

Research Projects of Tani's Group

1. Synthesis and photoelectronic properties of novel polycyclic pi-electron compounds

Aromatic diimide compounds such as naphthalene diimide (NDI) and perylene diimide (PDI) have attracted much attention as electron acceptors, n-type semiconductors, chromophores in visible region and building blocks of supramolecular architectures. Besides NDI and PDI, tetracene diimide (TDI) is also expected to exhibit intriguing electronic and photophysical properties since TDI possesses linearly extended π -conjugated system. However,

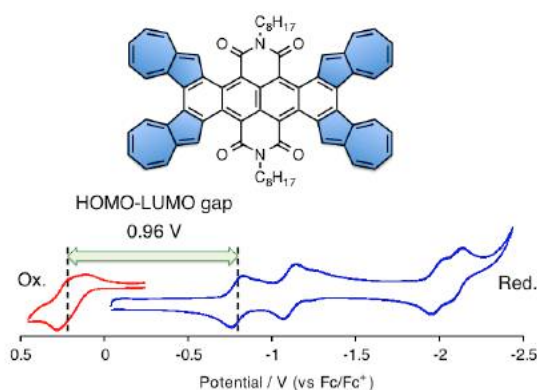


Figure 1) Chemical structure of **TA-fused TDI** and its cyclic voltammogram (CV)

there have been only limited TDI derivatives reported in a few papers. Herein, we have designed a further π -extended TDI by fusing azulene as a 10π -conjugating unit. Azulene is a unique molecule, which has a dipole moment of about 1.08 D along the C2-C6 axis to afford electron-donating five-membered ring and electron-withdrawing seven-membered ring. Hence, bonding of five-membered ring of azulene to a diimide core is anticipated to realize effective donor-acceptor interaction and π -extension, leading to a smaller HOMO-LUMO gap and characteristic photophysical and electronic properties. **TA-fused TDI** exhibited four reversible one-electron reduction processes at -0.77 , -1.08 , -1.97 , -2.12 V versus the Fc/Fc^+ with a remarkable small HOMO-LUMO gap (0.96 eV). Absorption spectrum of **TA-fused TDI** exhibited intense absorption bands at 343, 410, 426, 600, 651 nm derived from TDI skeleton, and a broad low-energy band centered at 946 nm. The edge of the lowest-energy absorption band reached *ca.* 1400 nm corresponding to the energy gap of 0.89 eV, which is in good agreement with the electrochemical HOMO-LUMO gap. The Two-photon absorption (TPA) cross-section of **TA-fused TDI** was determined to be $\sigma^{(2)} = 2140$ GM at 950 nm ($1 \text{ GM} = 10^{-50} \text{ cm}^4 \text{ s photon}^{-1} \text{ molecule}^{-1}$). The

electron mobility of a thin film of **TA-fused TDI** prepared on an ITO /glass substrate was revealed to be $\mu = 1.7 \times 10^{-4} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ by space charge limited current (SCLC) method.

[1] T. Koide, M. Takesue, T. Murafuji, K. Satomi, Y. Suzuki, J. Kawamata, K. Terai, M. Suzuki, H. Yamada, Y. Shiota, K. Yoshizawa, F. Tani, **Chem Plus Chem**, **2017**, *82*, 1010-1014.

2. Photochemical energy conversion based on supramolecular assemblies of porphyrin and fullerene

We have prepared nickel complexes and free-bases of cyclic porphyrin dimers linked by butadiyne or phenothiazine groups. The porphyrin dimers have self-assembling pyridyl groups at the opposite *meso* positions and include fullerenes such as C_{60} , PCBM, C_{70} and $\text{Li}^+@C_{60}$ to give π -complexes. In particular, the phenothiazine-bridged cyclic porphyrin dimers exhibit notable high affinities toward C_{60} ($K_{\text{assoc}} > 10^6 \text{ M}^{-1}$) and C_{70} ($K_{\text{assoc}} > 10^7 \text{ M}^{-1}$). In the crystal structures, the π -complexes of C_{60} and PCBM within the butadiyne-bridged nickel dimer and the phenothiazine-bridged free-base dimer afford self-assembled porphyrin nanotubes containing the linear arrays of the fullerenes. These self-assemblies are formed by the $\text{C-H} \cdots \text{N}$ hydrogen bonds and π - π interactions of the *meso* pyridyl groups. On the other

hand, the π -complexes of C_{60} and C_{70} within the butadiyne-bridged free-base dimer gave the zigzag chains of the fullerenes through van der Waals contacts with each fullerene. These well-ordered C_{60} arrays yield high electron mobilities

