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A Review of Visible-to-UV Photon Upconversion Systems Based on Triplet–triplet Annihilation Photon Upconversion

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ABSTRACT

Due to the tunable spectrum range and potential application under non-coherent solar irradiation, triplet-triplet annihilation based molecular photon upconversion (TTA-UC) systems represent a compelling study field for a variety of photonic implementations. There were studies on the incorporation of TTA-UC technology with photovoltaic technology, which made it possible to further improve the energy harvest performance through the utilisation of the wasted spectrum. However, many TTA-UC studies are limited to energy upconversion within the visible spectrum range. For photovoltaic cells with a higher band gap, which harvest the higher energy spectrum (UV region), an efficient Vis-to-UV upconversion is preferred. The Vis-to-UV TTA-UC system was first introduced in 2006. Recently, more studies were conducted to discover the Vis-to-UV upconversion system with high quantum efficiency and low excitation intensity such as the nanocrystal sensitizer-based system and the thermally activated delayed fluorescence sensitizer-based system. Recent studies in the solvent system of Vis-to-UV upconversion system had demonstrated the dependence of the couple photostability on the solvent and extended the solvent selection to inorganic solvent. In this review, we are reviewing the research background of the Vis-to-UV TTA-UC system and discussing the current challenges and potential developments in this research area.

Keywords: Fluorescence, sensitizer-annihilator, triplet-triplet annihilation based molecular photon upconversion (TTA-UC), upconversion system, Vis-to-UV

1. INTRODUCTION

With the global awareness of carbon neutral energy production for environmental sustainability, photovoltaic (PV) technology had received significant attention as a potential approach to sustainable energy production [1]. As compared with other renewable energy sources [2] and fossil-based conventional energy sources, solar energy is rather abundant, delivering several kilowatt-hours per square meter on a daily basis [3]. There are different types of PV technologies: crystalline silicon (Si) cells, perovskite cells, dye-sensitized solar cells (DSSC) [4,5,6,7,8], thin film cells, organic cells, and inorganic cells.

A perovskite material such as strontium titanate requires a higher energy photon due to its large bandgap, where it requires light from the UV region, and it only consists of 7% of the solar spectrum. It indicates that the rest of the spectrum, including visible and infra-red regions, is not utilized. Due to the performance limitation of the active material to utilize spectrum with photon energy below its energy bandgap, the photon conversion performance of single-junction photovoltaic systems is restricted to the Shockley-Queisser limit [3,4]. Hence, there is a trade-off

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between using a wider solar spectrum and having a large open circuit voltage. Even though the metal halide perovskite offers a wider absorption spectrum into the visible light region, it exhibits low chemical resistance.

The incorporation of an upconverter system that could upconverts lower energy photons into higher energy photons appear to be a potential solution to widen the absorption spectrum of the photovoltaic system [3,5]. The most studied upconverter system is constructed based on lanthanide materials, with reported upconversion efficiencies of 3–5% under monochromatic irradiation [12]. However, lanthanide-based upconverter systems possess the limitation of a very small absorption spectrum and high excitation intensities. The triplet–triplet annihilation upconversion (TTA-UC) system with broader absorption bands and lower excitation intensities appeared as an alternative solution.

However, many TTA-UC studies are primarily focused on energy upconversion within the visible spectrum range. For photovoltaic cells with a higher bandgap, which harvest the higher energy spectrum (UV region), an efficient Vis-to-UV upconversion is preferred. In this review study, we are reviewing the research progress of the Vis-to-UV TTA-UC system and discussing the challenges and future directions in this research field.

