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AUTHOR STATEMENT

Jae Moon Lee: Conceptualization, Methodology, Investigation, Writing -Original Draft. Jeong Min Park: Performing TTA-UC experiments and editing in the section of TTA-UC Hyun Kyu Lee: Methodology and analysis of photophysical properties. Hong Mo Kim : Methodology. Jae Hyuk Kim: Project administration of TTA-UC experiments and Writing review & editing in the section of TTA-UC Jae Pil Kim: Conceptualization, Project administration, Writing review & editing the whole manuscript.

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Synergistic effects of photoinduced electron transfer and neavy atom effect

based on BODIPY for efficient triplet photosensitizers

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KEYWORDS Singlet oxygen quantum yield (SOQY), Photoinduced electron transfer (PET), Heavy atom effect (HAE), donor-acceptor-heavy atom (D-A-H), BODIPY, Triplet–triplet annihilation upconversion (TTA-UC).

1 ABSTRACT: Achieving a long triplet lifetime and a high triplet quantum yield for efficient triplet sensitizers 2 are crucial for commercializing triplet-triplet annihilation-upconversion (TTA-UC). Although many donor-3 acceptor (D-A) or heavy atom-based triplet sensitizers have been extensively studied, each strategy 4 suffers from major drawbacks, such as low triplet quantum yield of D-A and short triplet lifetime of heavy 5 atoms. Herein, we propose the integration of a donor-acceptor with a heavy atom, which improves both 6 triplet lifetime and quantum vield because of the simultaneous utilization of photoinduced electron trans-7 fer and the heavy atom effect. To prove this, we synthesized Triphenylamine(D)-BODIPY(A)-bromine(H) 8 (AM6, AM7, and AM8), which were compared with standards such as Triphenylamine(D)-BODIPY(A) 9 (AM2) and BODIPY-Bromine (AM9). The donor-acceptor-heavy atom (D-A-H) compounds (AM6, AM7, 10 AM8) exhibited excellent TTA-UC emission efficiency (3.9 - 6.5%), which were high compared to AM2 11 (1.5%) and AM9 (1.7%). Moreover, threshold intensity (I_{th}) of AM6, AM7 and AM8 were lower (176 -12 465mW/cm²) than AM9 (1,916mW/cm²), even though they had heavy atom. This demonstrates that D-13 A-H is an effective molecular design for triplet sensitizers with a synergistic effect.

14 **1.** Introduction

Triplet sensitizers are molecules capable of generating electrons in excited triplet states; these have applications in several fields such as photocatalytic organic reactions, OLEDs, and photodynamic therapy (PDT)[1]. In particular, triplet–triplet annihilation-based upconversion (TTA-UC), in which triplet sen-

- sitizers play a key role, nave attracted more attention owing to their unique anti-Stokes photoluminescence properties. Porphyrin-based sensitizers have been the most widely used as triplet sensitizers; however, because of their major disadvantages, such as low absorption coefficient, dark toxicity, and long lasting photosensitivity, recently, there has been growing demand for the non-porphyrin-based triplet photosensitizers. However, non-porphyrin-based sensitizers generally have a low intersystem crossing (ISC) yield and short triplet lifetime than that of porphyrin-based ones; thus, it becomes challenging to enhance triplet properties.
- Among the various strategies for developing non-porphyrin-based triplet photosensitizers, the heavy atom effect (HAE) and photoinduced electron transfer (PET) are the most widely used.[2-7] In HAE, heavy atoms such as selenium and bromine in the photosensitizer generate spin-orbit coupling (SOC), which results in a higher ISC yield between the singlet and triplet states.[8] The magnitude of the SOC is determined based on the probability of electrons encountering a heavy atom.[8, 9]
- In contrast, PET in donor-acceptor (D-A) molecules generates a charge transfer state, which results in ISC from the singlet state to the triplet state. ISC by PET is caused by spin-orbit charge transfer (SOCT) or hyperfine coupling (HFC). Although it is not clear which mechanism is more prevalent, it is obvious that increasing the charge separation between D and A enhances the ISC.[10]

