Enhanced Triplet–Triplet Energy Transfer and Upconversion Fluorescence through Host–Guest Complexation

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Ⓢ *Supporting Information*

ABSTRACT: Perylene-tethered pillar[5]arenes and C_{60}–boron-dipyrromethene (BODIPY) dyads were synthesized acting as emitters and organic triplet photosensitizers, respectively, for the purpose of improving the efficiency of triplet–triplet annihilation upconversion (TTA-UC). The photophysical properties of the sensitizers (guests) and the emitters (hosts) were not greatly influenced by the chemical modifications except for a notable decrease in the fluorescence quantum yields of the perylene emitters due to the high local concentration. The perylene-tethered pillar[5]arenes form stable 1:1 complexes with a nitrile-bearing C_{60}–BODIPY dyad, showing association constants as high as 4.0×10^4 M^{-1}. Through host–guest complexation, the efficiencies of both triplet–triplet energy transfer and TTA were significantly enhanced, which overcompensated for the loss of the fluorescence quantum yield of the emitters (hosts). Thus, an improved TTA-UC efficiency of 3.2% was observed even at a diluted concentration of 6×10^{-5} M, demonstrating for the first time the effectiveness of the supramolecular motif for enhancing TTA-UC without varying the inherent photophysical properties of sensitizers and emitters.
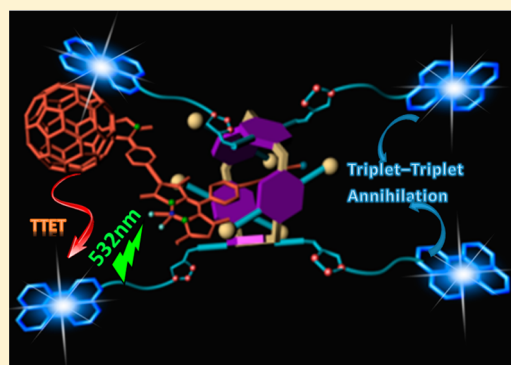
INTRODUCTION

Studies on triplet–triplet annihilation (TTA)-based upconversion (UC) have recently attracted increasing attention from researchers in various fields, such as solar cells,[1] photocatalysis,[2] bioimaging,[3] and optical oxygen sensors.[4] TTA-based UC systems demonstrate several advantages in efficient light-harvesting of incoherent visible/near-IR light[5] and high UC quantum yields,[6] while also allowing for facile tuning of absorption and emission photoenergy profiles by rational design of the photosensitizers and acceptors.[7] In general, a TTA-UC process comprises intersystem crossing (ISC) of sensitizers excited by a low-energy photon (Figure 1, left), triplet–triplet energy transfer (TTET) from the sensitizers to the emitters or acceptors and the triplet–triplet annihilation (TTA) of two sensitized emitters to produce one singlet excited state emitter, which finally emits upconverted fluorescence.[8]

As illustrated in Figure 1a, both TTET and TTA processes, pivotal in TTA upconversion, follow the Dexter energy transfer mechanism. The components involved must diffuse within a distance smaller than the Dexter radius during their excited triplet lifetimes to complete the energy transfer.[8g] Previous efforts to achieve and improve TTA-UC have been devoted to elongating the triplet-state lifetimes of the components, improving the light-absorption features of the sensitizers and increasing the energetic matching between the donor and the acceptor.[9] A variety of photosensitizers with optimized

photophysical properties, such as Pt–Pd(II) porphyrin complexes,[3,7a,10] Ru(II),[11] Pt(II),[12] Ir(III),[6b,13] Re(I),[14] and Cu(I)[15] complexes, and organic triplet sensitizers,[16] have been employed for generating TTA-UC. The metal-coordinated sensitizers are the widest studied and have met significant success, affording UC quantum yields up to 20%.[8b] Recently, heavy atom-free light-harvesting fullerene dyads have been explored as universal organic triplet photosensitizers for TTA-UC.[16e,f,h] This kind of photosensitizer is attractive as it does not possess a heavy atom and the triplet energy centered on the C_{60} unit is highly predictable. We first explored triphenylamine ethynyl C_{60}–boron-dipyrromethene (BODIPY) dyads as heavy atom-free organic triplet photosensitizers and observed 0.18%–0.36% UC quantum yields at annihilator concentrations of 3.3×10^{-4} M.[16h] The large size of the C_{60}-based sensitizers, which causes relatively low diffusion rates in solution, is partially responsible for the poor UC quantum yields. A high concentration of both sensitizers and donors is generally required in order to improve the collision probability among the components, leading such systems to inevitably suffer from serious inner-filter effects.[12e,17,18]