2. MOLECULAR TTA-UC

A triplet state is an excited quantum state in which two electrons in different molecular orbitals have the same spin. In a TTA-UC scheme, a sensitizer serves as a donor while an annihilator serves as an acceptor. Through the spectrum irradiation within the absorption spectrum range of the sensitizer, a ground (^DS_o) state sensitizer absorbs a photon with lower energy, which then becomes the singlet excited sensitizer ($^DS_1{}^*$). The singlet excited sensitizer immediately transforms into the triplet excited sensitizer ($^DT_1{}^*$) via intersystem crossing (ISC) process. ISC is a nonradiative process involving an electronic state transition from an excited singlet state into an excited triplet state, where a little energy must be lost during the process. Through the process of triplet-triplet energy transfer (TTET), the sensitizer then transfers the triplet state energy to the annihilator, creating a ground state sensitizer (^DS_o) and a triplet excited annihilator ($^AT_1{}^*$). By complying with the spin statistical law, a singlet excited annihilator ($2{}^AT_1{}^* = {}^AS_1{}^*$) molecule with higher energy will be produced through the phenomenon of triplet-triplet annihilation (TTA). It occurs during the collision of two excited triplet state annihilator ($^AT_1{}^* \leftrightarrow {}^AT_1{}^*$) molecules. The radiative disintegration of the annihilator in a singlet excited state ($^AS_1{}^*$) results in the emission of anti-Stokes upconverted fluorescence, where the energy of the upconverted emission is higher than the excitation spectrum absorbed by the sensitizer. The upconversion process results in the anti-Stokes delayed fluorescence. The Jablonski diagram of the TTA-UC system is illustrated in Figure 1.

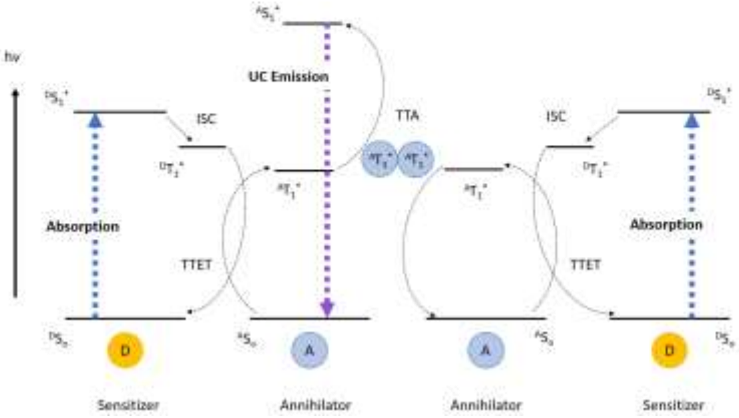

Figure 1. Jablonski diagram for the demonstration of TTA-UC system.

2.1 Stokes Shift

The Stokes shift is defined as the variance between the band maxima positioned in the absorption and emission spectra, which displays the energy difference between the incident and emitted photons. Rayleigh scattering occurs when there is no energy variance between an absorbed photon and an emitted photon. When the emitted photon exhibits energy below the incident photon, this energy variance is called a Stokes shift. An anti-Stokes shift (ΔE_{UC}) occurs while the emitted photon possesses higher energy than the incident photon. In the study of upconversion systems, the anti-Stokes shift (ΔE_{UC}) is an essential parameter to determine the excitation wavelength of the donor and the upconverted emission wavelength of the acceptor.

2.2 Upconversion Properties

Triplet energy transfer is a process involving the exchange of energy and spin between a couple of triplet excited molecules *via* the Dexter energy transfer (DET) mechanism [7,8]. DET only occurs at a short donor-acceptor distance (within 10 A°), whereby the DET rate decays at an exponential gradient as the donor-acceptor width increases. In the TTA-UC system, the distance between the chromophores must be within 10 A° to ensure an effective DET performance. The correlation of the DET rate (k_{ET}) with the donor-acceptor width is shown in Equation (1).

$$k_{ET} \propto J_{exp}[\frac{-2r}{L}] \tag{1}$$

where L represents the total of the donor-acceptor van der Waals radii, r represents the donor-acceptor width, and J represents the spectral overlap integral between the normalized emission spectrum of the donor and the absorption spectrum of the acceptor as defined in Equation (2).

$$J = \int f_D(\lambda)\varepsilon_A(\lambda)\lambda^4 \, d\lambda \tag{2}$$

where λ represents the spectrum wavelength, ε_A represents the molar attenuation coefficient at that wavelength and f_D represents the fluorescence spectrum of the donor. For an efficient spectral overlap of an electron exchange to happen, an optimal donor-acceptor distance (r < 1 nm) is required [8,9].

