

Controlled Orientations of Neighboring Tetracene Units by Mixed Self-Assembled Monolayers on Gold Nanoclusters for High-Yield and Long-Lived Triplet Excited States through Singlet Fission

Toshiyuki Saegusa,[†] Hayato Sakai,[†] Hiroki Nagashima,[‡] Yasuhiro Kobori,^{*,‡,◇}
Nikolai V. Tkachenko,^{*,§} and Taku Hasobe^{*,†}

[†]Department of Chemistry, Faculty of Science and Technology, Keio University, 3-14-1 Hiyoshi, Kohoku-ku, Yokohama, Kanagawa 223-8522, Japan

[‡]Molecular Photoscience Research Center, Kobe University, 1-1 Rokkodai-cho, Nada-ku, Kobe 657-8501, Japan

[◇]Department of Chemistry, Graduate School of Science, Kobe University, 1-1, Rokkodai-cho, Nada-ku, Kobe 657-8501, Japan

[§]Chemistry and Advanced Materials Group, Faculty of Engineering and Natural Sciences, Tampere University, Korkeakoulunkatu 8, FI33720 Tampere, Finland

DOI: [10.1021/jacs.9b06567](https://doi.org/10.1021/jacs.9b06567)

Cite this article: *J. Am. Chem. Soc.* 2019, 141, 14720–14727

Received: June 20, 2019

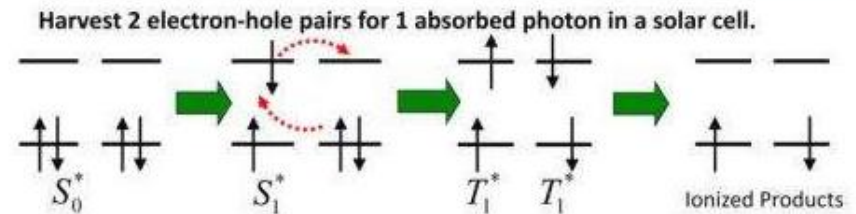
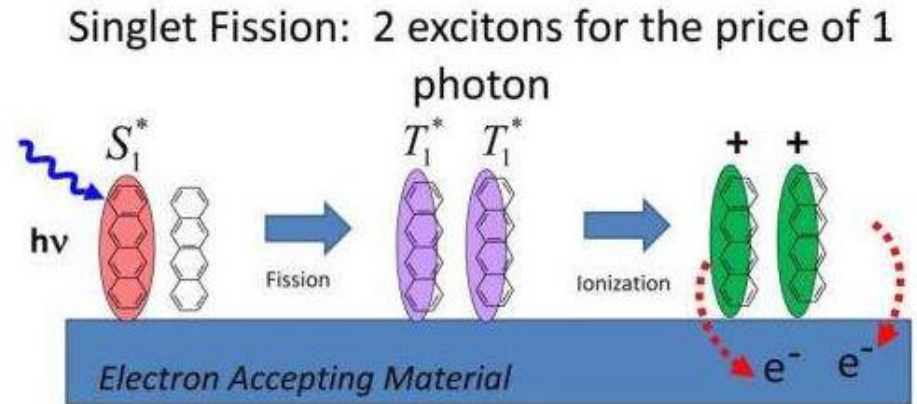
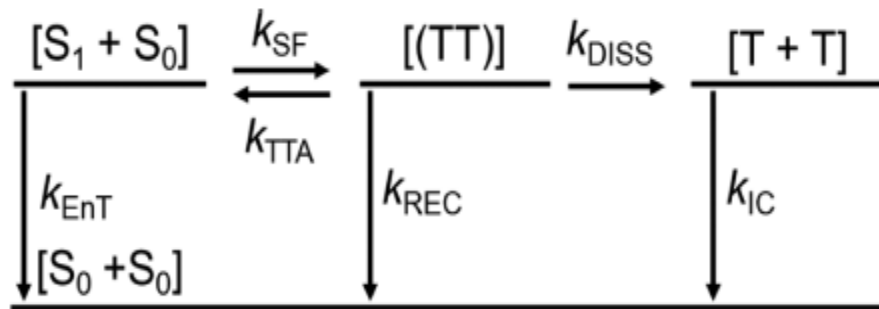
Published: September 6, 2019

Arijit Jana

18.01.2020

❖ Singlet Fission (SF) :

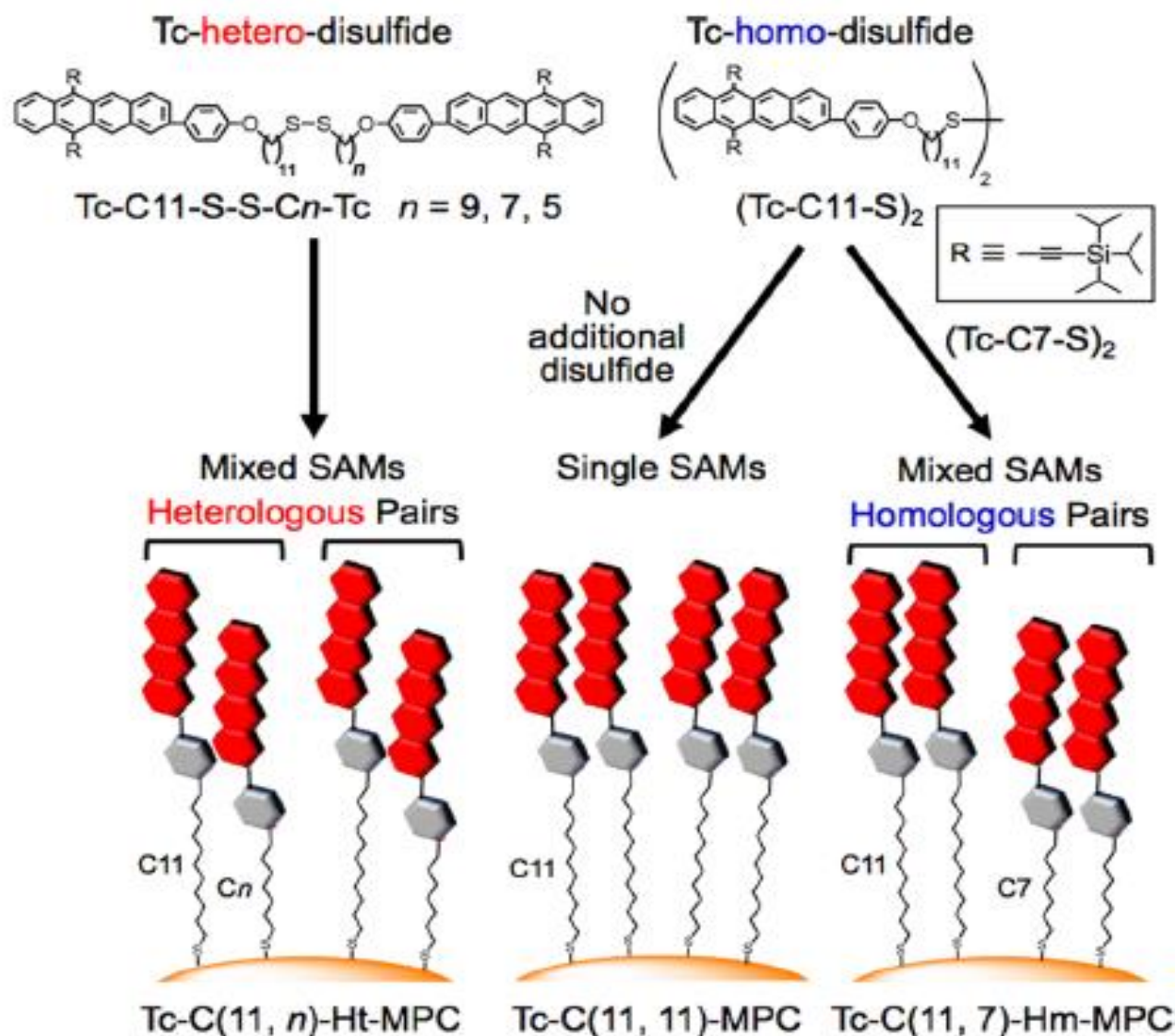
Singlet fission (SF) is a spin-allowed multiexciton generation process in which a singlet exciton is converted into two triplet excitons in two neighboring molecules.



