At

this conference, participants are expected to decide on measures to prevent global climate change after 2020. Each country has already submitted proposals, and it seems that global recognition for CCS has risen in this milestone year. The timing is ideal, since preparations for CCS verification testing, which may be our “trump card” among the measures against climate change, have entered the final stage in Japan. If this project kicks into gear, the positioning of CCS in Japan will become even clearer.

Tsuji: Have the preparations been going smoothly so far?

Ishii: Monitoring facilities, including three observation wells, are almost completed. The digging for one injection well has also been finished. In March 2015, we started digging the second well, targeting a total depth of 3,500 meters. We will store CO₂ in the layer 1,100 meters below the surface of the earth, and we have already dug to a depth of approximately 1,400 meters. The facilities on land are going up fast, and are scheduled to be put into trial operation in the second half of fiscal 2015.

Tsuji: The project is now in the phase just before the start of the injections. I imagine you overcame a variety of challenges to get to this point.

Ishii: Yes, we have. In particular, after the Great East Japan Earthquake, public opinion regarding CCS changed dramatically. It cannot be helped that the issue of faults attracts a lot of attention in Japan, considering how many earthquakes we have. So first, we selected a storage site in an area that is free of faults, and confirmed that a shielding layer exists over the storage layer. Another point we must always consider is the need for local consent. In Tomakomai, we received support from the locals.

I²CNER's Role in Promoting CCS

Tsuji: I²CNER has three divisions related with CCS: the CO₂ Storage Division, the CO₂ Capture and Utilization Division and the Energy Analysis Division. What kind of research do you think we should pursue when considering the promotion of CCS?

Ishii: I have been engaged in oil resource development for over 40 years. However, I am not an engineer. I specialize in managerial matters. What I want to emphasize here, especially from my years of experience, is that there are differences between ground-based structures and underground structures.

Tsuji: Of course, we understand there are large differences between structures above and under the ground. But what specifically do you mean by that?

Ishii: Consider the influence an earthquake has underground. Large transportation pipelines for petroleum and natural gas are laid at a depth of 1.5 meters underground. This is the case with the pipelines connecting Niigata and Sendai. Do you know how they were affected by the Great East Japan Earthquake?

Tsuji: I heard they had almost no damage.

Ishii: Correct. That's why the gas supply in Sendai City recovered with such extraordinary speed after the disaster. When the Great Hanshin-Awaji Earthquake took place, gas lines suffered almost no damage in that case, as well. As for CCS, when the Niigata Prefecture Chuetsu Earthquake occurred, there were no accidents or any other problems in any plant in Nagaoka.

Tsuji: It is true that the shaking caused by an earthquake affects the areas above ground and underground very differently.

Ishii: Indeed, the same seismic intensity has a completely different effect above ground and underground. During the Great East Japan Earthquake, above-ground gas storage tanks located in one port were destroyed by the tsunami and the whole surrounding area was in flames. So the question is, if a CCS site is hit by an earthquake, what are the chances of underground CO₂ leakage? Although people generally worry



Takeshi Tsuji

Lead Principal Investigator,
Associate Professor, CO₂ Storage Division,
International Institute for Carbon-Neutral Energy Research (I²CNER),
Kyushu University

Prof. Tsuji completed his doctoral course in the Graduate School of Science at the University of Tokyo in 2007. After serving as an Assistant Professor at Kyoto University from 2007-2012, he assumed his post at I²CNER in 2012. Prof. Tsuji currently holds research positions at the Japan Agency for Marine-Earth Science and Technology and Stanford University as a Visiting Research Scholar and a Co-Chief Scientist in the International Ocean Discovery Program, respectively. Prof. Tsuji is pursuing research in a wide range of fields, covering everything from the earth to the universe, and leading cross-divisional interdisciplinary research on underground CO₂ storage as a Lead Principal Investigator at I²CNER. Prof. Tsuji is currently focused on the estimation of underground mechanics and physical properties, the development of monitoring technology, and the elucidation of multiphase flow behaviors.

about what will happen after such leakage, the fact is that no gas from an underground natural gas field has leaked for over 1,000 years. To help people better understand the situation, I expect that researchers will compare and verify the relative ratio of leaks from tanks that sustain damage above ground with leaks of CO₂ from underground CCS sites, for example.