Compared to efforts focused on tuning the inherent photophysical properties of the components, the development
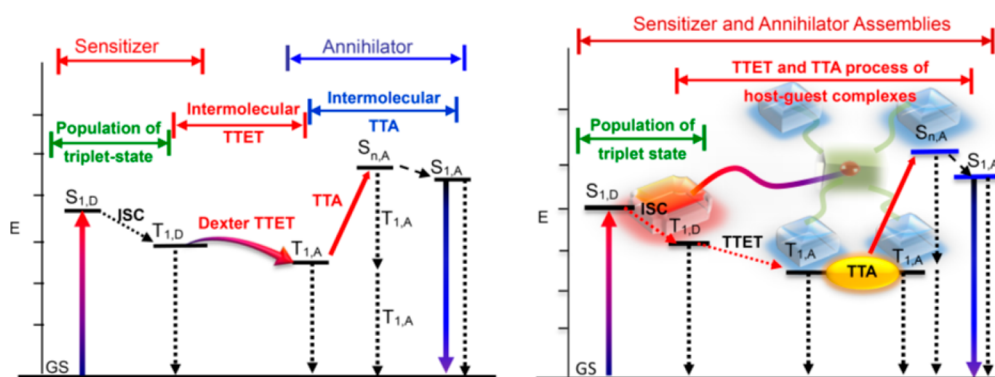
Figure 1. Schematic illustration of (a) a conventional TTA-UC process and (b) TTA-UC through host–guest complexation. GS represents the ground state, $S_{1,D}$ and $T_{1,D}$ represent the singlet and triplet excited states of the donor (sensitizer), respectively. ISC, TTET, and TTA represent intersystem crossing, triplet–triplet energy transfer, and triplet–triplet annihilation, respectively. $S_{1,A}$ and $T_{1,A}$ represent singlet and triplet excited states of the acceptor, respectively. The solid upward and downward arrows and the dotted downward arrows represent the absorption, emission, and nonradiative transition, respectively.

Scheme 1. (a) Chemical Structures of Sensitizers and Emitters and (b) Schematic Illustration of the Host–Guest Complexation-Facilitated TTA-UC of B-2@A-2
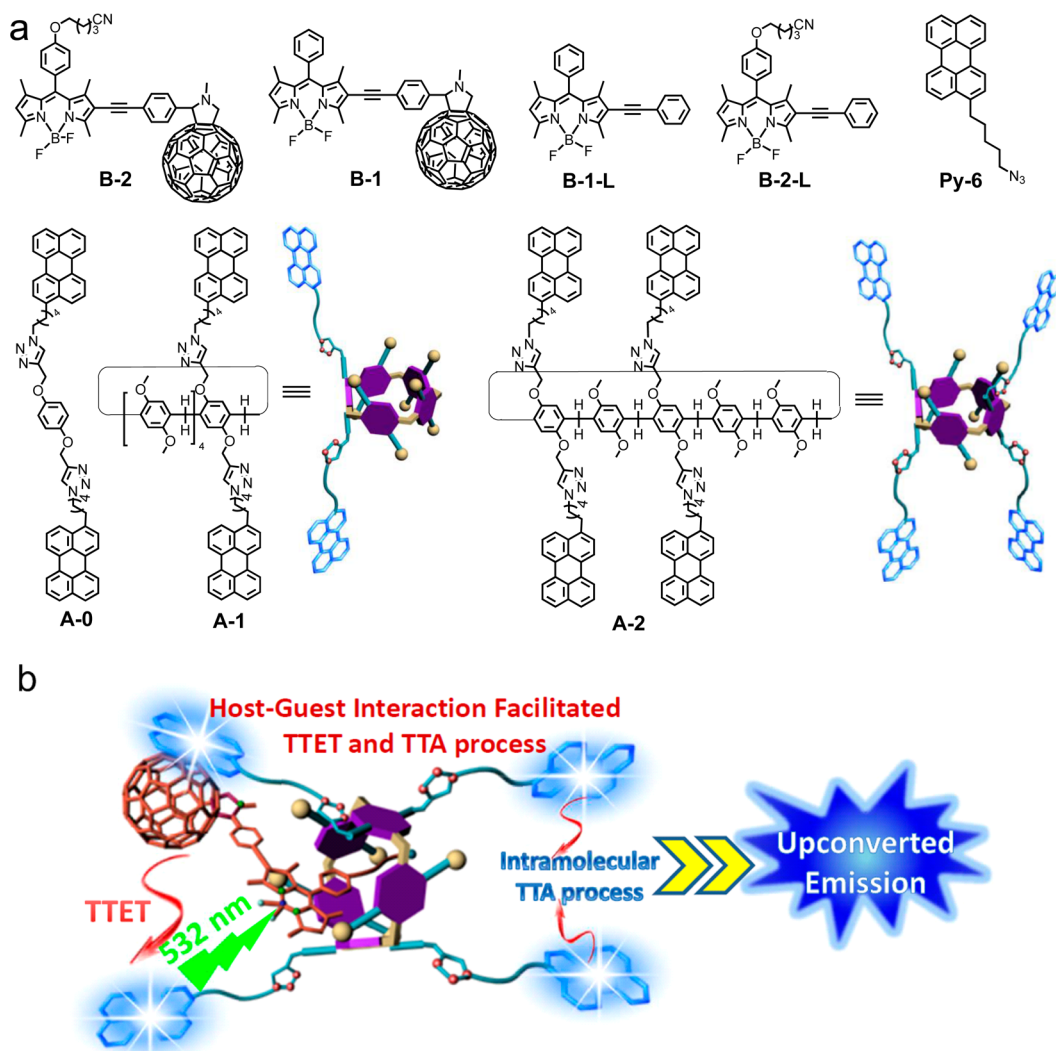
of methods for improving the TTET and TTA processes, both following the Dexter energy transfer mechanism, are still limited.[11g,12e,17] Positioning the sensitizer and annihilator in close proximity to each other in the solution was expected to improve the TTET and TTA processes, as the triplet energy loss due to molecular diffusion could be significantly reduced (Figure 1b).[11g,12e,17] Previous efforts have been devoted to improving TTET efficiency by directly connecting the
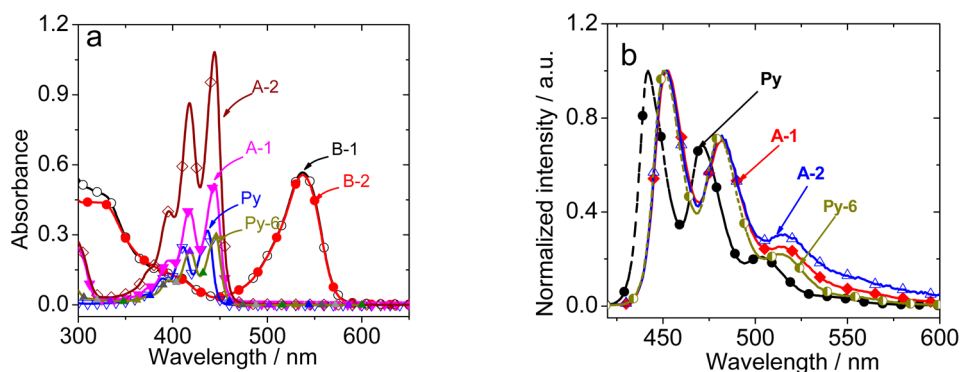
Figure 2. (a) UV−vis absorption spectra of the sensitizers (**B-1**, **B-2**) in CHCl$_3$, acceptors (**A-1**, **A-2**), and model compound (**Py**, **Py-6**) in CHCl$_3$, c = 1.0×10^{-5} M. (b) Normalized fluorescence emission spectra of **Py** (2.0×10^{-6} M), **Py-6** (2.0×10^{-6} M), **A-1** (1.0×10^{-6} M), and **A-2** (5.0×10^{-7} M), λ_{ex} = 405 nm, slit = 1.0 nm (Ex), 1.0 nm (Em), in CHCl$_3$ at 20 °C.