❖ The goal of this work : -

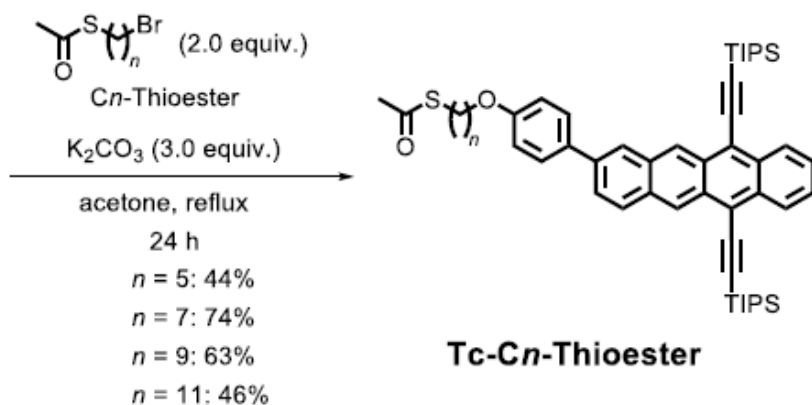
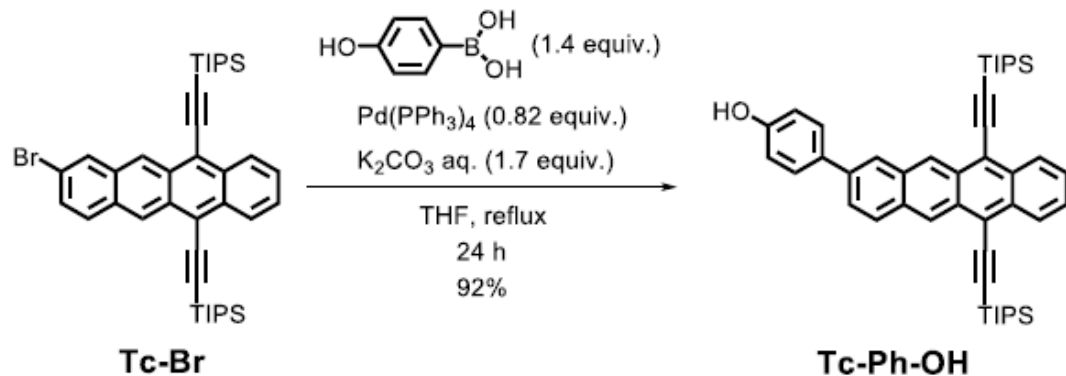
- To find out a way for making High yield and long lived triplet states through Singlet-Fission (SF) of tetracene molecule.
- Proposing a new type of supramolecular strategy utilizing self assemble monolayers (SAMS) with different chain length.
- Mixed SAM layer was crated such a way that systematically control the electronic interaction between two tetracene molecules, which can leads to highest singlet Fission.

Scheme 1. Schematic Illustration of Organization Process of Tc Units on MPCs^a

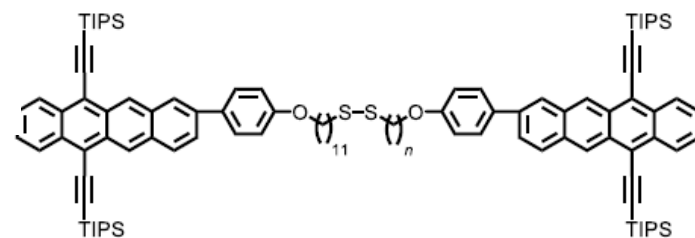


^aRed- and gray-colored units demonstrate Tc and linker chain units, respectively.

