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Supramolecular Photocatalysis Utilizing Host-Guest Charge-Transfer Interaction: Visible Light-Induced Generation of Triplet Anthracenes for [4+2] Cycloaddition Reactions

Tatsuhiro Uchikura,[a,b] Mari Oshima,[a] Minami Kawasaki,[a] Kohei Takahashi,[a] and Nobuharu Iwasawa*[a]

Abstract: A supramolecular photocatalysis via charge-transfer excitation of a host-guest complex was developed by use of the macrocyclic boronic ester **[2+2]**$_{BTH\text{-}F}$ containing highly electron-deficient difluorobenzothiadiazole moieties. In the presence of a catalytic amount of **[2+2]**$_{BTH\text{-}F}$, triplet excited state of anthracene was generated from charge-transfer excited state of anthracene@**[2+2]**$_{BTH\text{-}F}$ by visible light irradiation, and cycloaddition of the excited anthracene with several dienes and alkenes proceeded in a [4+2] manner in high yields.

Supramolecular catalysis has attracted considerable attention due to the unique reactivities utilizing characteristic properties of the host molecules.[1] Although there are many reports of catalytic acceleration of reactions by inclusion of guest substrates in host molecules, supramolecular photocatalysis has not been explored extensively and is mainly limited to two types, that is, i) direct excitation of included guest molecules, which would lead to specific reactions inside the hosts, and ii) use of host molecules bearing photo-sensitizing moieties, which would induce electron transfer or energy transfer reactions with guest molecules.[2-4]

Charge-transfer interaction between aromatic molecules, which often has absorption in visible light region, is frequently observed in host-guest complexes.[5] However, to the best of our knowledge, there is no obvious example of utilization of the charge-transfer excitation within discrete host-guest complexes for catalytic carbon-carbon bond formations.[6]

Previously, we have reported the electrophilic activation of aromatic aldehydes via donor-acceptor interaction of aromatic molecules by use of the macrocyclic boronic ester **[2+2]**$_{BTH\text{-}F}$, which has highly electron-deficient difluorobenzothiadiazole moieties.[7] We expected that visible light-irradiation of **[2+2]**$_{BTH\text{-}F}$ including an appropriate electron-rich aromatic guest molecucle would induce charge-tranfer excitation to realize supramolecular photocatalytic reactions. In this paper, we report a successful realization of this approach, which has enabled the visible light-induced generation of *not the cation radical but the triplet state of anthracenes* via charge-transfer excitation of a host-guest complex derived from **[2+2]**$_{BTH\text{-}F}$ (Figure 1). Subsequent [4+2] cycloaddition with dienes and alkenes and specific activation of the guest molecule are also demonstrated.

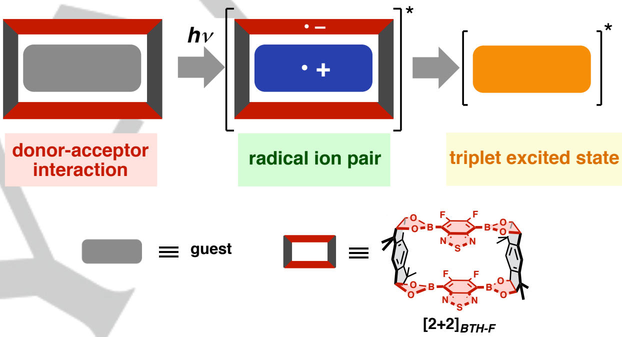

Figure 1. Schematic representation of the concept.