Based on the research in [9] and [10], the quantitative TTA performance in terms of excitation intensity dependence was determined through the threshold excitation intensity (I_{th}). The I_{th} the value represents the transition excitation intensity of the upconversion system from quadratic to linear dependence, which is used to define the optimum incident excitation range. During the excitation irradiance with a weak intensity, the upconverted fluorescence intensity will show a quadratic regime. As the incident excitation intensity increased above the I_{th}, the excitation intensity dependence changed into a linear regime, where the upconversion efficiency was approaching its maximum. In this situation, TTA serves as the main $^{A}T_1^*$ decay channel, where the spontaneous decay rate of $^{A}T_1^*$ approaches the TTA rate. The I_{th} was defined as Equation (3):

$$I_{th} = (\alpha \Phi_{ET} 8\pi D_T a_0)^{-1} (\tau_T)^{-2} \tag{3}$$

where α represents the attenuation coefficient under the excitation wavelength, Φ_{ET} represents the sensitizer-annihilator TTET efficiency, D_T represents the diffusion constant of annihilator triplets, a_0 represents the annihilation distance between annihilator triplets and τ_T represents the lifetime of the annihilator triplet. The τ_T is determined from the decay time of the UC emission with the consideration of the dependence of each parameter in Equation (4) in a longer time period, where the annihilation efficiency becomes insignificant when compared with the spontaneous decay of the triplets. With the double logarithmic plot of upconverted fluorescence intensity against the excitation intensity, the I_{th} can be experimentally calculated through the crossing section of the slopes between the quadratic and linear gradients.

$$I_{UC}(t) \propto exp\left(^{-t}/_{\tau_{UC}}\right) = exp(^{-2t}/_{\tau_T}) \tag{4}$$

The TTA-UC quantum yield (Φ_{UC}) was obtained to quantify the efficiency of the TTA-UC system, where it correlates with the ISC yield of a sensitizer (Φ_{ISC}), sensitizer to annihilator triplet energy transfer (Φ_{ET}), statistical probability to produce an excited singlet after TTA (f), annihilator-annihilator TTA (Φ_{TTA}) and fluorescence of an annihilator (Φ_{FL}). The Φ_{TTA} represents the ratio of annihilator triplets involved in the TTA-UC system to the total sensitizer triplets, which was commonly considered to be 1 in a concentrated regime. The Φ_{UC} was defined as Equation (5):

$$\Phi_{UC} = \frac{1}{2} f \Phi_{ISC} \Phi_{ET} \Phi_{TTA} \Phi_{FL} \tag{5}$$

$$\eta_{UC} = \Phi_{UC}' = 2 \times \Phi_{UC} \tag{6}$$

Based on Equation (5), the maximum theoretical quantum yield obtained is 50 %. To obtain the maximum quantum yield of 100 %, since an upconverted photon is produced from the absorption of two lower energy photons, Equation **Error! Reference source not found.** is defined through the multiplication of Equation **Error! Reference source not found.** with a factor of 2 [17]. To avoid confusion, Φ_{UC} is used for the evaluation of quantum yield in this review.

3. DEVELOPMENT HISTORY OF MOLECULAR TTA-UC

In 1962, the concept of a sensitizer-annihilator upconversion system that generates anti-Stokes fluorescence was first introduced in [18]. A couple of phenanthrene/ naphthalene and a couple of proflavine hydrochloride/ anthracene in ethanol exhibited delayed fluorescence with the UC performance of ΔE_{UC} = 0.21 eV (362 nm to 322 nm) and ΔE_{UC} = 0.24 eV (436 nm to 402 nm), respectively. The obtained quantum efficiency of the couples were ~1 % and 0.1 %, respectively. However, the couples showed the phenomenon at -72 ± 3 °C and -66 ± 3 °C. The molecules that are performable under ambient temperature have become the main challenge for the development of the TTA-UC system.