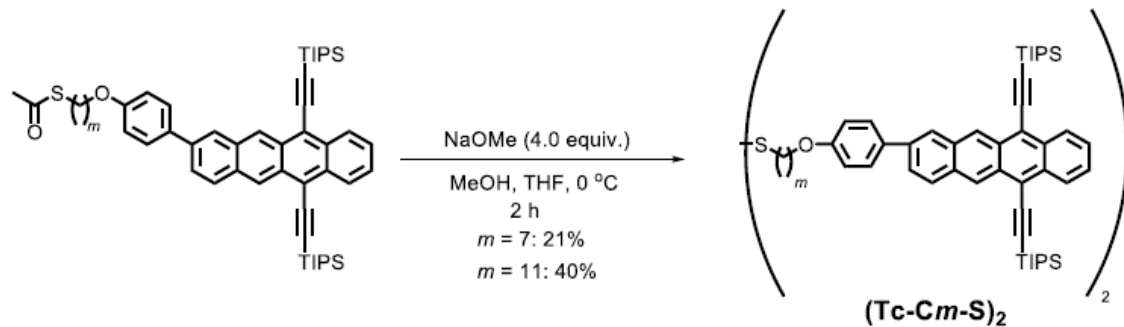
Synthesis of the ligands:



MeOH, THF, 0 °C
2 h
 $n = 5$: 5.7%
 $n = 7$: 17%
 $n = 9$: 6.0%



Tc-C11-S-S-C_n-Tc



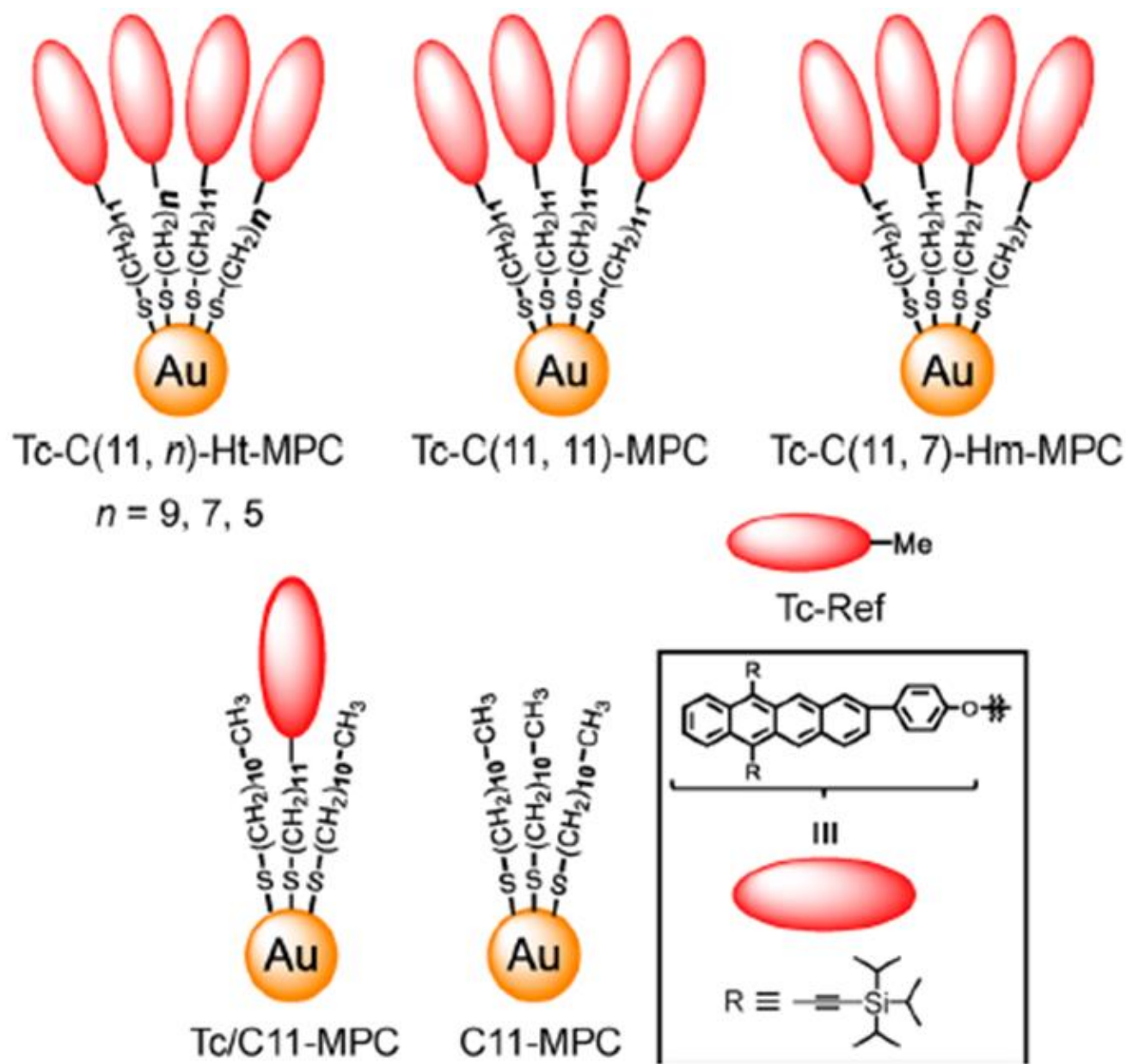
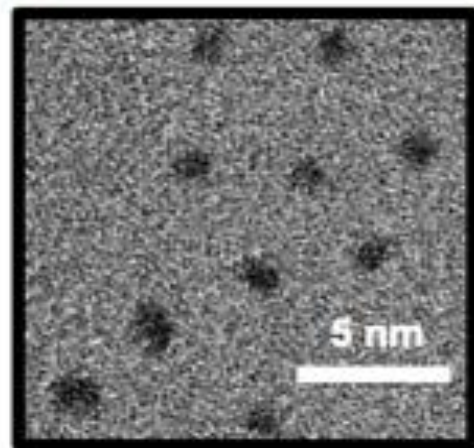
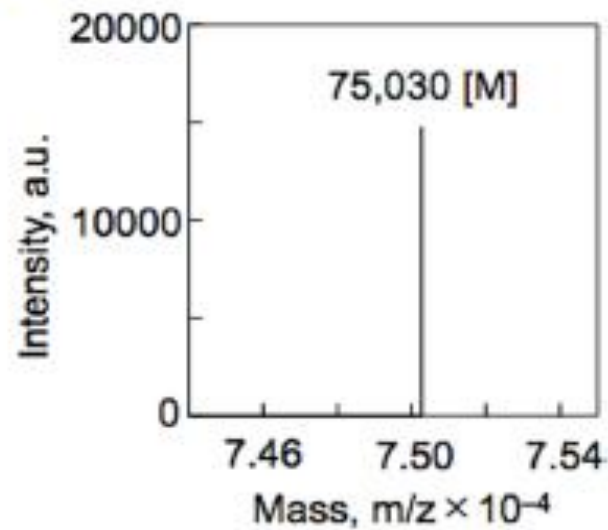


Figure 1. Structures of Tc-C(11, n)-Ht-MPCs ($n = 9, 7, 5$) and reference materials in this study.