When anthracene was mixed with **[2+2]**$_{BTH\text{-}F}$ in dichloromethane, the solution turned yellow and a new absorption band was observed at 400-500 nm by UV-Vis spectra (Figure 2a, b). Furthermore, according to the DFT calculation of the molecular orbital of anthracene@**[2+2]**$_{BTH\text{-}F}$, HOMO was

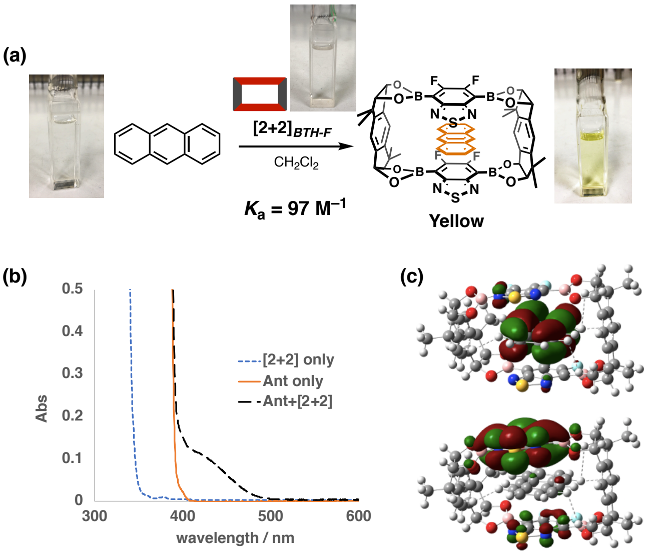

Figure 2. Properties of anthracene@**[2+2]**$_{BTH\text{-}F}$. (a) Color change via inclusion. (b) UV-Vis spectra of anthracene@**[2+2]**$_{BTH\text{-}F}$ in CH_2Cl_2. (c) Frontier orbitals of anthracene@**[2+2]**$_{BTH\text{-}F}$; top: HOMO, bottom: LUMO (M062X/6-31G).

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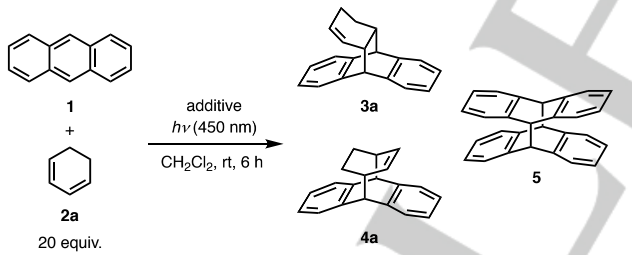
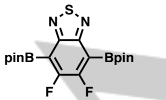
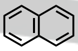
distributed on anthracene and LUMO was distributed on the benzothiadiazole ring of **[2+2]$_{BTH-F}$** (Figure 2c). Therefore, irradiation of 400-500 nm visible light would induce the charge-transfer from anthracene to **[2+2]$_{BTH-F}$**.

We then investigated the photocycloaddition reaction of anthracene (**1**) with 1,3-cyclohexadiene (**2a**)[8] in the presence of **[2+2]$_{BTH-F}$** under irradiation of visible light (450 nm) (Table 1). A dichloromethane solution of anthracene with 20 equivalents of 1,3-cyclohexadiene was irradiated with visible light in the presence of 0.1 equivalent of **[2+2]$_{BTH-F}$**. Interestingly, [4+2] cycloadduct **3a** of anthracene with **2a** was obtained almost quantitatively accompanied by a trace amount of anthracene [4+4] dimer **5**,[9] and other cycloadducts such as [4+4] cycloadduct **4a** of anthracene with **2a** and self-dimers of **2a** were not obtained at all (Table 1, entry 1).[10]

As control experiments, several reactions were examined. First, in the absence of **[2+2]$_{BTH-F}$** or in the presence of monomeric pinacol ester of difluorobenzothiadiazolediboronic acid **6**, which didn't form the charge-transfer complex with anthracene, the cycloaddition didn't proceed at all by the irradiation with 450 nm light (entries 2,3). Thus, the host structure of **[2+2]$_{BTH-F}$** was necessary for the reaction. Next, competitive experiment by naphthalene (K_a = 103 M^{-1}), which has almost the same association constant with anthracene (K_a = 97 M^{-1}), was examined, and addition of 5 equivalents of naphthalene retarded the reaction considerably (entry 4). Thus, inclusion of anthracene into **[2+2]$_{BTH-F}$** was found to be essential for the photocycloaddition reaction.