Tsuji: Using all the information available, we need to consider carefully what would happen if highly concentrated CO₂ were to leak.

Ishii: Exactly. In the first place, we all exhale CO₂ into the air on a daily basis. Considering this, it makes no sense to look at a CCS site in the same way we look at a treatment plant for toxic materials, for example. This is a common misunderstanding. I also expect that research into using CO₂ as an energy source will be promoted, which will cause the public to view it in a more positive light, rather than just as a cause of climate change.

The Shift from CCS to CCU

Tsuji: It may be a little too early to talk about at this point, but how do you think CCS will develop in Japan after the Tomakomai Project?

Ishii: While the experiment in Nagaoka was a 10,000-ton project, it is expected that one plant will store a million tons per year during the practical stage around 2020. For the future, we need to find an appropriate site that can handle 100 million tons of storage per year, and sort out the technological challenges and operational issues we face. If we reach the 100 million ton level, we may be able to use CCS to manage approximately 10% of Japan's CO₂ emissions.

Tsuji: Realistically, when do you think this might be?

Ishii: Our experiment at the 10,000-ton level in Nagaoka was in 2003. Only ten years after that, we have come to a verification test stage where we can scale it up to the 1 million ton level, 100 times greater in approximately 10 years. Taking future technological progress into consideration, we see a strong possibility that storage at the 100 million ton level will be realized within ten years - or even seven or eight if all goes smoothly.

Tsuji: To ensure the success of CCS, we need to solve the problem of cost. For example, if a joint crediting mechanism is established, it might be possible for private corporations to initiate a CCS project.

Ishii: From a global viewpoint, CCS is positioned as an EOR (enhanced oil recovery) facility that can deal with the increased production of petroleum and natural gas. However, it will be tough to introduce this idea into Japan without large gas fields. As for the cost issue, one of the ideas is to fundamentally change the way we view CO₂.

Tsuji: To be more specific, you are talking about CCU (carbon dioxide capture and utilization), right?

Ishii: Yes. CO₂ can be a valuable resource. To cite one example, a company in Tomakomai has already started tri-generation. Cogeneration refers to combined heat and power. They separate and collect CO₂ from emissions and use it for hydroponic agriculture. They say increasing CO₂ concentration in the air facilitates plant growth.

Tsuji: Regarding another use for CO₂, artificial photosynthesis shows a lot of promise. With this, CO₂ could become a new, revolutionary energy source.

Ishii: If that happens, I think private companies will be more enthusiastic about storing CO₂. The meaning of CCS would

also change dramatically, and it would then be considered an asset to have a huge CO₂ reserve underground. We will be able to open a valve to draw CO₂ when necessary and use it to generate energy via artificial photosynthesis, or use it to help make petroleum products.

Tsuji: In addition to the achievements in monitoring research for the verification test, underground storage technology used for other research themes seems useful.

Ishii: In the longer term, we may be able to use bacteria to turn CO₂ into methane gas. This is exciting, but I think the priority should be looking for a site to store large amounts of CO₂, and a way to conduct less costly CCS.

The Power of I²CNER's Young People

Tsuji: Just a few years ago, nobody imagined that CCS could be an energy storage facility. Changes in the energy field have been incredibly fast. What do you expect lies ahead for young people who want to contribute to this field?

Ishii: First of all, I want young people to keep in mind that graduating from a university is only one step in the process. The roles they will need to play in their 30s and 40s may be quite different. In order to respond to current circumstances appropriately, it is necessary to pay close attention to ever-changing world affairs and the economic situation.

Tsuji: Public opinion regarding CCS has changed greatly.

Ishii: People used to say CCS was out of the question, because they believed it would trigger an earthquake. However, now CCS is attracting attention both at home and abroad, and is better understood by the local

community.