The first discovery of a room temperature TTA-UC system was reported in [8] and [13]. By introducing the Pd(II) octaethylporphyrin as the dopant in the poly(9,9-bis(2-ethyl-hexyl)fluorene) ($PF_2/6$) solid film, it emitted upconverted emission of ~450 nm (blue) under the excitation irradiance at 532 nm (green) with relatively high intensity (13.5 kw/ cm^{-2}). In 2006, the demonstration of the excitation irradiance of noncoherent sunlight on TTA-UC system was demonstrated in [20], where the couple of Pd(II)octaethylporphyrin (PdOEP)/ diphenylanthracene (DPA) emitted the blue upconverted fluorescence when excited with the low intensity (10 W cm^{-2}) of noncoherent green solar spectrum. The low excitation intensity initiated the future direction of the TTA-UC system in its incorporation with the solar system under standard AM 1.5 solar irradiance.

The TTA-UC system is applied in several other fields in addition to photovoltaic systems, such as photocatalysis, bioimaging, sensing, theranostics, and optogenetics. However, more studies are needed to determine the viability of these applications because there are still challenges to be resolved before the TTA-UC system can be widely utilized in these applications. Recent studies had expanded the upconversion range from Vis-to-Vis to NIR-to-Vis and Vis-to-UV. The UC performance of the Vis-to-UV TTA-UC systems is summarized in Table 1, with regard to the couple design, ΔE_{UC}, Φ_{UC} and I_{th}.

Table 1 Vis-to-UV molecular TTA-UC systems along with their respective UC performance

Sensitizer	Annihilator	Solvent/ Solid State	UC Range (nm)	ΔE_{UC} (eV)	I_{th} (mW cm^{-2})	Φ_{UC} (%)	Ref.
$Ir(ppy)_3$	Pyrene	Dichloromethane	450 to 390	0.42	-	-	[21]
2MeOTX	PPO	PMMA	450 to 350	0.79	-	-	[22]
Biacetyl	PPO	Benzene	442 to 360	0.64	-	0.58 ± 0.02	[23]
$Ir(ppy)_3$	2,7-diaryltetrahydropyrenes	Toluene	488 to 411	0.8	-	-	[24]
$Ir(C6)_2(acac)$	DBP	DMF	455 to 370	0.54	0.78	1	[25]
CdS/ZnS	PPO	Hexane	405 to 355	0.43	-	2.6 ± 0.25	[26]
$CsPbBr_3$/ 1-NCA	PPO	Hexane	443 to 353	0.7	1900	5.1	[27]
CdS/ 3-PCA	PPO	Toluene	405 to 350	0.48	0.95	10.4	[24, 25]
CdS/ 3-PCA	Naph	Toluene	405 to 320	0.81	-	0.04	[28]
4CzIPN	QP	Benzene	445 to 353	0.73	775	1.95	[29]
4CzIPN	TP	Benzene	445 to 343	0.83	1800	1.4	[29]
4CzBN	TIPS-Naph	Toluene	405 to 375	0.24	220	13.1	[28]
BN-2Cz	1,5-DTNA	Toluene	517 to 375	0.91	9.2	3.8	[30]
BN-2Cz-tBu	1,5-DTNA	Toluene	532 to 367	1.05	41.8	2.0	[30]
Irsppy	NDS	Water	447 to 321	1.09	-	0.03	[31]

4. BACKGROUND OF VIS-TO-UV MOLECULAR TTA-UC

In 2006, the upconverted emission within the UV spectrum from the couple of tris(2-phenylpyridine)iridium(III), ($Ir(ppy)_3$)/ pyrene in deoxygenated dichloromethane solvent using 450 nm light excitation was firstly demonstrated in [21]. The fluorescence spectrum of pyrene exhibits upconverted emission in the range of 360 and 420 nm, showing the $\Delta E_{\mathrm{UC}} \sim 0.42$ eV (450 nm to 390 nm). The upconverted emission in the UV region had initiated the inspiration in Vis-to-UV upconversion system based on TTA-UC.

Merkel and Dinnocenzo reported the observation of upconverted UV fluorescence (in the range of 350 nm to 380 nm) excited by blue light for the couple of 2-methoxythiox-anthone (2MeOTX)/ PPO in poly(methyl methacrylate) (PMMA) film in 2009 [22]. It is the first time that blue-to-UV TTA-UC in a polymer solid film has been discovered. It is also the first UC system that avoids the use of an organometallic sensitizer that contains heavy metals. It pioneered the solid-state Vis-to-UV TTA-UC system. It is the only solid-state Vis-to-UV TTA-UC system demonstration throughout this review.