Table 1. Photocycloaddition of anthracene (**1**) and 1,3-cyclohexadiene (**2a**).[a]



entry	additive	Yield 3a	Yield 4a	Yield 5[b]
1	0.1 equiv. **[2+2]$_{BTH-F}$**	>95%	0%	1%
2	none	0%	0%	0%
3	 **6** 0.2 equiv.	0%	0%	0%
4	0.1 equiv. **[2+2]$_{BTH-F}$**  5.0 equiv.	47%	0%	0%

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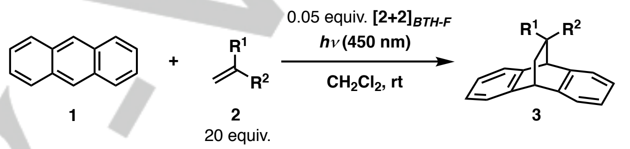
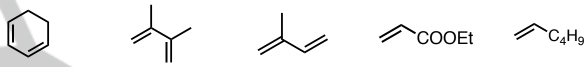
[a] NMR yield. Performed with **1** (9 μmol), **2a** (180 μmol), and additives in CH_2Cl_2 (0.5 mL). [b] Based on the amount of anthracene used.

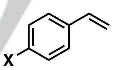
Then we examined the generality of alkenes (Table 2). The dienes such as 2,3-dimethyl-1,3-butadiene (**2b**) and isoprene (**2c**) reacted efficiently in a [4+2] cycloaddition manner. Ethyl acrylate (**2d**) as an electron-deficient alkene was also applicable and gave the product in good yield although it required much longer irradiation. Styrene derivatives (**2f, 2h-2l**) were also employable. In particular, electron-poor styrenes reacted faster. *p*-Methoxystyrene (**2g**) gave the product in low yield due to the competitive polymerization. A simple alkene (**2e**) was not applicable to this reaction.

Table 2. Generality of alkenes.[a]

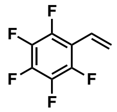




2a	2b	2c	2d	2e
quant (12 h)	95% (36 h)	91% (6 h)[b]	81% (139 h)	0% (24 h)



X = H (**2f**): 93% (30 h)
OMe (**2g**): 17% (20 h)[c]
Cl (**2h**): 97% (36 h)
Br (**2i**): 88% (30 h)
^{t}Bu (**2j**): 95% (30 h)
CF$_3$ (**2k**): 96% (11 h)

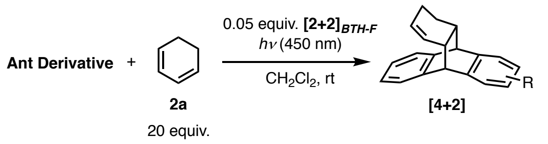


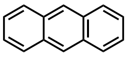
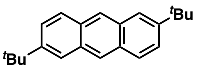
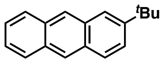
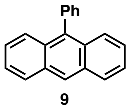
2l
99% (4 h)

[a] Isolated yield. Performed with **1** (90 μmol), alkenes (1.8 mmol), and **[2+2]$_{BTH-F}$** (4.5 μmol) in CH_2Cl_2 (0.7 mL). [b] Two positional isomers were obtained in 7 : 3 ratio. [c] NMR yield.