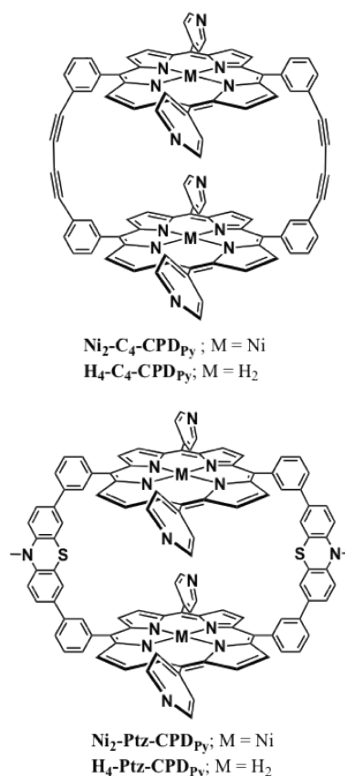


Figure 2 Cyclic porphyrin dimers

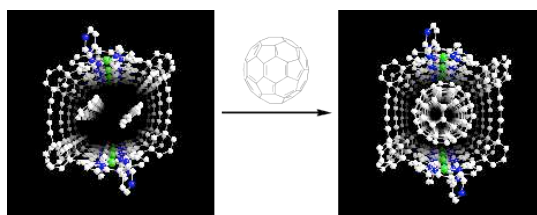


Figure 3) Porphyrin nanotube and C_{60} in porphyrin nanotube

($\Sigma\mu > 10^{-1} \text{ cm}^2\text{V}^{-1}\text{s}^{-1}$). The π -complexes of C_{60} and $\text{Li}^+\text{@C}_{60}$ within the butadiyne-bridged dimers perform photoinduced electron transfer from the porphyrins to the fullerenes to give the CS states. The π -complexes of $\text{Li}^+\text{@C}_{60}$ with

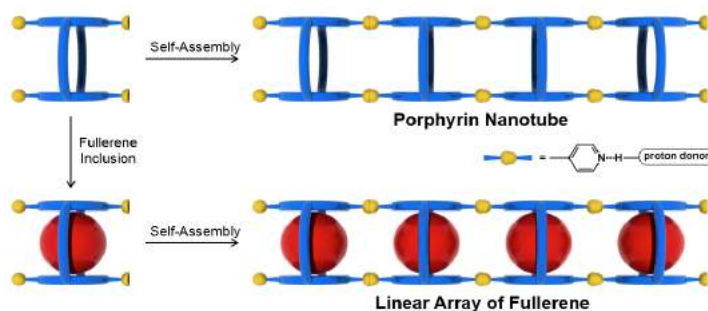


Figure 4 Formation of self-assembled porphyrin nanotube and linear array of fullerene

the butadiyne-bridged dimers afford the CS states of remarkably long lifetimes reaching submillisecond order.

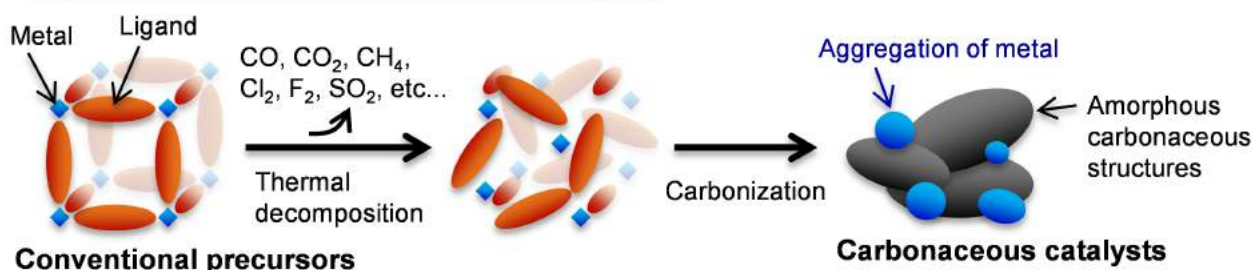
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3. Development of new carbon materials made from organic molecular crystals

We have developed a new synthesis route for alternative catalysts of noble metals for versatile chemical reactions that could help address environmental concerns.

Noble metals such as platinum are useful as catalysts for versatile chemical

(a) Conventional carbonaceous catalysts



(b) This work

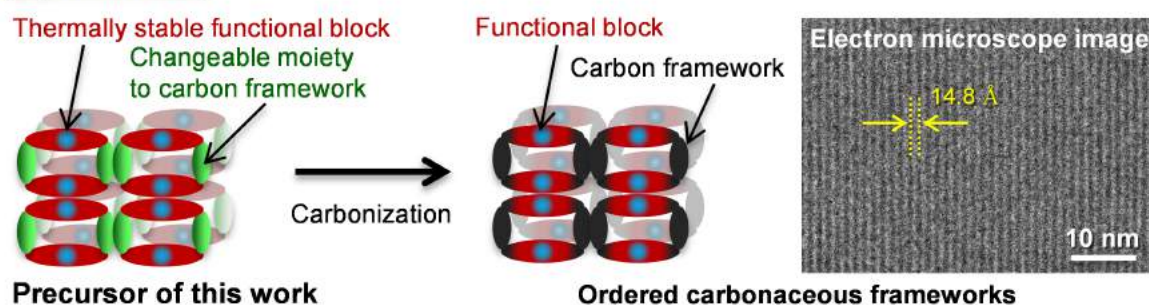


Figure 5 Synthesis schemes of (a) conventional carbonaceous catalysts and (b) this work for ordered carbonaceous frameworks.

reactions including fuel cell vehicles and reduction of CO₂ emission. However, they are too costly to be used for these purposes.

As inexpensive alternatives, organic-based catalysts and carbonaceous catalysts were explored, but were ultimately found to be impractical. This was because organic-based catalysts tend to be active but unstable, while carbonaceous catalysts are stable but less active.

In this work, we have found a solution by developing a new synthesis route for intermediate materials of organic-based catalysts and carbonaceous catalysts. While conventional carbonaceous catalysts have amorphous carbonaceous structures that cause a decline in catalytic activities (Figure 5a), the new synthesis route enables the formation of carbonaceous catalysts with controlled chemical structures like organic-based catalysts (Figure 5b). This synthesis route is capable of developing alternative catalysts of noble metals for many eco-friendly technologies such as fuel cell vehicles, hydrogen generation from water and CO₂ reduction.

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