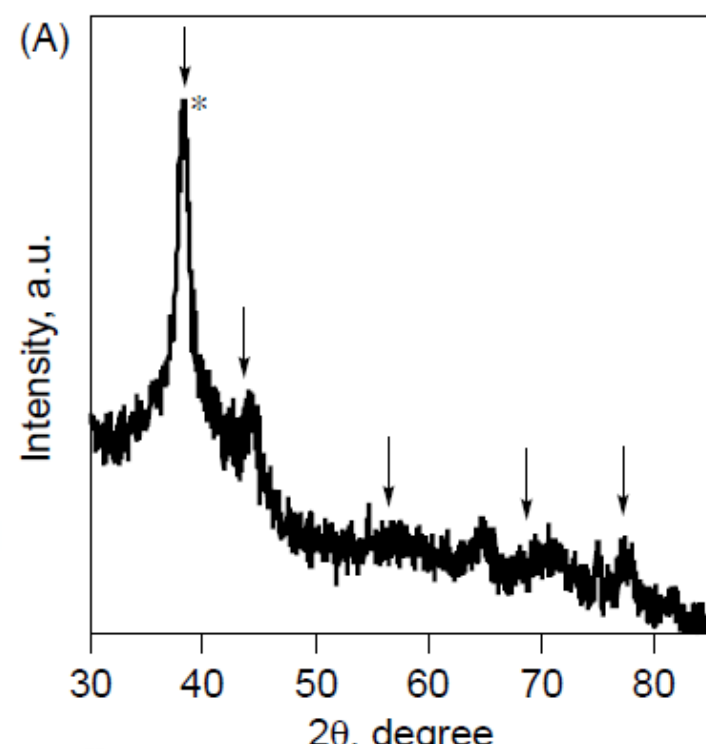
(A)



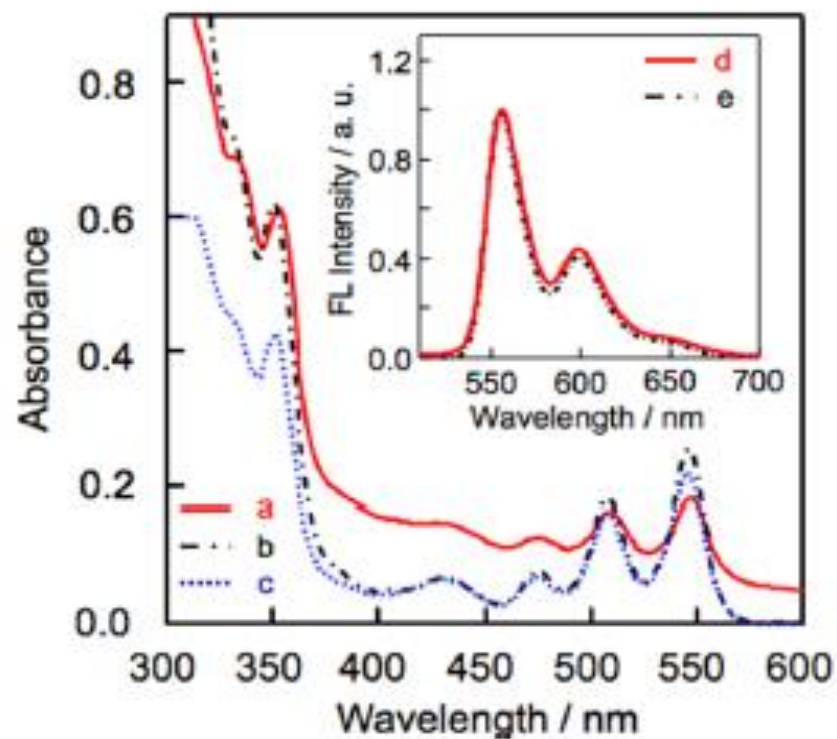
(B)



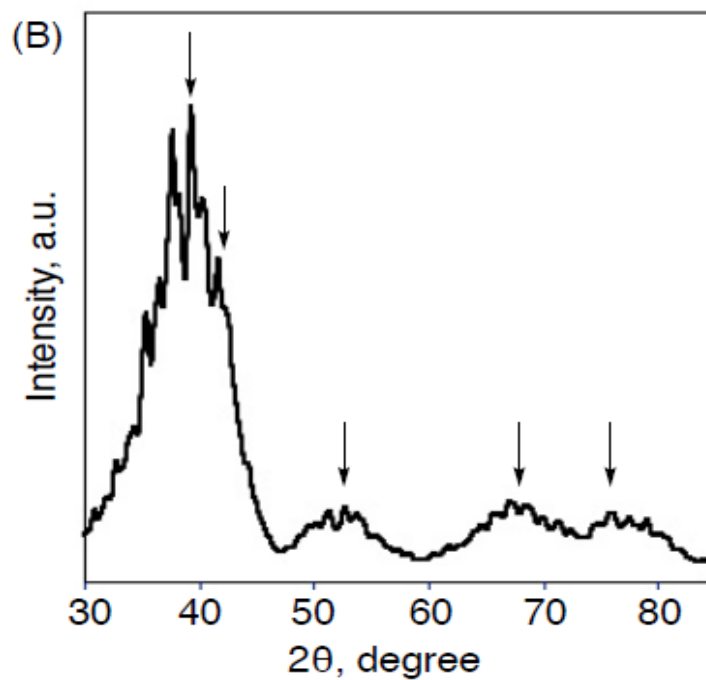
(A)