Next, generality of the anthracene derivatives was investigated (Table 3). The reaction proceeded as well with several substituted anthracenes which are included in **[2+2]$_{BTH-F}$**, but the reactions were slower as the association constants of anthracene derivatives became smaller (2-*tert*-butylanthracene (**7**): 80% for 14 h, K_a = 71 M^{-1}; 2,6-di-*tert*-butylanthracene (**8**): 82% for 42 h, K_a = 23 M^{-1}). Furthermore, the photocycloaddition didn't proceed using 9-phenylanthracene (**9**), which was not included in **[2+2]$_{BTH-F}$** as judged by ITC measurement. This correlation is consistent with the assumption that the included guest molecule was selectively activated (Table 1).[11]

Table 3. Generality of anthracene derivatives.[a]

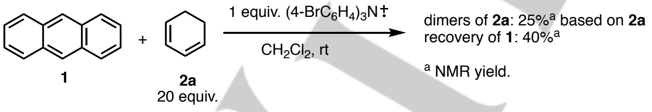


Ant derivative (association const.)	yield (time)	Ant derivative (association const.)	yield (time)
 **1** (97 M^{-1})	quant (12 h)	 **8** (23 M^{-1})	87%[c] (42 h)
 **7** (71 M^{-1})	80%[b] (14 h)	 **9** (~0 M^{-1})	0% (6 h)

[a] Isolated yield. Performed with anthracene derivatives (90 μmol), **2a** (1.8 mmol), and **[2+2]**$_{BTH-F}$ (4.5 μmol) in CH_2Cl_2 (0.7 mL). [b] Obtained as Inseparable 3 isomers. [c] Obtained as inseparable 2 isomers.

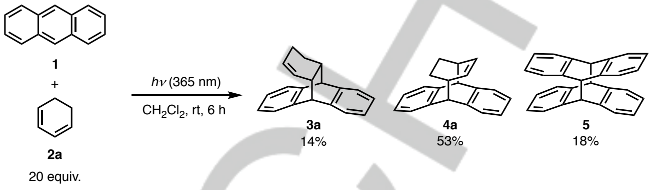
We next carried out several examinations to clarify the nature of the generated excited state of anthracene. There are three possible active species, that is, the cation radical directly released from the CT excited complex,[12] and the singlet and the triplet excited states which are known to undergo photocycloaddition reactions.[8,9]

Firstly, the reaction was examined using tris(4-bromophenyl)ammoniumyl hexachloroantimonate as catalyst to examine the possibility of the cation radical [4+2] cycloaddition reaction.[13] Treatment of a mixture of anthracene and 1,3-cyclohexadiene (**2a**) with the ammoniumyl salt turned out to give only dimers of **2a**[14] with moderate recovery of anthracene and none of the [4+2] cycloadduct **3a** was obtained. As the oxidation potential of anthracene is lower than **2a**,[15] this result suggests that even when the radical cation of anthracene was generated, the [4+2]-cycloaddition did not proceed. Thus, it is not likely that the reactive species of the **[2+2]**$_{BTH-F}$-catalyzed reaction is the cation radical of anthracene generated by excitation of the CT complex (Scheme 1).



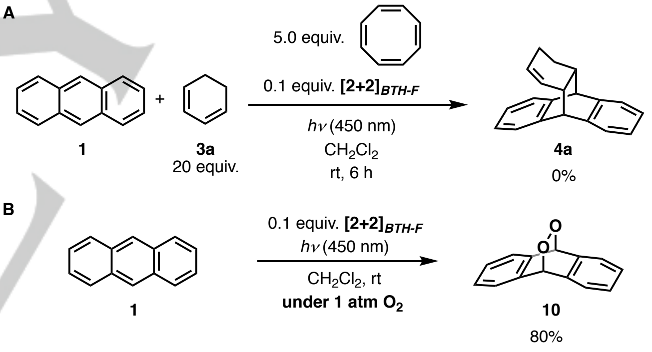
Scheme 1. Ammoniumyl salt-mediated reaction.