At the same year, the low power Vis-to-UV upconversion system was firstly demonstrated, with a couple of 2,3-butanedione (biacetyl)/ 2,5-diphenyloxazole (PPO) in deoxygenated benzene solvent [23]. It was reported with ΔE_{UC} = 0.64 eV (442 nm to 360 nm) with Φ_{UC} = 0.58 ± 0.02 % under the 442 nm light excitation intensity of 0.389 W/ cm^2. The author explained the low Φ_{UC} was due to the initial sensitization TET quenching and the low Φ_{FL} of PPO.

In 2013, El-Ballouli and his co-workers reported the combination of Ir(ppy)$_3$/ 2,7-diaryltetrahydropyrenes in deoxygenated toluene, showing the result of ΔE_{UC} = 0.8 eV (488 nm to 411 nm) under moderate excitation light intensity (> 100 mW/ cm^2) [24]. Under the visible light irradiance, the selective excitation of Ir(ppy)$_3$ can occur, with the triplet state properly situated for the TET process to 2,7-diaryltetrahydropyrenes as compared with pyrene [15,18,19]. It inspired another selection of annihilator for the couple of Ir(ppy)$_3$.

A further exploration for the use of sensitized iridium complexes was conducted in 2014, for the couple of Ir(C6)$_2$(acac) (C6 = coumarin 6, acac = acetylacetone)/ 2,7-di-tert-butylpyrene (DBP) in deaerated DMF solution [25]. The author introduced a new sensitizer, Ir(C6)$_2$(acac), to resolve the significant anti-Stokes fluorescence reabsorption issue of the sensitizer, which causing the low Φ_{UC} or high excitation intensity (> 100 mW/ cm^2) [15,17,18]. The upconverted fluorescence ranging from 370 to 420 nm was generated upon the excitation at 445 nm ($\Delta E_{\mathrm{UC}} \sim$ 0.54 eV). The Φ_{UC} and I_{th} values were reported as 1 % and 0.78 mW/ cm^2, respectively. As compared with the previous studies in the field of Vis-to-UV TTA-UC, it is the first study to achieve I_{th} value that is below the solar irradiance.

The early studies in Vis-to-UV molecular TTA-UC are primarily focused on the demonstration experiments to show the potential of the TTA-UC in the Vis-to-UV upconversion. The organic triplet sensitizers in Vis-to-UV TTA-UC are mainly restricted to biacetyl [23] and iridium complexes [15,18,20], which feature several limitations such as low photoluminescence properties, triplet energy transfer quenching and reabsorption of the upconverted fluorescence. Recent development in Vis-to-UV TTA-UC studies had introduced new direction in term of new molecular design, material selection and solvent system. In the next section, the recent research direction in Vis-to-UV TTA-UC will be introduced and discussed.

5. RECENT DEVELOPMENT IN VIS-TO-UV MOLECULAR TTA-UC

5.1 Nanocrystal Sensitizer-based Vis-to-UV Molecular TTA-UC

In 2017, the demonstration of nanocrystal (NC) sensitized Vis-to-UV TTA-UC system was reported in [26]. The demonstration of sensitized CdS NC a ZnS core–shell coupled with PPO in the deaerated hexane solvent had achieved the results of ΔE_{UC} = 0.43 eV (405 nm to 355 nm) with Φ_{UC} = 2.6 ± 0.25 % under the 405 nm light excitation intensity of 7.1 W/ cm^2. The ZnS shell coated on the CdS had contributed to the quantum efficiency improvement of the system, where the ZnS shell passivated the surface traps showing the increase in the photoluminescence quantum yield (Φ_{PL}) of the CdS NC. However, as the shell thickness increased, the tunnelling barrier for TET from Cds core to PPO increase, resulting in a reduction in the TET rate [22,23]. This study had extended the application of nanocrystal sensitized TTA-UC system from the NIR and visible into UV.