sensitizer and emitter through a covalent bond.[11g,12e] Such materials, however, suffer from significant back-energy-transfer processes from the acceptor to the sensitizer. Accordingly, the observed UC quantum yields were as low as 0.22% in spite of the improved TTET efficiency. More recently, MOF-based preorganized sensitizer−emitter assemblies have demonstrated success in facilitating both TTET and TTA efficiencies,[17b,c] affording UC quantum yields as high as 1.9%.[17c]

In this paper, we present a new strategy for improving TTA-UC through host−guest complexation (Figure 1b).[19] Our central hypothesis is that TTET should be facilitated by positioning the sensitizer and emitter in close proximity through host−guest complexation, and intramolecular singlet back energy transfer should be avoided because the sensitizer and the emitter are brought in close proximity by noncovalent interactions. Following this hypothesis, we designed and synthesized host molecules **A-1** and **A-2** (Scheme 1a) by grafting either two or four perylene units onto one macrocyclic compound, pillar[5]arene, a recently developed molecular host that shows versatile complexation properties and a wide range of potential applications.[20−22] Light-harvesting C$_{60}$−BODIPY dyads **B-1** and **B-2** were employed as heavy atom-free sensitizers.[16e] An alkyl nitrile chain, known to strongly bind with pillar[5]arene,[20d] was introduced onto the *meso* phenyl moiety of BODIPY in **B-2**, so as to act as the binding site with pillar[5]arene. We envisioned that the supramolecular complexation between the sensitizer and emitter would significantly facilitate the TTET process (Scheme 1b). Moreover, the perylene units displayed on the same host should lead to intramolecular annihilation, allowing for efficient TTA even at concentrations below 10^{-5} M (Scheme 1b). A control compound, **Py-6**, which features a perylene group functionalized with an alkyl azide chain was also constructed.

■ RESULTS AND DISCUSSION

As shown in Figure 2, **A-1**, **A-2**, and **Py-6** showed slightly bathochromically shifted absorption (λ_{max} = 444 nm) and fluorescence spectra (λ_{em} = 449−451 nm) relative to perylene itself (**Py**, λ_{abs} = 437 nm, λ_{em} = 442 nm), presumably due to influences from the alkyl group substituent.[23] The molar extinction coefficients (ε) of **A-1** and **A-2** were higher than that of **Py-6** by factors of two and four, respectively, exactly proportional to the number of perylene units tethered onto the pillar[5]arenes. This indicates that there is no strong interaction between the perylene units in the ground state.