Tsuji: Another challenge is to further promote national recognition of CCS.

Ishii: The verification tests will start soon, with various challenges to be overcome. We must achieve tangible results and an annual storage level of 100 million tons as soon as possible. This process will surely require young and abundant intellectual power. I hold out much hope for the power of the young people within I²CNER.



Special
Interview



1 The study of heterogeneous two-phase flow around small-scale heterogeneity in porous sandstone by measured elastic wave velocities and Lattice Boltzmann Method simulation

Keigo Kitamura, Fei Jiang, Albert J. Valocchi, Shun Chiyonobu, Takeshi Tsuji and Kenneth T. Christensen

Journal of Geophysical Research: Solid Earth
DOI: 10.1002/2014JB011281

It is revealed that two-phase fluid flow (CO₂ and water) is strongly controlled by the small-scale heterogeneity of porous sandstone by the measurement of elastic wave velocity on the sub-core scale (mm-cm) and the two-phase fluid flow simulation based on the Lattice Boltzmann Method (LBM) on the pore-scale (nm- μ m). The lamina is a typical small-scale heterogeneity in the porous sandstone and has a smaller pore-size distribution than the surrounding porous zone. This study indicates that CO₂ cannot go through this lamina-rich zone in water-saturated porous sandstone with lamina structure. This restrictive CO₂ flow around the lamina-rich zone is caused by the gap of pore pressure. These results indicate that we can monitor pore scale CO₂ behavior from outside of the sample using geophysical methods. This study also indicates that small-scale heterogeneity has the potential to be a sub-seal in CO₂ reservoirs and to increase the integrity of CO₂ storage.

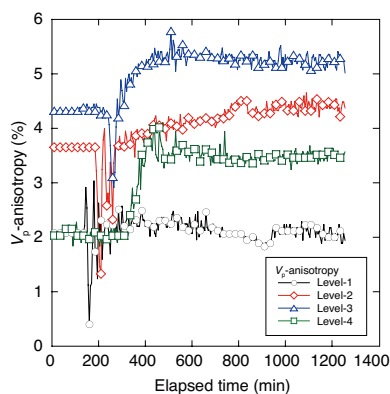


Fig. 1
The changes of V_p anisotropy with increasing CO₂ injection time. V_p -anisotropies of lower two-levels (Level-1 and 2) indicate no large changes but upper two-levels clearly point out the increasing of the V_p -anisotropies. This result implies that there is anisotropic CO₂-flow above the level-3.



Fig. 2
The result of a CO₂ flow simulation based on LBM. Anisotropic CO₂ flow is simulated in the porous model with slit-like structure, which has different pore-size distributions between the slit and the other part.

2 A compatible crosslinker for enhancement of CO₂ capture of poly (amidoamine) dendrimer-containing polymeric membranes

Ikuo Taniguchi, Teruhiko Kai, Shuhong Duan, Shingo Kazama and Hiroshi Jinnai

Journal of Membrane Science
DOI: 10.1016/j.memsci.2014.10.015

Membrane separation is a promising technology in CO₂ capture. Poly(amidoamine) (PAMAM) shows high specificity to CO₂, and PAMAM immobilized cross-linked PEG membranes exhibit excellent CO₂ separation performance over H₂. The PAMAM membranes are applicable for CO₂ capture at an IGCC plant, under elevated, high pressure CO₂ permeance (100 GPU). The PAMAM membranes have a macrophase-separated structure between PAMAM and PEG matrix, and do not work under pressure. A newly developed compatible cross-linker gives pressure tolerance and suppresses the phase separation. As a consequence, the membrane thickness can be reduced down to 10 μ m, and the CO₂ permeance under pressure is increased by 200 times (2.2 GPU), which can be further enhanced by additives or optimization of the membrane structures. The developed membranes are also used for CO₂ free H₂ generation in the CH₄-steam reforming process.