Next, direct excitation of anthracene with UV light was examined. When a mixture of anthracene and 1,3-cyclohexadiene was irradiated with 365 nm UV light without **[2+2]**$_{BTH-F}$, anthracene [4+4] dimer **5** and [4+4] cross cycloadducts **4a** were obtained as major products, along with [4+2] cycloadduct **3a** in only 14% yield (Scheme 2). This result suggests that while the direct excitation using UV light generated a species which favored [4+4] cycloaddition pathway, a different excited species of anthracene which favored [4+2] cycloaddition pathway was selectively generated in the presence of **[2+2]**$_{BTH-F}$.[8] It is assumed that the former is the singlet state[8a,b] and the latter is the triplet state of anthracene.



Scheme 2. Photocycloaddition of anthracene (**1**) with 1,3-cyclohexadiene (**2a**) by irradiation of 365 nm UV lamp.

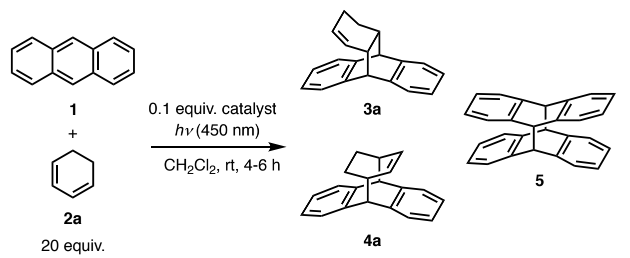
To confirm the generation of the triplet state of anthracene, the quenching experiment was carried out. Indeed, the reaction was completely inhibited in the presence of 5.0 equivalents of cyclooctatetraene, which is known as a triplet quencher (Scheme 3A). Furthermore, under oxygen, the cycloadduct **10** of anthracene and oxygen was obtained in good yield in the presence of **[2+2]**$_{BTH-F}$ under visible light irradiation (Scheme 3B). These results confirmed that triplet state of anthracene was actually generated as the active species in the **[2+2]**$_{BTH-F}$ catalyzed reaction.[16]



Scheme 3. Addition of triplet quenchers.

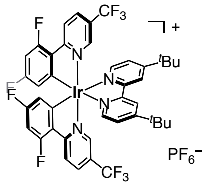
To clarify the characteristic properties of the present **[2+2]**$_{BTH-F}$-catalyzed reaction, the reaction was compared using iridium catalyst **I** and **II**, which have recently attracted attention as a triplet-triplet energy transfer catalyst in several reactions (Table 4).[17] When iridium catalysts **I** and **II** were employed instead of **[2+2]**$_{BTH-F}$, the same [4+2] cycloadduct **3a** between anthracene and 1,3-cyclohexadiene (**2a**) was obtained as a major product together with a small amount of anthracene [4+4] dimer **5**,[18] accompanied by a large amount of dimers of **2a**. This result also suggested that the triplet state of anthracene is generated as an active species of the cycloaddition in the presence of **[2+2]**$_{BTH-F}$. More importantly, **[2+2]**$_{BTH-F}$ could excite anthracene selectively and only [4+2] cross-adduct **3a** was obtained in high yield, while both **1** and **2a** were excited by energy transfer from iridium catalysts, and a large amount of 1,3-cyclohexadiene dimers were obtained.[19] It should be noted that the triplet excited energy of Ir catalyst **II** is somewhat lower than that of **2a** (E_T of catalyst **II** = 49.2 kcal/mol; E_T of **2a** = ~52 kcal/mol; E_T of **1** = ~42 kcal/mol), but still most of **2a** was dimerized under the present conditions, while **[2+2]**$_{BTH\text{-}F}$-catalyzed reaction gave none of dimerized products of **2a**. Thus, selective excitation of anthracene was achieved in the presence of **2a** by using **[2+2]**$_{BTH\text{-}F}$.