The fluorescence quantum yield of **A-1** in dichloromethane is 46.4% (Table 1), much lower than that of **Py-6** (78.2%) and **Py**

Table 1. Photophysical Parameters of BODIPYs and Perylenes[a]

	λ_{abs} (nm)	ε^{b} (M^{-1} cm^{-1})	λ_{em} (nm)	Φ_{F} (%)	τ_{F}^{f} (ns)	τ_{T}^{g} (μs)
B-1-L	536	62000	572	92.7^{c}	3.78	
B-2-L	537	61000	572	86.7^{c}	3.48	
B-1	538	56600	563	0.25^{d}	2.28	29.3
B-2	537	55500	563	0.17^{d}	1.52	30.5
A-1	444	52000	452	46.4^{e}	3.20	
A-2	444	110000	455	23.2^{e}	2.30	
Py	437	32000	442	73.3^{e}	4.40	
Py-6	444	29600	452	78.2^{e}	4.40	
A-0	444	51400	451	54.8^{e}	3.55	

[a]In chloroform at 1×10^{-5} M. [b]Molar extinction coefficient at the absorption maxima. [c]Fluorescence quantum yields estimated using BODIPY as the standard (Φ = 72.0%). [d]Iodo-BODIPY as the standard (Φ = 2.7%). [e]Absolute fluorescence quantum yields. [f]Fluorescence lifetimes. [g]Triplet state lifetimes, measured by transient absorptions.

(73.3%). Moreover, **A-2**, which bears four perylene units, shows an even lower quantum yield of 23.2%. The extremely high local concentration of perylene in **A-1** and **A-2** leads to significantly greater collisional quenching and, thus, decreasing fluorescence quantum yields in accord with the increasing number of perylene units.[17c] This is supported by the decreased decay times when the number of perylene units increased; **Py-6**, **A-1**, and **A-2** show lifetimes at 450 nm of 4.4, 3.2, and 2.3 ns, respectively. The inner filter effect is not evident since the relative intensities of the first and second vibrational bands of fluorescence emission for **A-1** and **A-2** are almost identical to that of **Py-6** (Figure 2b). Interestingly, the normalized fluorescence spectra of **A-1** and **A-2** show relatively stronger emission in the range of 550−600 nm. The differential fluorescence spectra between normalized **A-1** or **A-2** and **Py-6** afforded broad and unstructured spectra in the range of 490−600 nm (Figure S48d). Moreover, the fluorescence decay at 540 nm showed two components of 3.2 and 16.2 ns for **A-1** and 2.3 and 16.7 ns for **A-2** (Figure S49). The longer decay times were assigned to the excimer fluorescence, which also caused quenching of the monomer fluorescence of perylene.

The absorption maxima and extinction coefficients for **B-1** and **B-2** were almost identical, suggesting that the presence of the nitrile side chain hardly influenced the absorption
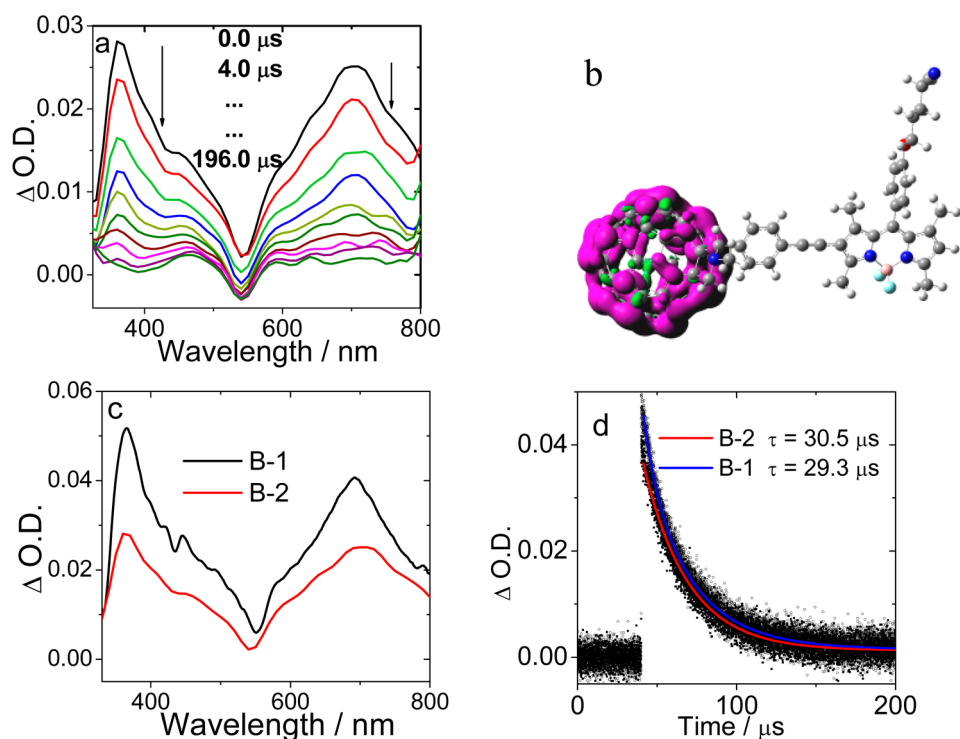
Figure 3. (a) Nanosecond time-resolved transient difference absorption spectra of **B-2** (λ_{ex} = 532 nm); (b) spin-density surface of **B-2** at the triplet excited state. Calculated at B3LYP/6-31G level with Gaussian 09W.[26] (c) The comparison of the transient difference absorption spectra of **B-1** and **B-2** and (d) decay traces of the transient absorption of **B-1** and **B-2** at 700 nm. [sensitizer] = 1.0×10^{-5} M in deaerated CHCl$_3$, 20 °C.