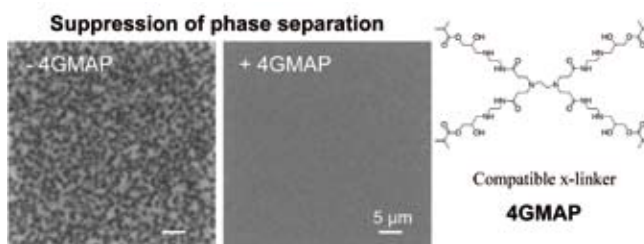


Fig. 1
Chemical structure of a compatible cross-linker, 4GMAP and confocal microscope images of PAMAM membranes with/without 4GMAP

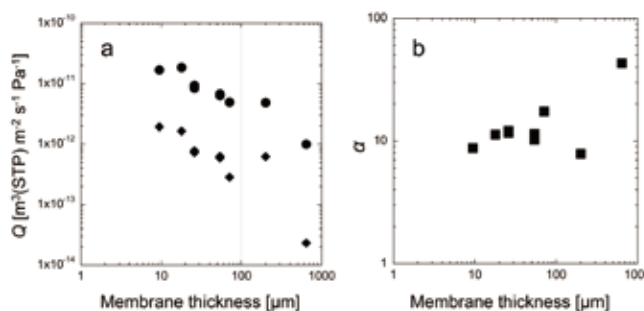


Fig. 2
Effect of the membrane thickness on the CO₂ separation properties of PAMAM dendrimer-containing polymeric membranes at 313 K and 90 % relative humidity under 0.56 MPa of $p(\text{CO}_2)$ and 0.70 MPa of total pressure; a) circle: CO₂ permeance; diamond: H₂ permeance; b) cube: CO₂/H₂ selectivity; PAMAM dendrimer/PEGDMA/4GMAP=50/42.5/7.5 by wt.



3

Effect of ambient pressure on Leidenfrost temperature

Daniel Orejon, Khellil Sefiane and Yasuyuki Takata

Physical Review E, Volume 90 Issue 5, 053012 (2014)
DOI: 10.1103/PhysRevE.90.053012

The precise prediction and control of the interactions of liquids with hot surfaces is paramount in numerous applications, such as cooling or liquid manipulation. Depending on the temperature of the substrate, three different regimes can be clearly identified; wetting, transition and levitating regime (Leidenfrost), as shown in Fig. 1. Moreover, mentioned physical interactions between the droplet and the substrate were found to be dependent on pressure. In this communication, we introduce a unifying theory for the dependence of Leidenfrost temperature, T_L , on system pressure. This physical approach is based on an analogy with the Clausius-Clapeyron equation: $1/T_L$ versus $\log_{10}[P]$, as presented in Fig. 2. Being able to induce and predict the Leidenfrost phenomenon at low temperatures makes the use of this phenomenon more practical and at reduced energetic costs with the consequent decrease in CO₂ emissions.

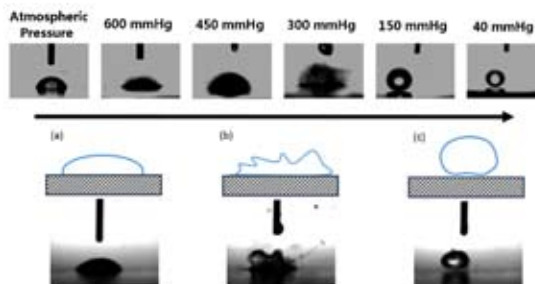


Fig. 1 Snapshots of the droplet deposited on a heated substrate at different pressures; (a) wetting, (b) transition and (c) levitating regimes.

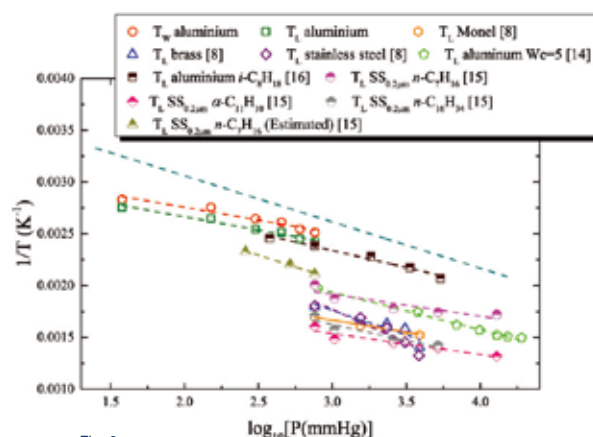


Fig. 2 Experimental results and linear trends as $1/T_L$ versus $\log_{10}[P]$.