To improve charge separation, various strategies are commonly used to increase the electron donating or accepting capability of the molecule or to ensure that the dihedral angle between D and A is close to 90°.[11] Theoretically, both mechanisms, HAE and PET, are local effects wherein electrons adjacent to heavy atoms induce ISC because of the HAE, and the electrons transferred from D to A induce ISC because of the SOCT or HFC. Therefore, if both strategies are introduced in the same molecule, the ISC may be independently generated according to the spatial distribution of electrons, resulting in an increased ISC yield.

Several researchers have studied triplet sensitizers, independently investigating HAE and PET.[2-7] However, to the best of our knowledge, the simultaneous utilization of HAE and PET has not been investigated. Here, we developed novel non-porphyrin-based donor-acceptor-heavy atom (D-A-H) photosensitizers, in which both HAE and PET strategies were involved in the same molecule. The triplet characteristics and their singlet oxygen quantum yield (Φ_{Δ}), triplet lifetime (τ_T), and photophysical dynamics

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- 46 were thoroughly investigated. Finally, the synthesized triplet sensitizers were employed to achieve ITA-
- 47 UC and photochemical characteristics, which were observed to be precisely correlated with triplet char-
- 48 acteristics.



- Scheme 1 Synthesis of the photosensitizers (AM2-AM9). A triphenylamine (TPA), a BODIPY (BDP) and
 a perylene moiety for measuring cyclic voltammetry and TTA-UC preperties
- 52 2. Experimental

49

53 2.1 General information

54 **Materials** All of the commercial reagents were purchased from Sigma-Aldrich or Tokyo Chemical Indus-55 try (TCI) and used without further purification. Anhydrous solvents used in the reactions were purchased 56 from Sigma-Aldrich or Alfa aesar.

57 Instruments 1H NMR spectra were recorded on a Bruker Avance 500 spectrometer (National Center for 58 Inter-University Research Facilities at Seoul National University) at 500 MHz using chloroform-d with 59 tetramethylsilane (TMS). High resolution mass experiments were operated on a Q-TOF 5600 mass spec-60 trometer (AM2, AM6, AM7, and AM8) equipped with an ESI source (National Instrumentation Center for 61 Environmental Management) and on JMS-700 (JEOL, Japan), 6890 Series (AM9). Solvatochromic ab-62 sorption and fluorescence solutions were measured by an UV-vis spectrophotometer (LAMBDA 25, Per-63 kin Elemer Co.) and a fluorescence spectrometer (LS-55, Perkin Elmer Co.), respectively. Photolumi-64 nescence guantum yield (PLQY) of 10 µM photosensitizers in various solvents were estimated using an 65 integrating sphere (QE-1100, Otsuka electronics Co.).

66

2.2 Syntnesis and characterization of the photosensitizers (AIVIZ, AIVI6-AIVI9)

AM2 AM2 was synthesized through our previous report.[12] AM2 as red-brown solid. (250 mg, 13%
yield). 1H NMR (500 MHz, CDCl₃) δ 7.90 (s, 2H), 7.49-7.44 (d, J=8.7Hz, 2H), 7.39-7.32 (t, J=7.5Hz, 4H),
7.25-7.00 (d, J=7.5Hz, 4H), 7.19-7.13 (t, J=7.4Hz, 2H), 7.13-7.08 (d, J=8.6Hz, 2H), 7.08-7.04 (d,
J=4.0Hz, 2H), 6.5 (m, 2H) 13C NMR (500 MHz, CDCl₃) δ 151.1, 147.7, 146.6, 142.9, 134.8, 132.5, 131.3,
129.9, 126.4, 126.1, 124.9, 120.2, 118.2; HRMS-ESI (M+H+) Calcd for C27H21BF2N3: 436.1796.
Found: 436.1772