properties of these sensitizers. Both **B-1** and **B-2** showed negligible fluorescence from the BODIPY unit with fluorescence quantum yields Φ_F < 0.25% (Table 1) and weak fluorescence at 710 nm assignable to the emission of C$_{60}$ (Figures S39 and S40).[24] The control compounds without C$_{60}$, **B-1-L** and **B-2-L**, however presented significantly high fluorescence quantum yields of >87%. These results indicate an efficient intramolecular singlet energy/electron transfer from BODIPY to the C$_{60}$ unit,[25] with a quantum yield close to 100%.[16e] Moreover, the nanosecond time-resolved transient difference absorption spectra of **B-2** (Figure 3a) showed only the characteristic absorption of the triplet excited state of C$_{60}$ at 360 and 700 nm. No significant bleaching of BODIPY was observed, suggesting that the triplet excited state of **B-2** was located on the C$_{60}$ moiety. This is consistent with the results from density functional theory studies,[16e,26] which demonstrated that the spin densities of electronically excited **B-2** localized exclusively on the C$_{60}$ moiety, with negligible electron spin density around the BODIPY antenna (Figure 3b and Figure S43[24]).

The host–guest complexation between perylene-tethered pillar[5]arenes and sensitizers was studied by spectroscopic methods. Addition of **A-1** or **A-2** to solutions of **B-2** led to an apparent increase in the main absorption band (λ_{max} = 536 nm) of BODIPY (Figures S53,S54).[24] Job's plots based on the continuous variation method showed that the maximum UV–vis changes at 0.5 molar fraction, demonstrating a 1:1 complexation stoichiometry (Figures S50,S51).[24,27] The 1:1 association constants (K_a) were 3.7×10^4 M^{-1} for **B-2/A-1** and 4.0×10^4 M^{-1} for **B-2/A-2** (Table 2), both of which are slightly higher than the association constant for complexation between **B-2** and pillar[5]arene (2.9×10^4 M^{-1}). The significantly stronger complexation of **B-2** versus **B-1** with pillar[5]arene,

Table 2. K_a Values for 1:1 Complexation between BODIPYs and Pillar[5]arenes[a]

	K_a (10^2 M^{-1}) (population of 1:1 complex)[b]		
	B-2-L	**B-1**	**B-2**
A-1	190 (33.6%)	9.8 (2.83%)	370 (48.2%)
A-2	189 (33.2%)	13 (3.71%)	400 (50.0%)
pillar[5]arene	200 (33.9%)	c	290 (42.7%)

[a]Measured in chloroform at 20 °C, error < 10%. [b]Calculated based on the K_a values obtained at 25 °C at [guests] = 1×10^{-5} M and [hosts] = 3×10^{-5} M. [c]Not determined due to weak complexation.

representative of the typical association strength of an alkyl nitrile to a pillar[5]arene,[20d,e] could be ascribed to multiple dipole–dipole and C–H···π interactions as well as hydrogen bonding. Relatively weak complexation (K_a = 1.9×10^4 M^{-1}) was observed between **A-1** and **B-2-L**, indicating the existence of additional interactions from the C$_{60}$ component, presumably due to π–π interactions between the perylenes and C$_{60}$. The slightly improved K_a found with **B-2/A-2** versus **B-2/A-1** suggests that the additional perylene units are also involved partially in the complexation. On the other hand, **B-1** afforded weak complexation with both **A-1** (K_a = 9.9×10^2 M^{-1}) and **A-2** (K_a = 1.3×10^3 M^{-1}), but no apparent complexation could be seen with pillar[5]arene, providing further demonstrates that the interaction between C$_{60}$ and the perylene units plays a role in the complexation between the sensitizers and hosts.