The quantum-confined perovskite NCs were introduced as the sensitizer, to ensure effective TET and reduce the ISC energy loss, which is due to the quantum confinement of the sensitized NCs. It ensures a strong donor-acceptor wavefunction overlap needed for DET [27]. The couple of confined $CsPbBr_3$ NCs/ PPO with 1-naphthoic acid (1-NCA) as the mediator in the deaerated hexane solution reported the E_{UC} = 0.7 eV (443 nm to 353 nm) with the Φ_{UC} of 5.1 % and I_{th} of 1.9 W/ cm^2. The author explained the high quantum yield was due to the high-emissive and quantum-confined $CsPbBr_3$ NCs, which ensure the effective triplet energy transfer process to NCA.

Previous sensitized NCs-mediator-annihilator Vis-to-UV TTA-UC system had reported a relatively poor quantum efficiency [21,24]. To further understand the mechanism of the sensitized NC-mediator-annihilator upconversion system, the photoluminescence performance of three CdS NCs with their respective sizes, four mediators and four annihilators with their respective energy levels were evaluated in [28]. The couple of CdS 405/ phenanthrene-3-carboxylic acid (3-PCA)/ PPO in deaerated toluene showed the highest Φ_{UC} of 10.4 % under 405 nm excitation of 14 W/ cm^2 with the ΔE_{UC} = 0.48 eV (405 nm to 350 nm) and I_{th} of 0.95 W/ cm^2. The result had achieved the highest Φ_{UC} for the use of PPO annihilator as compared with the previous work [17,21,24]. Furthermore, the couple of CdS NCs/ 3-PCA/ naphthalene (Naph) had achieved the upconverted emission of 320 nm (3.9 eV) upon the 405 nm irradiance, which is comparable with the highest upconverted emission based on TTA-UC system achieved [31]. The author had provided the guidelines for designing a sensitized NCs TTA-UC system: (1) The T_1 level of the mediator should be a minimum of 200 meV lower than the NCs, (2) The T_1 level of the annihilator should not be higher than the mediator, and (3) High quality NCs improve the UC system quantum efficiency.

5.2 Thermally Activated Delayed Fluorescence Sensitizer-based Vis-to-UV Molecular TTA-UC

The energy losses that occurred during the donor ISC process through the S_1-T_1 energy gap (ΔE_{ST}) will reduce the overall energy gain in the TTA-UC system. In 2016, Yanai research group issued the problem significantly hindered the sensitizer-annihilator combination since the T_1 level of the annihilator was required to be lower than the sensitizer [29]. In this study, a thermally activated delayed fluorescence (TADF) molecule-based sensitizer, carbazolyl dicyanobenezene (4CzIPN), was coupled with p-quarterphenyl (QP) and p-terphenyl (TP) in the deaerated benzene solvent. Due to the small ΔE_{ST} value of 4CzIPN (0.083 eV), it minimizes the energy loss that occurred in the ISC process and expands the selection of annihilators. The couple of 4CzIPN/ QP showed the ΔE_{UC} = 0.73 eV (445 nm to 353 nm) with the Φ_{UC} of 1.95 % and I_{th} of 775 mW/ cm^2, whereas 4CzIPN/ TP showed the ΔE_{UC} = 0.83 eV (445 nm to 343 nm) with the Φ_{UC} of 1.4 % and I_{th} of ~ 1.8 W/ cm^2.

In 2022, the first Vis-to-UV TTA-UC system achieving the upconversion performance closer to the classical spin statistical limit (20%) was demonstrated in [35]. The organic TADF molecule based on 2,3,5,6-tetra(9H-carbazol-9-yl)benzonitrile (4CzBN) acted as the sensitizer coupled with 1,4-bis((triisopropylsilyl)ethynyl)naphthalene (TIPS-Naph) in deoxygenated toluene showed the ΔE_{UC} = 0.24 eV (405 nm to 375 nm) with the Φ_{UC} of 13.1 % and I_{th} of 220 mW/ cm^2. The high quantum yield is due to the small ΔE_{ST} value of 4CzBN (0.28 eV) and the high f factor of TIPS-Naph (0.54). However, the ΔE_{UC} value for the couple is relatively low. The author issued the drawback of the sensitized 4CzBN that limits the achieved anti-Stokes shift. It leads to a significant energy loss through the ISC process and TET process when the excitation wavelength exceeds 430 nm.