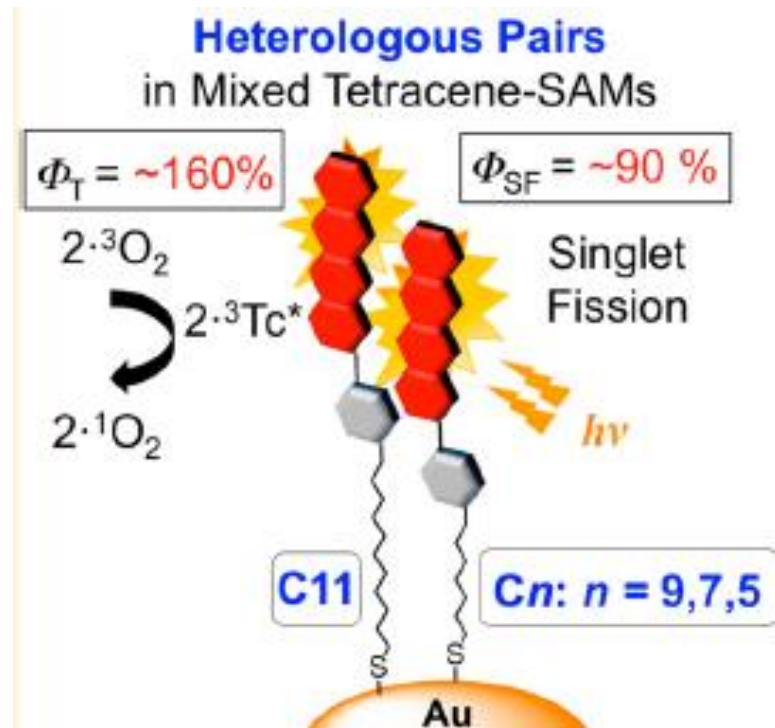
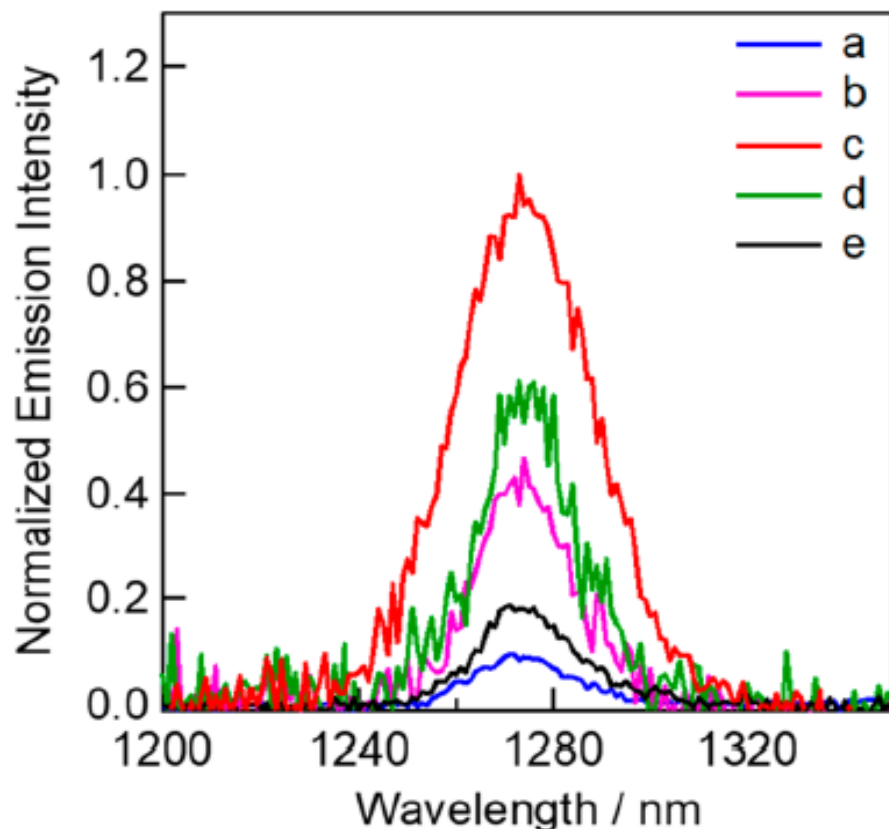


(C)



(B)





$$\Phi_T(\text{Tc-C(11, 7)-Ht-MPC}) = \Phi_T(\text{benzophenone}) \times \frac{I_{em}(\text{Tc-C(11, 7)-Ht-MPC})}{I_{em}(\text{benzophenone})} \times \frac{1 - 10^{A_{350\text{ nm}}(\text{benzophenone})}}{1 - 10^{A_{350\text{ nm}}(\text{Tc-C(11, 7)-Ht-MPC})}}$$

Table S9. Calculation of Φ_T in Tc-C(11,7)-Ht-MPC at different five observation wavelengths.

Wavelength, nm	1270	1273	1274	1275	1277
Φ_T , %	164	156	163	152	155

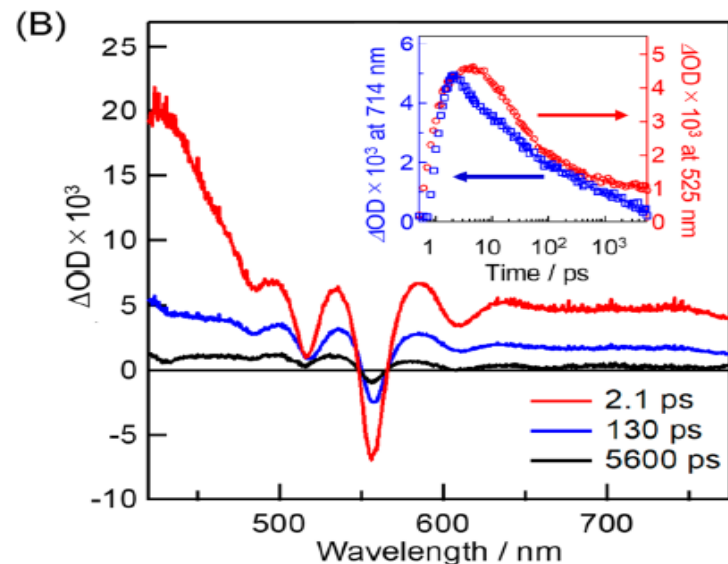
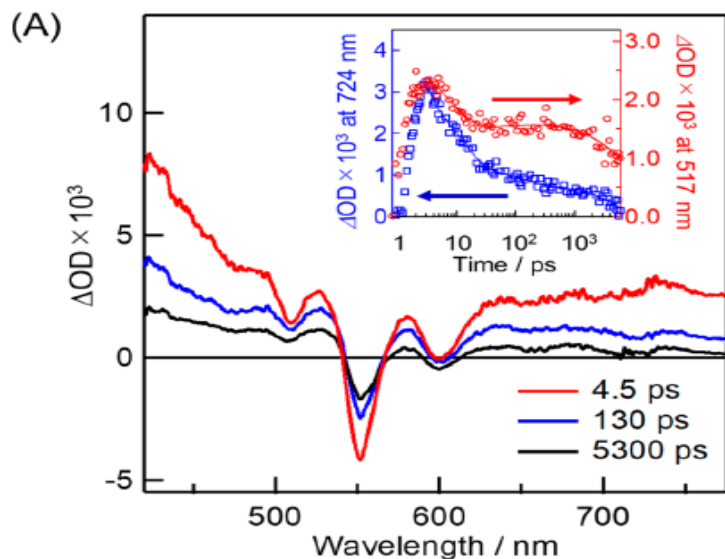
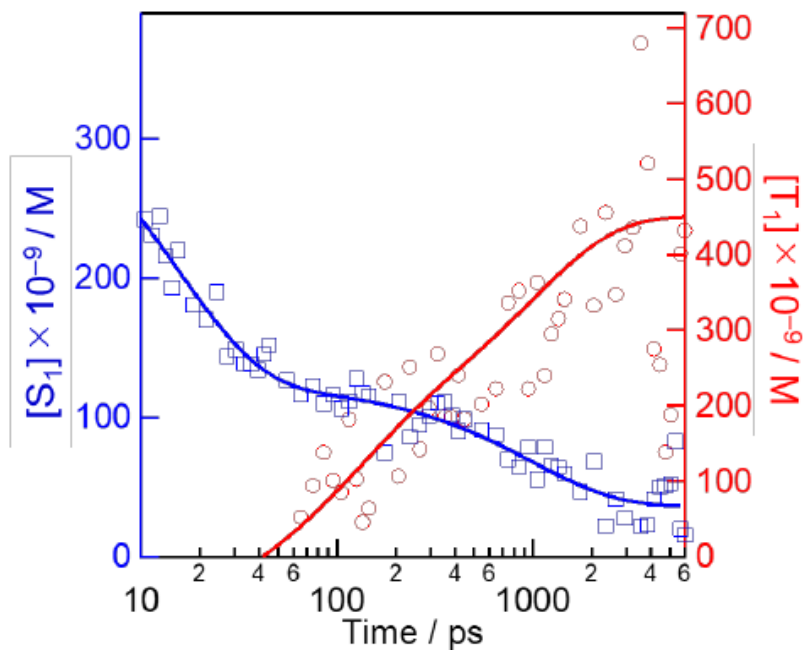