Such strong binding between **B-2** and **A-1** and **A-2** guaranteed a high complexation ratio even at low concentrations of sensitizers and acceptors. For example, at [**B-2**] = 1×10^{-5} M and [**A-2**] = 3×10^{-5} M, a very low concentration condition for TTA-UC, 50% of the **B-2** exists as a 1:1 complex with the pillar[5]arene host (Table 2). This should allow for
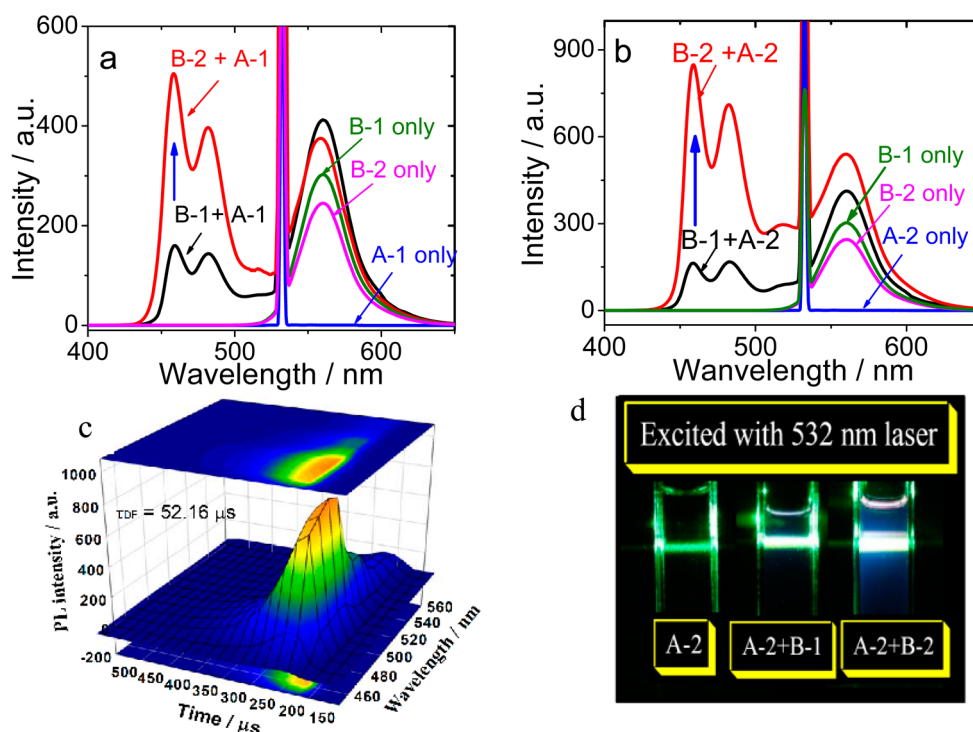
Figure 4. TTA-UC fluorescence with **B-1** and **B-2** as the triplet photosensitizers (1×10^{-5} M) and (a) **A-1** and (b) **A-2** as the acceptors (3×10^{-5} M), measured in $CHCl_3$ and excited with a CW laser (532 nm, 170 mW/cm^{-2}) at 20 °C. (c) Time-resolved emission spectra (TRES) of the upconverted fluorescence of **A-1** using **B-2** as the triplet photosensitizer. (d) Photographs of the emission of the acceptor **A-2** alone and in the presence of sensitizers **B-1** and **B-2**.

efficient TTET from the sensitizer to the acceptor to occur due to their close proximity to each other.

The TTETs were investigated based on the variation in triplet lifetimes for **B-1** and **B-2** with changes in the concentration of the acceptors. **B-1** exhibited similar transient absorption spectrum to that of **B-2**, confirming that the nitrile group essentially did not alter the triplet state localization (Figure 3c). The triplet state lifetimes of **B-1** and **B-2** were determined as 29.3 and 30.5 μs, respectively. Increasing the concentration of **A-1** and **A-2** led to a progressive decrease of the triplet lifetimes for **B-1** and **B-2** (Figure S58)[24] due to TTET from the sensitizers to the emitters. It should be noted that the TTET should be a mixture of dynamic and static quenching processes among free and complexed sensitizers and emitters (Figure S75),[24] in which static quenching should hardly change the lifetime of the sensitizer. The Stern−Volmer analysis of the lifetime quenching data shows an approximately linear relationship (Figure S59).[24] The observed k_q values derived from the Stern−Volmer plots of **B-1** are comparable for **A-1** and **A-2** (($0.96−0.97) \times 10^9$ M^{-1} s^{-1}), while the nitrile-bearing **B-2** gave higher observed k_q values of (1.24 and $1.38) \times 10^9$ M^{-1} s^{-1}, respectively, presumably due to the higher local concentration caused by host−guest interaction.

The TTA-UC efficiencies in the supramolecular assemblies of **B-2** with **A-1** and **A-2** were studied by fluorescence measurements. **A-1** or **A-2** alone produces no emissions when photoirradiated with a 532 nm laser. The addition of the sensitizers **B-1** and **B-2**, however, led to an apparent anti-Stokes fluorescence ranging from 420 to 530 nm, in addition to the prompt fluorescence of the sensitizers in the range of 530−700 nm (Figure 4a,b). Time-resolved emission spectra (TRES) of **A-1/B-2** showed exceptionally long-lived emission (Figure 4c) versus a 3.2 ns lifetime of the prompt fluorescence of **A-1**

without **B-2**.[11f,16c] The fluorescence intensity increased with the laser power (Figures S62−S65),[24] and followed a quadratic dependence, suggesting a two-photon process. These results unambiguously demonstrated the TTA-UC nature of the observed blue emission.

