Tomoya Nakamura

Templated Assembly of Photoswitches Significantly Increases the Energy-Storage Capacity of Solar Thermal Fuels

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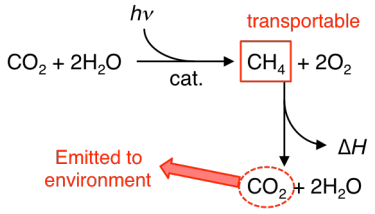
1. Introduction

1-1. Solar thermal batteries: storing solar energy as chemical potential

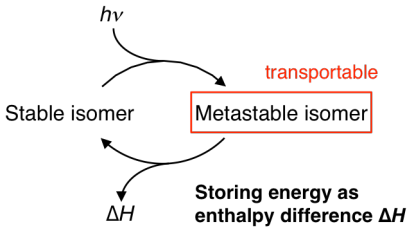
➢ Utilization of solar energy (largest source of renewable energy) →**Need of energy storing technique**

(a) Generation of conbustible fuels



×Not cyclable: emission of CO_2

(b) Solar thermal battery



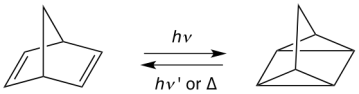
✓Cyclable: emission-free

Figure 1. Two approaches for solar energy storage.

➔ **Solar thermal battery is a promising candidate for solar energy storage**

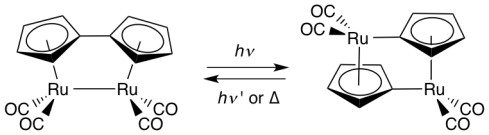
1-2. Conventional approaches for solar thermal batteries

(a) Norbornadiene-quiadricyclane



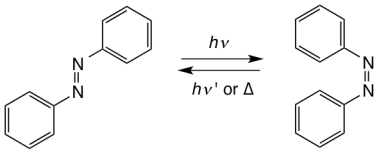
×Degradation in only a few cycles

(b) Tetracarbonyl-diruthenium fulvalene



×Rare and expensive Ru

(c) Azobenzene



✓Low cost and high cyclability

×Small Δ*H* and short storage lifetime

Figure 2. Chromophores previously studied as solar fuels.[1]

➔ **How to increase Δ*H* and storage lifetime?**

1-3. This work: new approach for increasing Δ*H* and storage lifetime

Author's Concept (Figure 3)

Templating photoswitches to nanostructures →Increasing steric restriction →Increasing Δ*H* and thermal stability

✓ Tuning of Δ*H* and storage lifetime without changing photochemical parameters

✓ Applicable to various combinations of photoisomer and template materials

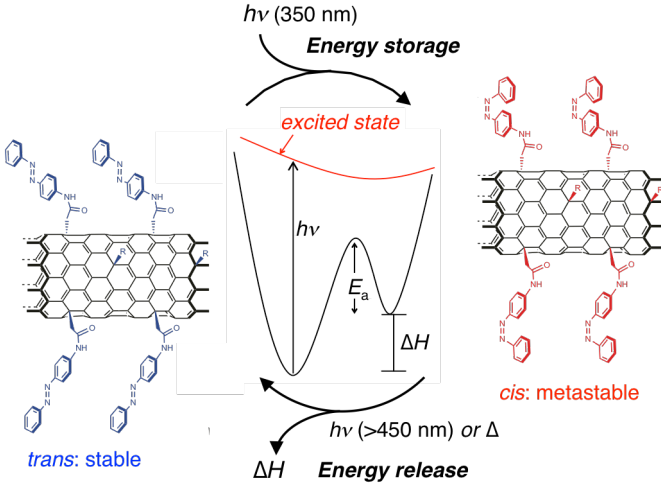


Figure 3. Concept of templating azobenzene to SWCNT.