Figure 3. fsTA spectra of (A) Tc-C(11,7)-Ht-MPC and (B) Tc-C(11,11)-MPC in toluene. The excitation wavelength is 350 nm.



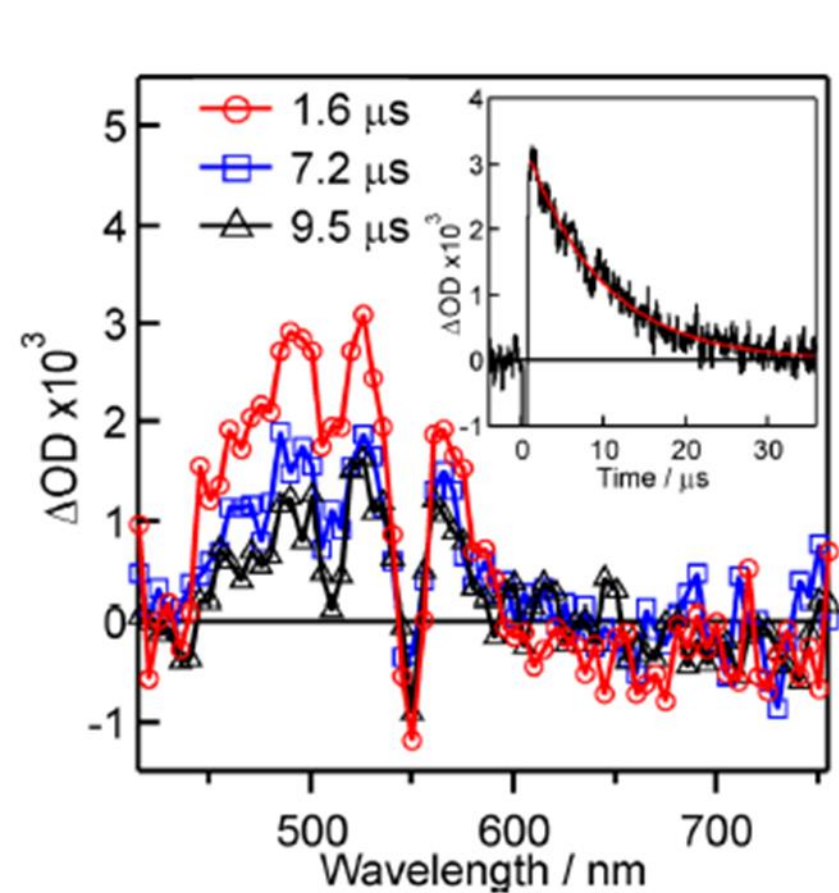


Figure 5. Nanosecond transient absorption spectra of Tc-C(11,7)-Ht-MPC in toluene. Inset shows the corresponding time profile at 525nm. Excitation wavelength is 532 nm. The lifetime of the triplet state is determined to be 9.3 μ s.