4

Strongly coupled thermal and chemical expansion in the perovskite oxide system Sr(Ti,Fe)O_{3-α}

Nicola H.Perry, Jae Jin Kim, Sean R.Bishop and Harry L.Tuller

Journal of Materials Chemistry A
DOI: 10.1039/C4TA05247A

The operating lifetime of efficient, fuel-flexible solid oxide fuel cells is limited, in part, by mechanical failure of the brittle oxides, caused by thermo-chemical expansion-induced stresses. We therefore seek to identify factors controlling chemical expansion in perovskite oxides, using both *in situ* experiments and atomistic simulations. In the present paper, we 1) provide the first comprehensive measurements of coefficients of chemical expansion (CCEs) in the emerging electrode material Sr(Ti,Fe)O_{3-α}, 2) uncover strong coupling between thermal and chemical expansion: thermal expansion coefficients are higher for lower oxygen contents, and CCEs are higher at higher temperatures, and 3) confirm our earlier results, showing that charge delocalization on multivalent cations correlates to significantly lower CCEs. This work thus develops some of the first design principles for low chemical expansion perovskites.

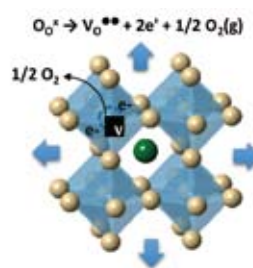


Fig. 1 Reduction process in a perovskite oxide leading to chemical expansion. Electrons formed often localize on multivalent cations, causing them to enlarge.

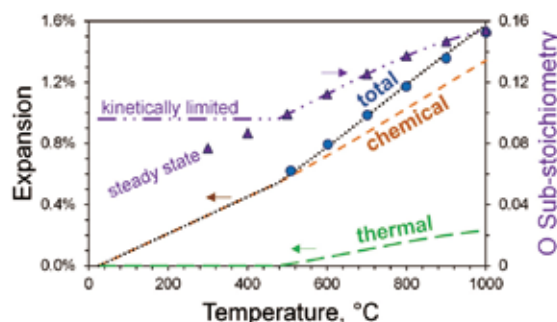


Fig. 2 Comprehensive measurements of oxygen content, iso-thermal coefficients of chemical expansion, and iso-stoichiometric coefficients of thermal expansion enables the fitting shown in the figure. Here the total thermo-chemical expansion taking place upon heating in air can be modeled fully, separating the strongly coupled thermal and chemical expansion contributions.

5

Absorption kinetics and hydride formation in magnesium films: Effect of driving force revisited

Helmut T. Uchida, Stefan Wagner, Magnus Hamm,
Jochen Kürschner, Reiner Kirchheim,
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Magnesium is a light metal and it absorbs two hydrogen atoms per metal atom, leading to a higher density than in liquid hydrogen. This makes magnesium a favorable storage medium, as needed in mobile applications like in fuel cell cars, where weight and capacity of the storage devices play a crucial role. Unfortunately, the use of magnesium for hydrogen storage is hindered by a slow reaction rate. In the present study, it was shown that a high density of grain boundaries in magnesium is favorable for higher rates, because MgH_2 , which inhibits hydrogen transport, is not generated there. The blocking effect of MgH_2 can also be reduced by decreasing the driving force during absorption. This unusual result is explained by the formation of less hydride nuclei at low driving forces, which favors an in-depth growth of the hydride before the hydride regions coalesce to a blocking layer. Knowing the kinetics of hydride formation will enable us to develop magnesium alloys with a higher efficiency for energy storage, especially for storing excess energy produced by renewable energy sources, such as solar and wind energy.