Due to the weak absorption of TADF molecule-based sensitizer in the range of visible spectrum, which resulted in the large excitation threshold, two types of multi-resonance TADF (MR-TADF) molecules (BN-2Cz and BN-2Cz-tBu) that had achieved high ΔE_{UC} and low $I_{th}$was introduced in [30]. The couple of BN-2Cz/ 1,5-DTNA showed the ΔE_{UC} = 0.91 eV (517 nm to 375 nm) in deoxygenated toluene with the Φ_{UC} of 3.8% and I_{th} of 9.2 mW/ cm^2; while the couple of BN-2Cz-tBu/ 1,5-DTNA showed the ΔE_{UC} = 1.05 eV (532 nm to 367 nm) in deoxygenated toluene with the Φ_{UC} of 2.0 % and I_{th} of 41.8 mW/ cm^2. The MR-TADF molecule successfully outperformed the previous carbazolyl TADF molecules in term of the ΔE_{UC} and I_{th}.

5.3 Solvent System in Vis-to-UV Molecular TTA-UC

As the solvents used for TTA-UC system were so far limited to the organic solvent, a water-soluble sensitizer-annihilator couple was developed, where in this case water was used as the solvent in the TTA-UC system [31]. The sensitizer-annihilator couple of Irsppy/ 1,5-naphthalenedisulfonate (NDS) in Ar-saturated water showed the ΔE_{UC} = 1.09 eV (447 nm to 321 nm) with the Φ_{UC} of ~ 0.03 % under excitation intensity of ~ 230 mW/ cm^2. The author demonstrated that Vis-to-UV TTA-UC system is feasible in water solvent. This study also achieved a high ΔE_{UC}, which is completable with the previous studies [30, 31], and outperform the highest ΔE_{UC} previously reported for a blue-to-UV TTA-UC system [29], despite its low quantum yield. More studies are required to discover the couple that is functional in water solvent.

To study the effect of solvent selection on the TTA-UC system, the upconversion performance in each different solvent was studied by coupling the 10-butyl-2-chloro-9(10H)-acridinone as the sensitizer and 2,6-di-tert-butylnaphthalene as the annihilator [38]. It was reported that the both the Φ_{UC} and photostability of the couple correlate with the solvent, where it shows negative correlation with the solvent polarity. The Φ_{UC} and photostability increase when the polarity decreases, and vice versa. Among the solvents studied, the couple in hexane solvent exhibits the best photostability due to the low polarity of hexane. However, the solvents studied were only limited to the commonly used solvents, where more studies are required to understand the solvent system for Vis-to-UV TTA-UC system. This study could provide a solvent guideline for the use of Vis-to-UV TTA-UC system.

6. CONCLUSION, CHALLENGES AND FUTURE DIRECTIONS

Based on the previous Vis-to-UV TTA-UC system, most of the studies were conducted in solution based except the couple of 2-methoxythiox-anthone (2MeOTX)/ PPO in poly(methyl methacrylate) (PMMA) film [22]. However, it is impractical from an engineering and technological perspective to apply a solution-based system for practical and commercialized implementations. There were recently studies conducted to fabricate the solid state upconversion system, which could provide the future direction in solid-based Vis-to-UV TTA-UC system. It is possible to integrate the TTA-UC system with the sol gel technology [39] and epoxy resin film fabrication technology [40].

Another current challenge faced in the TTA-UC system is the oxygen quenching issue, which resulting the degradation of the system. Since most of the sensitizer-annihilator couples were synthesized in N_2 atmosphere and performed in deaerated condition, it is rather undesirable in the practical use. A TTA-UC system with oxygen acted as the mediator, called as singlet oxygen mediated upconversion (SOMUC) [41], could provide an inspiration in resolving the oxygen sensitivity issue. For solid-based TTA-UC system, a film fabrication technology with excellent oxygen blocking ability should be developed.

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