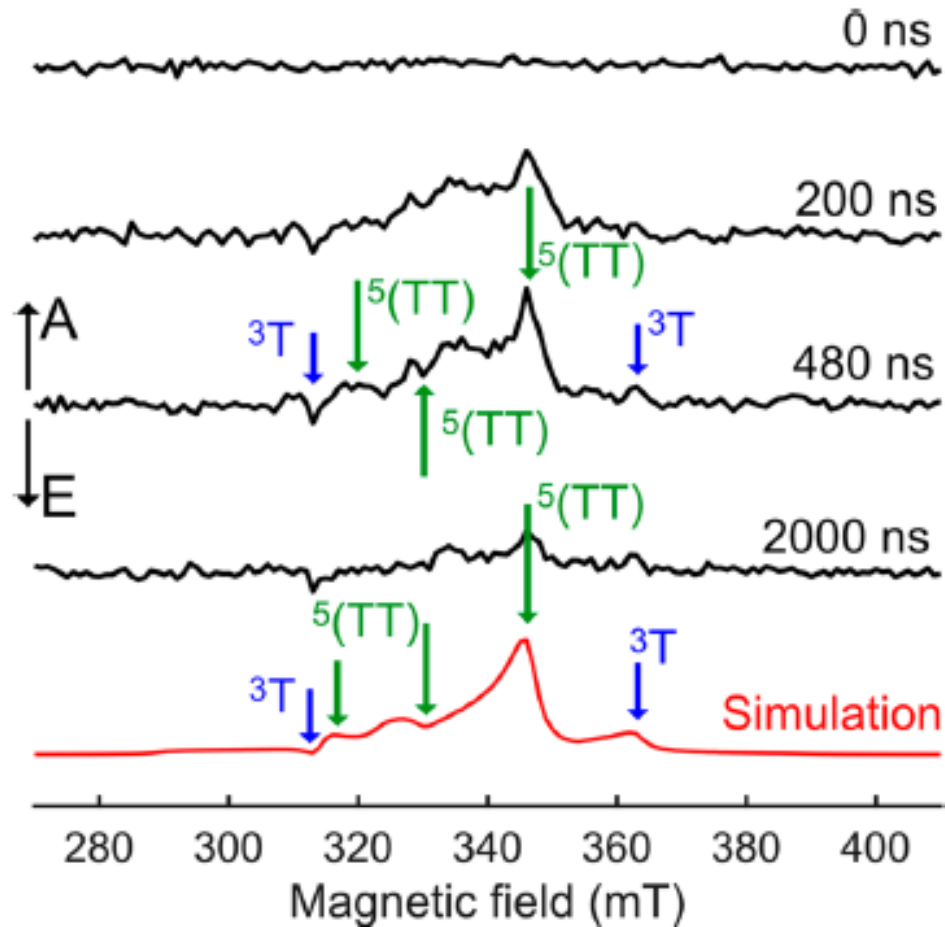
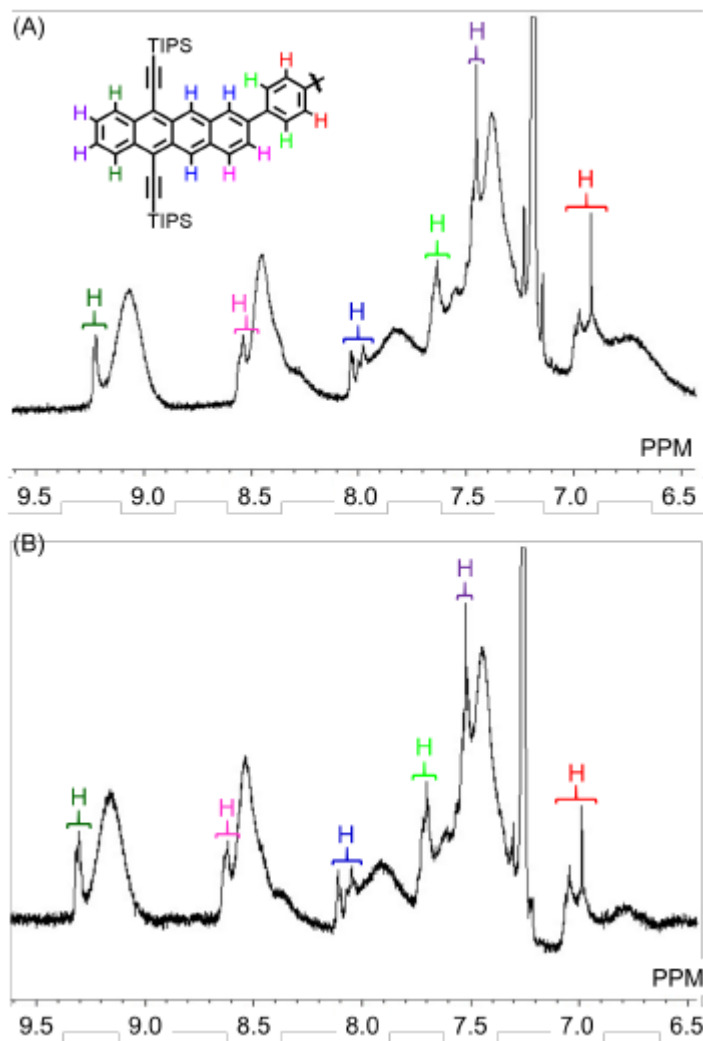
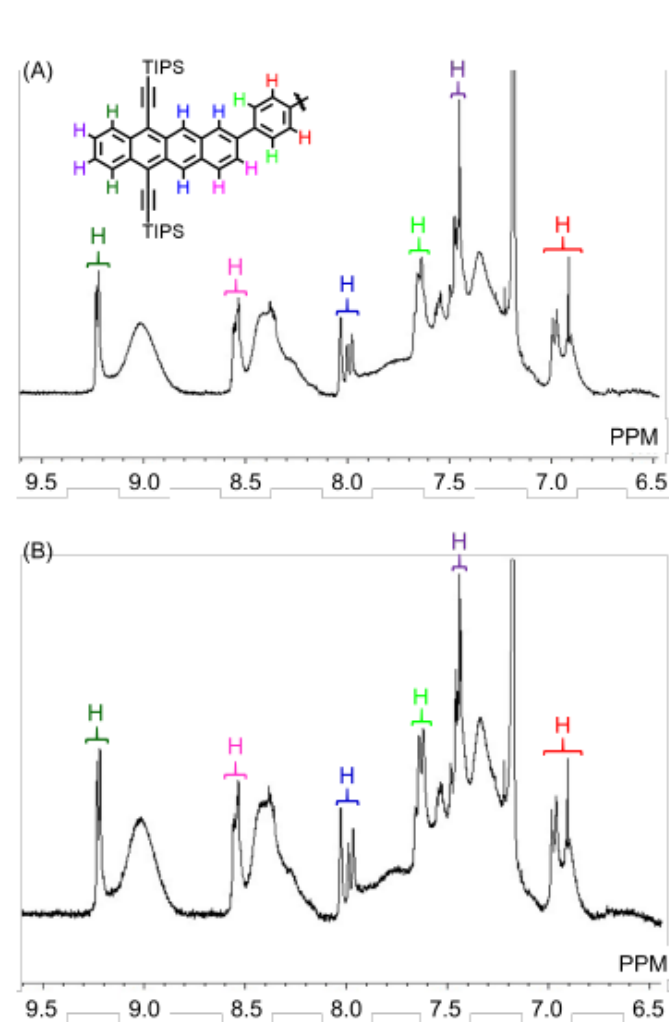


Figure 6. TR-ESR spectra of Tc-C(11,7)-Ht-MPC in methylcyclohexane at 120 K ($\lambda_{\text{exc}} = 532$ nm). A and E denote microwave absorption and emission, respectively. Simulated spectra were obtained by setting spin sublevel populations to be 0.455, 0.242, 0.303, 0, 0 for the quintet in $m_S = -2, -1, 0, +1$, and $+2$, respectively.