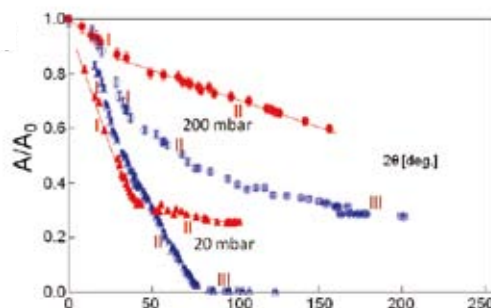


Fig. 1 It shows the fraction of the magnesium surface A/A_0 not covered by MgH_2 as a function of the square root of hydriding time for Mg-films of thickness $2.8 \mu\text{m}$ (red symbols) and $0.5 \mu\text{m}$ (blue symbols) being exposed to gaseous hydrogen of 20 and 200 mbar corresponding to a lower (triangles) and higher (circles) driving force for hydride formation.

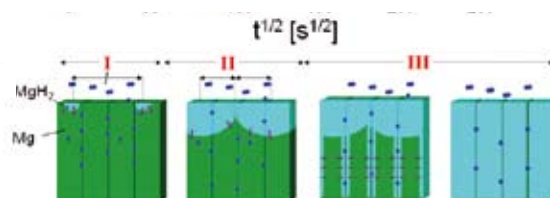


Fig. 2 It shows the three stages of hydride (light blue MgH_2) formation by nucleation and growth (stage I), coalescence of hydride regions (stage II), further fast transport along grain boundaries until total transformation (stage III). Grain boundaries are shown as vertical lines and hydrogen atoms as dark blue dots.

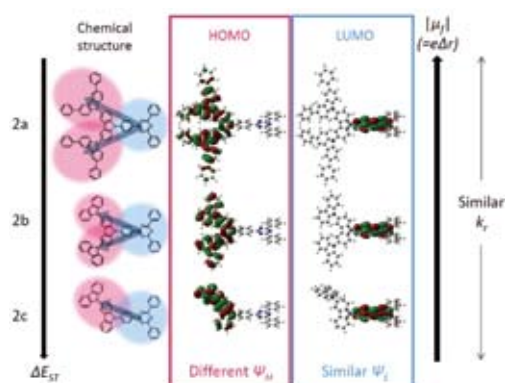
6

Highly efficient blue electroluminescence based on thermally activated delayed fluorescence

Shuzo Hirata, Yumi Sakai, Kensuke Masui, Hiroyuki Tanaka, Sae Youn Lee,
Hiroko Nomura, Nozomi Nakamura, Mao Yasumatsu, Hajime Nakanotani, Qisheng Zhang, Katsuyuki Shizu,
Hiroshi Miyazaki and Chihaya Adachi

Nature Materials
DOI: 10.1038/nmat4154

Organic compounds that exhibit highly efficient, stable blue emission are required to realize inexpensive organic light-emitting diodes (OLEDs) for future displays and lighting applications. Here, we define the design rules for increasing the electroluminescence efficiency of blue-emitting organic molecules that exhibit thermally activated delayed fluorescence. We show that a large delocalization of the highest occupied molecular orbital and lowest unoccupied molecular orbital in these charge-transfer compounds enhances the rate of radiative decay considerably by inducing high oscillator strength, even when there is a small overlap between the two wave functions. A compound based on our design principles exhibited a high rate of fluorescence decay and efficient up-conversion of triplet excitons into singlet excited states, leading to both photoluminescence and internal electroluminescence quantum yields of nearly 100%. Our result will contribute to energy conservation in society by saving energy in display and lighting applications. Also, our scientific result will provide a guideline for high efficiency photo-electron conversion processes, such as organic solar cells.



Chemical structures and distribution of HOMO and LUMO showing TADF activity. Our molecular design clarifies the compatibility of large oscillator strength and small (DEST). Optimized structures of the HOMO and LUMO were calculated by TD-DFT (Gaussian09/B3LYP/6-31G(d)).