- Azo-SWCNT as initial proof-of-principle

  ＊Computational modeling[2]

  →30% increase of ΔH with a functionalization densities of 1/8

  (one azobenzene for every eight SWCNT carbon atoms)

2. Results and Discussion

2-1. Synthesis and characterization

(i) Synthesis (Figure 4)

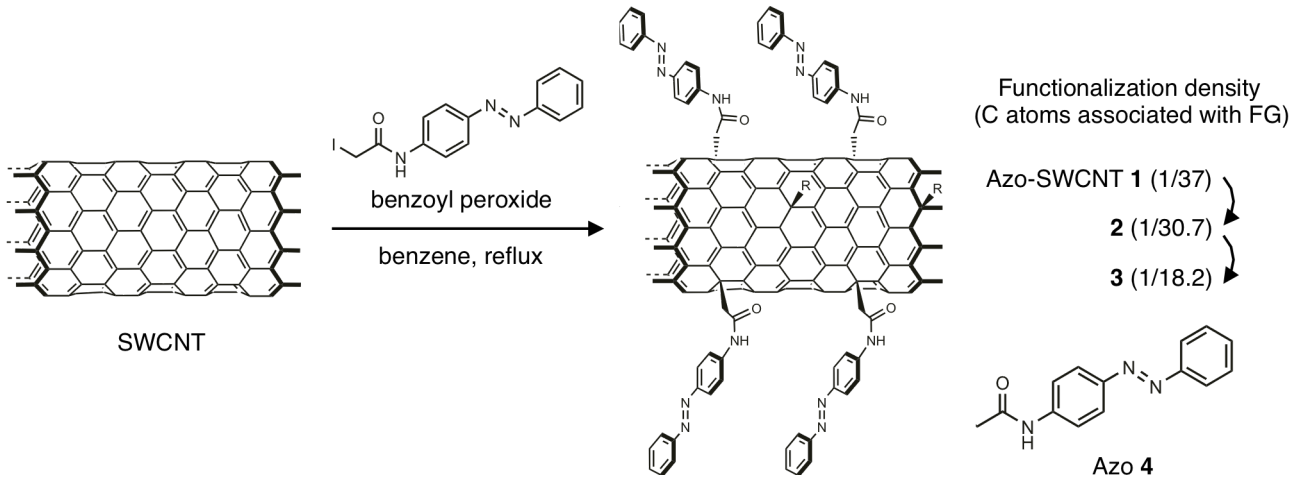


Figure 4. Functionalization of SWCNT.

- Direct functionalization of SWCNT with amide-linked azobenzene via radical process

  ➔ Repeating the process three times to achieve high functionalization density (1/18.2 for Azo-SWCNT **3**)

(ii) Characterization (Figure 5)

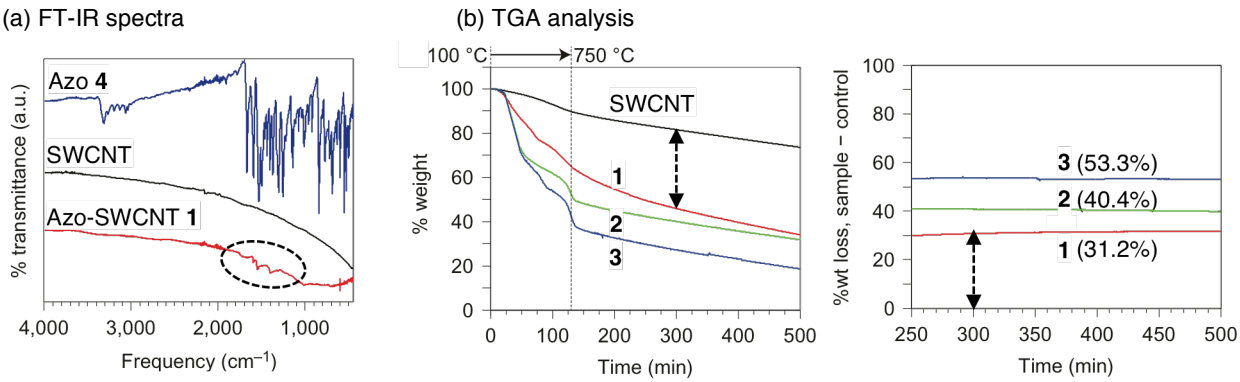


Figure 5. Characterization of Azo-SWCNT.