Tc-C(11,7)-Hm-MPC in CDCl₃.



Tc-C(11,7)-Ht-MPC in CDCl₃.



Relatively sharpened proton peaks of Tc were observed at high temperature (323 K) as compared to those at 298 K. These results suggested the stacked interaction of two Tc unit was reduced in Tc-C(11,7)-Ht-MPC as compared to Tc-C(11,7)-Hm-MPC.

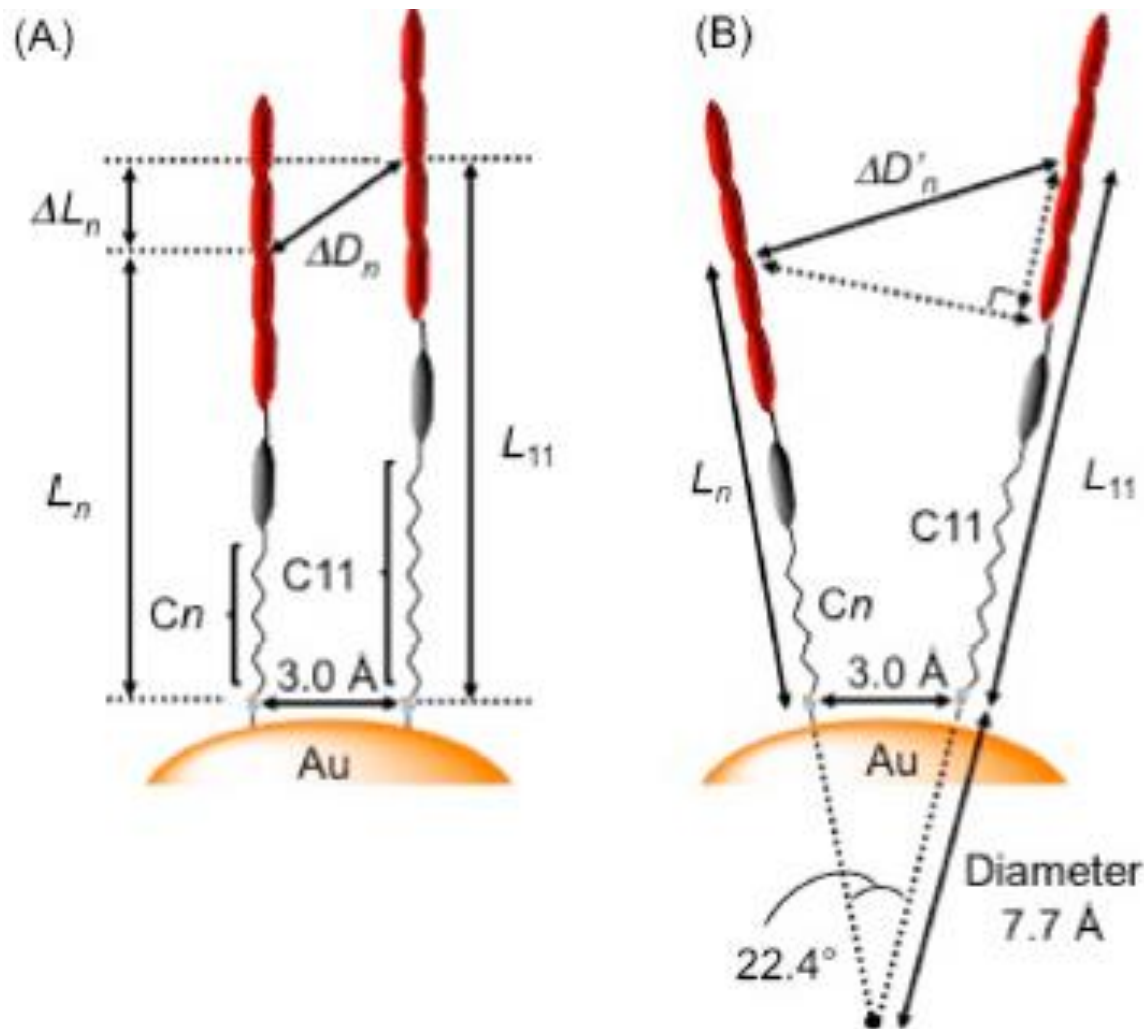


Figure 7. Proposed dimeric structures of Tc units in Tc-C(11,n)-Ht-MPCs. (A) Close-stacking models for $n = 11$ ($\Delta D_{11} = 3.0 \text{ \AA}$), $n = 9$ ($\Delta D_9 = 4.2 \text{ \AA}$), $n = 7$ ($\Delta D_7 = 5.8 \text{ \AA}$), and $n = 5$ ($\Delta D_5 = 8.5 \text{ \AA}$) and (B) equally spaced models for $n = 11$ ($\Delta D'_{11} = 12.5 \text{ \AA}$), $n = 9$ ($\Delta D'_9 = 12.3 \text{ \AA}$), $n = 7$ ($\Delta D'_7 = 12.7 \text{ \AA}$), and $n = 5$ ($\Delta D'_5 = 13.4 \text{ \AA}$).

Conclusion :

- ❖ We have newly synthesized a series of mixed Tc- SAMs on gold nanoclusters prepared from a Tc-modified heterodisulfide with two different chain lengths (Tc-C11-S-SC_n-Tc (n = 9, 7, 5)) [Tc-C(11,n)-Ht-MPC]. The detailed structures of these Tc-modified MPCs were successfully assigned by steady-state spectroscopy, MALDI-TOF mass, TEM and XRD.
- ❖ Temperature-dependent ¹H NMR measurements suggested smaller interaction of two Tc units in Tc-C(11,7)-Ht-MPC as compared to mixed SAMs by two different Tc-homo-disulfides: (Tc-C11-S)₂ and (Tc-C7-S)₂ [Tc-C(11,7)-Hm-MPC].
- ❖ Such control of electronic interaction between two neighboring Tc units in C(11,7)-Ht-MPC resulted in the highest $\Phi_{SF} \approx 90\%$ among Tc derivatives in homogeneous solution (together with $\Phi_T \approx 160\%$).

Thank you