4-(di(1H-pyrrol-2-yl)methyl)-N,N-diphenylaniline (1) In three neck round bottom flask, 4-(Diphenylamino)benzaldehyde (1.05g, 3.85 mmol) and and pyrrole (1.033g, 15.4 mmol, 4eqn) were dissolved into dry dichloromethane (250 ml), then a solution of trifluoroacetic acid (0.5 mmol, 0.13eqn) in dry dichloromethane (2.5 ml) were slowly added to the mixture at room temperature under N2 atmosphere. Then the reaction mixture was quenched by 2 ml, trimethylamine and evaporated. The brown, oily residue is simply purified by column chromatography on silica with CH₂Cl₂:n-hexane = 1:1 to produce **1** as brown solid (1.47g)

/9 (1.47g)

80 AM6 - 8 In a three neck flask, a crude mixture of compound 1 (584 mg, 1.5 mmol) was dissolved into dry THF (30 ml) and the mixture was cooled to -78 °C under nitrogen atmosphere. N-bromosuccinimide, 81 82 (587mg, 3.3 mmol) was slowly added over 30 min. After 2 h, 2,3-Dichloro-5,6-dicyano-1,4-benzoquinone, 83 DDQ (341 mg, 1.5 mmol) in 5 ml dry THF was added dropwise over 10 min at same temperature. Then 84 the reaction temperature was increased to RT and the solvent was distilled on rotary evaporator. Then 85 the crude compound was dissolved in 50 ml dichloromethane, neutralized with triethylamine (7.30 ml, 52 86 mmol) and treated with BF₃.Et₂O (9.4 ml, 74.6 mmol) at room temperature for additional 2-3 h. The re-87 action mixture was guenched with 20 ml 0.1 M NaCl solution and extract from water. The organic layer 88 was dried over MgSO₄, filtered, and evaporated. The crude product was purified by silica gel column 89 chromatography eluting with hexane/dichlorometane (1:1) to produce compound AM6 (44 mg, 5.7% 90 vield) AM7 (86 mg, 9.6% vield) and AM8 (37 mg, 3.6% vield) as violet solid.

AM6: 1H NMR (500 MHz, CDCl₃) δ 7.92 (s, 2H), 7.43-7.39 (d, J=8.7Hz, 2H), 7.38-7.33 (t, J=8.2Hz, 4H),
7.23-7.20 (d, J=7.5Hz, 4H), 7.19-7.14 (t, J=7.4Hz, 2H), 7.12-7.07 (d, J=7.3Hz, 2H), 7.04 (m, 1H), 6.96
(d, J=4.2Hz, 1H), 6.57 (m, 1H), 6.55-6.51(d, J=4.3Hz, 1H) 13C NMR (500 MHz, CDCl₃) δ 151.0, 146.4,

Journal Pre-proof 120.0, 125.4, 124.8, 120.0, HKIVIS-ESI (IVI+H+) Caicd for 94 143.z. 132.2, 131.3, 131.1, 129.7 95 C27H20BBrF2N3: 514.0902. Found: 514.0870 **AM7**: 1H NMR (500 MHz, CDCl₃) δ 7.39-7.33 (m, 6H), 96 7.23-7.19 (d, J=7.6Hz, 4H), 7.19-7.14 (t, J=7.4Hz, 2H), 7.08 (d, J=8.7, 2H), 6.93 (d, J=4.1Hz, 2H), 6.55 97 (d, J=4.3Hz, 2H) 13C NMR (500 MHz, CDCl₃) δ 151.3, 146.6, 143.8, 135.4, 132.4, 131.5, 131.2, 130.0, 98 126.2, 125.1, 124.9 122.4, 120.1 HRMS-ESI (M+H+) Calcd for C27H19BBr2F2N3: 593.9987. Found: 99 593.9952 AM8: 1H NMR (500 MHz, CDCl₃) δ 7.41-7.33 (m, J=8.4Hz, 6H), 7.24-7.16 (m, J=7.4Hz, 6H), 100 7.11-7.06 (d, J=8.7Hz, 2H), 6.98 (s, 2H), 6.59 (d, J=4.4Hz, 2H) 13C NMR (500 MHz, CDCl₃) δ 151.6, 101 146.4, 143.6, 135.6, 134.4, 133.3, 132.6, 132.5, 131.1, 130.2, 130.0 126.4, 125.3, 124.3, 123.2 120.0, 102 110.4 HRMS-ESI (M+H+) Calcd for C27H18BBr3F2N3: 670.9056. Found: 670.9076