- FT-IR →C=O stretch, N-H bend, and N=N stretch by comparison to Azo **4**.
- TGA →Estimation of functionalization density by fractional mass loss on heating to 750 °C

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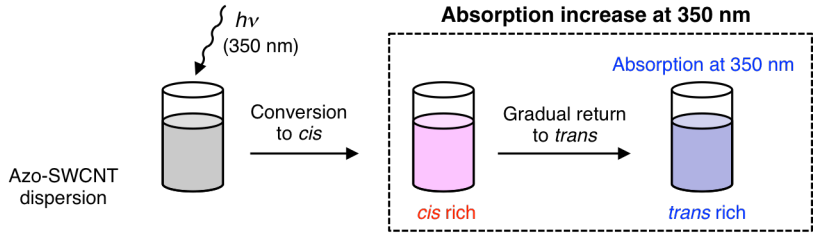
2-2. Photoisomerization and thermal isomerization

(i) In dilute dispersion (Figure 6)

(a) Experimental procedure



(b) Time-resolved UV-vis spectra

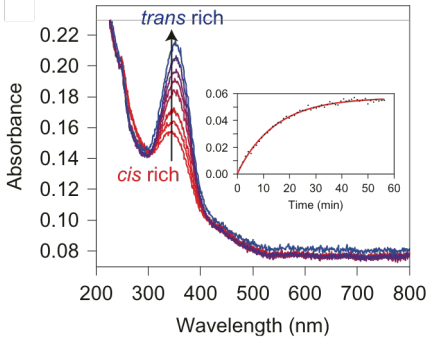


Figure 6. Isomerization process of Azo-SWCNT **3** in dilute dispersion.

- Monoexponential kinetics
  - ➔Activation parameters: no change

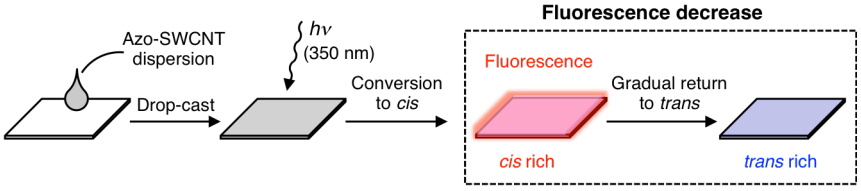
    Azo-SWCNT **3**: $\Delta H^{\ddagger} = 90$ kJ mol^{-1}, $\Delta S^{\ddagger} = -45$ J mol^{-1}K^{-1}

    Azo **4**: $\Delta H^{\ddagger} = 92$ kJ mol^{-1}, $\Delta S^{\ddagger} = -41$ J mol^{-1}K^{-1}
  - ➔**No inter-SWCNT interaction in dilute dispersion** (Figure 7)

Figure 7. Intertemplate interactions in dilute dispersion.

(ii) In solid state (Figure 8)

(a) Experimental procedure



(b) Time-resolved fluorescence spectra

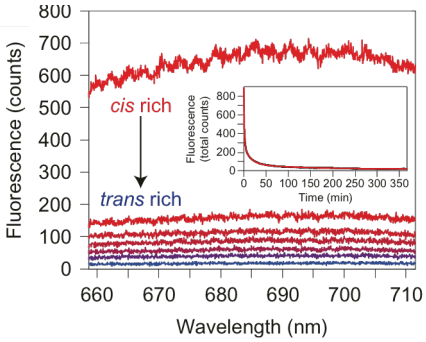


Figure 8. Isomerization process of Azo-SWCNT **3** in solid state.

- Not monoexponential kinetics
  - ➔ Estimation of activation parameters: impossible
- Increased *cis* form lifetime: increased storage lifetime
  - ➔**Interaction between neighboring functionalized templates** (Figure 9)

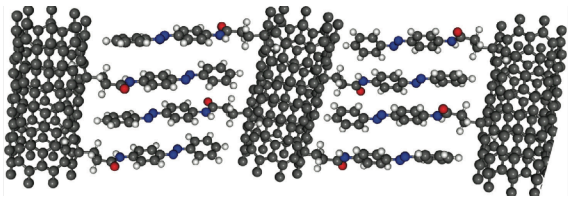


Figure 9. Intertemplate interactions in solid state.