Table 4. Photocycloaddition of anthracene (**1**) and cyclohexadiene (**2a**).[a]

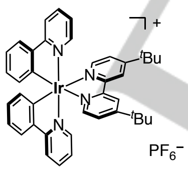


		yield[b]			
entry	catalyst	3a	4a	5	2a dimers
1	**[2+2]**$_{BTH\text{-}F}$	>95%	0%	1%	0%
2	Ir complex **I**	85%	0%	4%	92%
3	Ir complex **II**	89%	0%	7%	88%

[a] NMR yield. Performed with **1** (9 μmol), **2a** (180 μmol), and catalyst (0.9 μmol) in CH_2Cl_2 (0.5 mL). [b] For **3a**, **4a**, and **5**, the yield is based on the amount of anthracene used. For **2a dimers**, the yield is based on 1,3-cyclohexadiene used.



I Ir[dF(CF$_3$)ppy]$_2$(dtbbpy)PF$_6$



II Ir(ppy)$_2$(dtbbpy)PF$_6$

To obtain information on the pathway for the formation of the triplet state of anthracene, we have carried out DFT analyses of the triplet state of anthracene itself and that of anthracene@**[2+2]**$_{BTH\text{-}F}$ (Figure 3). The initial structure of anthracene@**[2+2]**$_{BTH\text{-}F}$ was constructed based on the X-ray data of 2-naphthaldehyde@**[2+2]**$_{BTH\text{-}F}$.[7] As shown in Scheme 4, LSOMO of anthracene@**[2+2]**$_{BTH\text{-}F}$ spreads over the anthracene moiety and its phase is nearly the same with LSOMO of anthracene itself. HSOMO of anthracene@**[2+2]**$_{BTH\text{-}F}$ spreads between anthracene and one of the benzothiadiazole moieties, and the appearance of the HSOMO over the anthracene moiety in **[2+2]**$_{BTH\text{-}F}$ is close to that of anthracene itself. These analyses suggest that the triplet state of anthracene@**[2+2]**$_{BTH\text{-}F}$ has a character close to the triplet state of anthracene without much perturbation from the **[2+2]**$_{BTH\text{-}F}$ moiety. Thus, with visible light irradiation, anthracene@**[2+2]**$_{BTH\text{-}F}$ undergoes CT excitation to generate a charge-separated singlet state, which undergoes intersystem crossing to give the triplet state of anthracene@**[2+2]**$_{BTH\text{-}F}$, from which the triplet state of anthracene is released into the solution (Scheme 4). Generation of the triplet state of guest molecules by CT-excitation of host-guest complexes has been reported in several cases,[20] but to our knowledge, this is the first example of successful application to the supramolecular catalysis for carbon-carbon bond formation.

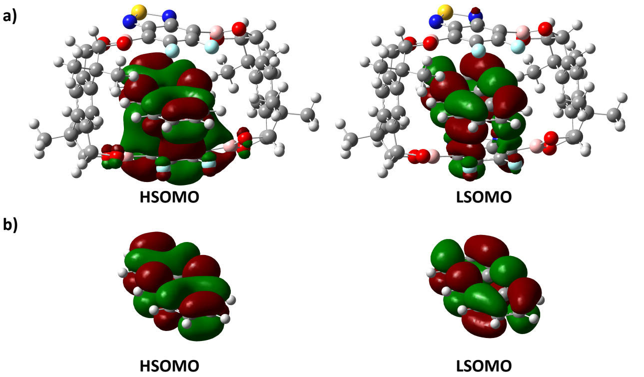
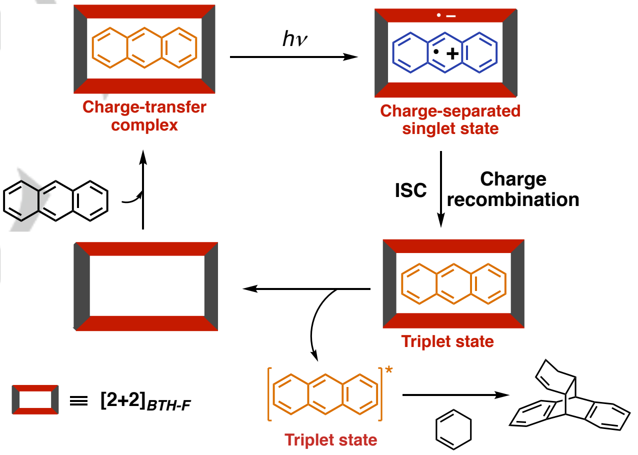


Figure 3. Molecular orbitals of the triplet state of a) anthracene@**[2+2]**$_{BTH\text{-}F}$ and b) anthracene (M062X/6-31G).