Intriguingly, the UC fluorescence intensity was evidently higher with **B-2** versus **B-1**. For example, at the diluted concentration of [sensitizer] = 1×10^{-5} M and [emitter] = 3×10^{-5} M, the UC intensity of **B-2** is about 2.8-fold greater than the value observed with **B-1** when using **A-1** as the acceptor (Figure 4a). A more apparent enhancement as high as 4.6 times was seen for **B-2** over **B-1** when using **A-2** as the acceptor (Figure 4b). In fact, the enhancement is so enormous that upconversion emission with different sensitizers is readily distinguishable with the unaided eye (Figure 4d). The much stronger upconversion fluorescence observed with **B-2** over **B-1** clearly demonstrates the effectiveness of supramolecular complexation. The efficiency of TTA-UC fluorescence is an accumulative result of the efficiencies of all of the processes involved in the upconversion, including the quantum yields of intersystem crossing (Φ_{ISC}), TTET (Φ_{TTET}), and TTA (Φ_{TTA}) and the fluorescence emission of the emitter (Φ_F, eq 1).[8b] The 2.8-fold higher Φ_{UC} of **B-2/A-1** versus **B-1/A-1** should arise principally from the greater Φ_{TTET} value, because of the very similar Φ_{ISC} between **B-1** and **B-2** (Table 1) and same Φ_F and Φ_{TTA} due to same emitter. Likewise, **B-2/A-2** should possess a Φ_{TTET} 4.6-fold higher than **B-1/A-2**, demonstrating the significant role of host−guest complexation in improving the energy transfer efficiency from sensitizer to emitter.

$$\Phi_{UC} = \Phi_{ISC}\Phi_{TTET}\Phi_{TTA}\Phi_F \tag{1}$$

The **A-2/B-2** system displayed higher TTA-UC than **A-1/B-2** (Figures S60,S61),[24] despite the fact that **A-2** possesses a
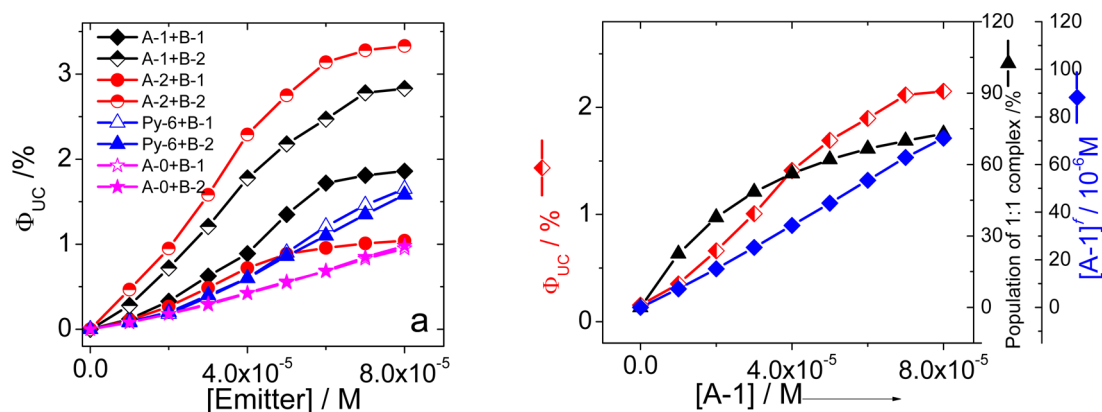
Figure 5. (a) TTA-UC quantum yields of **B-1** and **B-2** in the presence of different acceptors as a function of the concentration of acceptors. (b) TTA-UC quantum yield of **B-2** and **A-1** (red), population of 1:1 complex (black) and the concentration of free **A-1** (blue) as a function of the concentration of **A-1**. Solutions of sensitizers (1×10^{-5} M) and acceptors in $CHCl_3$ were irradiated with a CW laser (λ_{ex}= 532 nm, 170 mW/cm^{-2}).

comparable association constant and a much lower fluorescence quantum yield relative to that of **A-1**. This result implies that the TTET and TTA are improved further with **A-2**, thus compensating for the reduced fluorescence quantum yield.

The fluorescence intensity of **A-1** and **A-2** decreased when **B-1** or **B-2** was added (Figures S46,S48, Table S1).[24] For both **A-1** and **A-2**, however, increasing the concentration of **B-1** resulted in a decrease of emission essentially comparable to that found by increasing the concentration of **B-2** (Figures S47,S49).[24] This suggests that the supramolecular complexation does not seem to improve the back energy transfer from the excited singlet acceptor to the sensitizer, which could be rationalized by the weak absorption of **B-1** and **B-2** at the fluorescence emission bands of **A-1** and **A-2**. The emission decrease caused by **B-1** and **B-2** should be ascribed mainly to the absorption of excitation light as well as the emission of the emitters by **B-1** and **B-2**. This is validated by the fact that the fluorescence decay times of **A-1** and **A-2** were almost unchanged when adding **B-1** or **B-2** (Figure S44, 45, Table S1).