2-3. Energy storage

- Cyclability of energy storing and releasing (Figure 10)

(a) Cycling by 350 nm and >450 nm irradiation (1,890 cycles) (b) Cycling by 350 nm irradiation and dark at 75 °C (210 cycles)

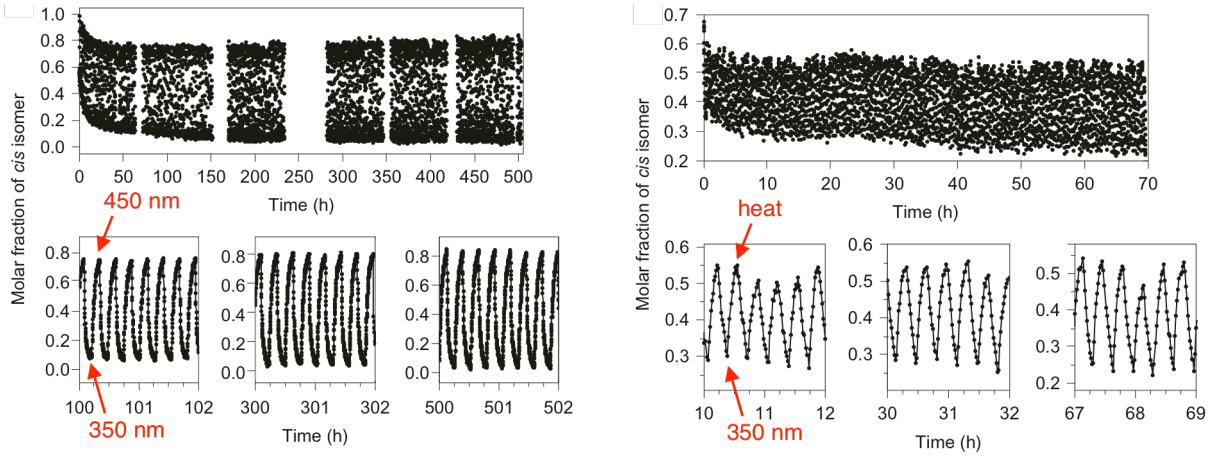


Figure 10. Photochemical and thermal cycling of Azo-SWCNT **3**.

➔ **Robust cyclability without any degradation**

- Estimation of energy density ΔH (by DSC)

  Azo **4**: $\Delta H_{cis\text{-}trans} = 58$ kJ mol^{-1}

  Azo-SWCNT **3**: $\Delta H_{cis\text{-}trans} = 120$ kJ mol^{-1}

  ➔ **Increase of ΔH by more than 200%**

- Origin of the increased $\Delta H_{cis\text{-}trans}$?

  ➔ *Cis* isomer being more conformationally restricted than *trans* isomer (Figure 11).

- Energy-storage efficiency

  14% (under 350 nm irradiation)

  0.3% (under AM1.5 irradiation)

(a) All-*trans* configuration (b) All-*cis* configuration

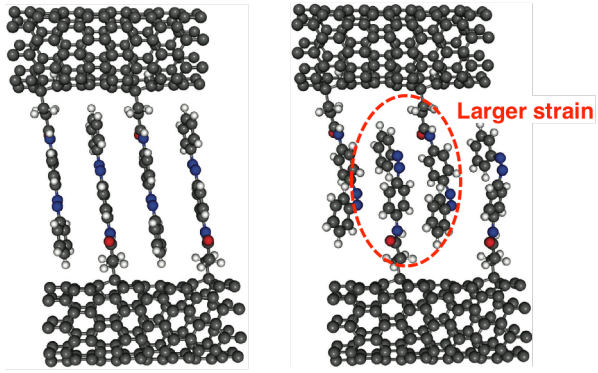


Figure 11. Packing structure in the solid state.

3. Conclusion

- Proof-of-principle for the approach of achieving high energy density by templating photoswitches to nanostructures
- Increase of energy density by more than 200% and storage lifetime by orders of magnitude due to the enforced conformational restriction
- Potential for further improvement by optimizing chromophore-template combination

4. References

(1) Kucharski, T. J.; Tian, Y.; Akbulatov, S.; Boulatov, R., *Energy Environ. Sci.*, **2011**, *4*, 4449–4472.

(2) Kolpak, A. M.; Grossman, J. C., *Nano Lett.* **2011**, *11*, 3156–3162.