Scheme 4. Proposed mechanism of the [4+2] cycloaddition in the presence of **[2+2]**$_{BTH\text{-}F}$.

In summary, we have developed a supramolecular photocatalysis which can generate the triplet state of guest molecules via charge-transfer excitation. By using this catalyst, photocycloaddition of anthracene derivatives with several dienes and alkenes proceeded smoothly by visible light irradiation. Control experiments revealed that inclusion of the guest molecule was crucial for this reaction, and the photocycloaddition proceeded only with guest molecules that can be included. Utilization of chage-transfer interacton between host and guest molecules for generation of reactive species would be a promising method for realization of a new type of selective reactions.

Acknowledgements

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Keywords: Supramolecular catalyst• Charge-transfer interaction • Anthracene • Photocatalysis

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[10] By using 1 equivalent of cyclohexadiene, [4+2] cycloaddition product **3a** was obtained in low yield (37%) and anthracene [4+4] dimer **5** was obtained in 12% yield. For details, see Supporting information, Table S2.

[11] The CT absorption band in UV-Vis spectra appeared only when guest molecules were included and the absorbance increased as the association constant of anthracene derivatives became larger (Figure S2, Supporting information). The reaction of **9** proceeded without problem by using Ir catalysts.

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[15] Oxidation potentials of anthracene: E = 1.1 ~ 1.3 V vs SCE; 1,3-cyclohexadiene: E = 1.4 ~ 1.6 V vs SCE.

[16] Additionally, the fluorescence quenching of anthracene@**[2+2]**$_{BTH\text{-}F}$ was not observed by the addition of **2a**. Hence, the charge-tranfer excitation state did not directly react with **2a** (Figure S4, Supporitng information).

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[18] A small amount of the [4+4] dimer **5** was thought to be produced via triplet-triplet annihilation to generate singlet anthracene. See ref. [9].

[19] In this reaction, the dimer of 1,3-cyclohexadiene was obtained as a mixture of 4 isomers as reported in the literature. The ammoniumyl-catalysed dimerization reaction of cyclohexadiene was reported to afford only two isomers,[13] which also supported that the present reaction proceeded via the triplet state of anthracene. See Supporting information, Tables S4 and S5 and the following references. (a) D. Valentine, N. J. Turro, Jr., G. S. Hammond, *J. Am. Chem. Soc.* **1964**,

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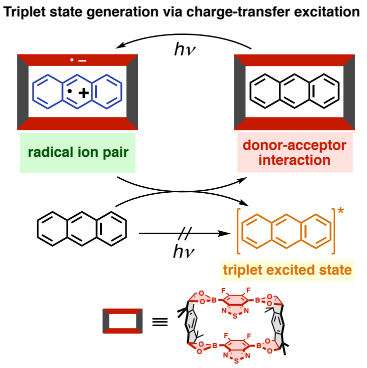
Layout 1:

COMMUNICATION

New type of supramolecular photocatalyst: A supramolecular photocatalysis via charge-transfer excitation of a host-guest complex was realized by use of macrocyclic boronic ester **[2+2]**$_{BTH\text{-}F}$ containing highly electron deficient difluorobenzothiadiazole moieties. Triplet excited state of anthracene was generated by visible light irradiation, and cycloaddition with several dienes and alkenes proceeded in high yields.



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Supramolecular Photocatalysis Utilizing Host-Guest Charge-Transfer Interaction: Visible Light-Induced Generation of Triplet Anthracenes for [4+2] Cycloaddition Reactions