As noted earlier, a relatively high concentration of acceptor ($10^{-2}-10^{-4}$ M) is generally required to maximize performance of TTET, and consequently upconversion quantum yield, at the cost of serious inner filter effects.[12e,17b,18] The present supramolecular systems, in contrast, allow for good TTA-UC quantum yields at dilute concentrations. As shown in Figure 5a, all emitters showed an increase in TTA-UC emission with a corresponding increase in the concentration of emitter. The TTA-UCs of **A-1** and **A-2** with **B-2** are significantly higher than **A-1** and **A-2** with **B-1**, and even higher than **A-0** and **Py-6** with **B-1** or **B-2**. This corresponds well with the order of host–guest complexation strength, further confirming the critical role of supramolecular assembly.

The TTA-UC quantum yields of **A-1**/**B-2** increased when the concentration of **A-1** was increased and reached a value of 3.2% when the concentration of **A-1** was 6.0×10^{-5} M, which is much lower than the concentration commonly used for TTA-UC.[12e,18] The quantum yields did not change significantly upon further increasing the concentration of **A-1**. Similar results were observed when **A-2** was used as an acceptor (Figure S74).[24] Almost no inner filter effects could be observed under the investigated concentration range (Figures S66−S69).[24] The higher quantum yields at lower concentration further confirmed the significance of supramolecular complexation for the TTA-UC efficiency, particularly when taking the much lower

fluorescence quantum yields of **A-1** and **A-2** into consideration. However, the increasing trends of the TTA-UC quantum yields with the emitter concentration did not completely coincide with the increasing population of the 1:1 complex. As exemplified in Figure 5b, the increase of TTA-UC did not completely coincide with the ratio of **B-2@A-1** or with the concentration of free **A-1**. The same was true in the **B-2**/**A-2** system (Figure S74). This could be rationalized by the fact that the 1:1 complex was not the only origin of the TTA-UC. Besides the doubly photoexcited process within the **B-2@A-1** complex (route 1, Figure S75), TTA between two different **B-2@A-1**, **B-2@A-1** and **A-1**, and two **A-1** (routes 2−4, Figure S75)[24] also should contribute jointly to the generation of TTA-UC. The supramolecular complexation should at least be partially responsible for the improvement in TTA-UC efficiency of routes 1−3 (Figure S75).[24]

It is interesting to note that the increasing trends of Φ_{UC} are gradual at the low concentration range of **A-1** but become more steep as the concentration of **A-1** becomes larger than 2×10^{-5} M, finally showing saturation at 6×10^{-5} M (Figure 5b, red line). This sigmoid-like change is different from the fast increase at the low **A-1** concentration range observed in the complexation curve (Figure 5b, black line), clearly demonstrating that more than one mechanism is involved in the Φ_{UC} curve. With the increase in complexation, contributions from TTA between triplet **B-2@A-1** and other intermolecular processes (routes 2−4 in Figure S75)[25] should become more and more evident, thus accounting for the steeper increase in Φ_{UC} at higher concentrations of **A-1**. Reasonably optimizing the complexation affinity, the distance of emitters in the same host, and the number of sensitizers to complex with the acceptors should lead to further improvements in TTA-UC efficiency for the supramolecular system.

■ CONCLUSIONS

In conclusion, we established a supramolecular complexation-based strategy for improving the efficiency of TTA-UC in the solution phase. The host–guest complexation facilitated the TTET and TTA processes between the sensitizers and emitters, and the TTA-UC intensity was significantly enhanced. A Φ_{UC} as high as 3.2% was observed even at the very low acceptor concentration of 6×10^{-5} M, which successfully avoided undesired inner filter effects. This work opens a new window for improving TTA-UC efficiency without changing the

inherent photophysical properties of the sensitizers and emitters. Further improvement in the TTA-UC by optimizing these procedures is in progress.

■ EXPERIMENTAL SECTION

Synthesis and structural characterization data of the organic triplet photosensitizers and pillararene-based triplet acceptors/hosts are presented in Supporting Information. A diode pumped solid state (DPSS) laser (532 nm) and a nanosecond pulsed OPO laser, which was synchronized with the spectrofluorometer, was used for the upconversion measurements. The samples were purged with Ar for at least 15 min before measurement, and the gas flow was maintained during the measurement (NOTE: the upconversions are sensitive to O_2). The upconversion quantum yields (Φ_{UC}) were determined with the prompt fluorescence of B-1 (Φ_F = 0.25% in $CHCl_3$) as the standard. All of the values were measured in three independent runs. The transient absorption of the sensitizers was measured with an Edinburgh LP920 laser flash photolysis instrument. For detailed experiment setups, please refer to the Supporting Information.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/jacs.6b07946.

> Detailed experimental procedures, the syntheses and characterization of compounds, host−guest complexation and photophysical characterization data (PDF)

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Notes
The authors declare no competing financial interest.

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■ REFERENCES

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