103 2 In three neck round bottom flask, benzaldehyde (0.32g, 3 mmol) and pyrrole (0.805g, 12 mmol, 4egn) 104 were dissolved into dry dichloromethane (200 ml), then a solution of trifluoroacetic acid (0.6 mmol, 105 0.2eqn) in dry dichloromethane (2 ml) were slowly added to the mixture at room temperature under N2 106 atmosphere. Then 2,3-Dichloro-5,6-dicyano-1,4-benzoquinone(DDQ) (0.68 g, 3 mmol) were added to 107 the RBF under ice bath cooling and stirred for 10 min. The solution is stirred for an additional 1 h at room 108 temperature. Triethylamine (43.2 mmol, 11.3eqn) is added, followed by slow addition of BF₃Et₂O (48.7 109 mmol, 12.6eqn). After 2 h, the reaction mixture was washed at room temperature with saturated aqueous 110 Na_2CO_3 solution (3 x 100 ml), dried over MqSO₄, and concentrated on a rotary evaporator. The brown, 111 oily residue is purified by column chromatography on silica with CH_2CI_2 :n-hexane = 1:1 to produce 2 (48 112 mg, 6% yield) as yellow solid. AM9 To 2 (25 mg, 0.093 mmol) in 10 ml of dry in CH₂Cl₂ was added 113 dropwise N-bromosuccinimide (NBS) (83mg, 0.465 mmol) in CH₂Cl₂ (5 ml) over a period of 0.5h. The 114 mixture was left stirring for an additional 24 h, washed with an aqueous solution of sodium chloride, and 115 extracted by CH₂Cl₂. Organic layers were extracted, dried over MgSO₄, and evaporated to dryness. Pu-116 rification was performed by column chromatography on silica gel using hexane/CH₂Cl₂ (1:1, v/v). AM9 117 was obtained as dark purple solid (13mg, 37% yield)

AM9 1H NMR (500 MHz, CDCl₃) δ 7.65-7.62 (t, J=7.5Hz ,1H), 7.57-7.54 (t, J=8Hz, 2H), 7.49-7.47 (d,
J=7.5Hz, 2H), 6.91 (s, 2H) 13C NMR (500 MHz, CDCl₃) δ 143.0, 135.4, 135.0, 131.8, 131.7, 130.5,
120 129.1, 112.3 HRMS-ESI (M+H+) Calcd for C27H18BBr3F2N3: 579.7404. Found: 579.7408

5

121

2.3 Photophysical and photochemical properties

Singlet oxygen quantum yield measurements SOQY were measured by using the indirect method in toluene. (standard : 2,3,7,8-tetrabromo-5,5-difluoro-10-phenyl-5H-4l4,5l4-dipyrrolo[1,2-c:2',1'-f][1,3,2]diazaborinine, $\Phi_{\Delta} = 0.49$ in toluene) [7] To determine SOQY, a following eqn 1 was used:

125
$$\Phi_{\Delta,sam} = \Phi_{\Delta,std} \left(\frac{m_{sam}}{m_{std}}\right) \left(\frac{1-10^{-A_{std}}}{1-10^{-A_{sam}}}\right) \left(\frac{n_{sam}}{n_{std}}\right)^2 \qquad \text{eqn. 1}$$

Where $\Phi_{\Delta,sam}$ – SOQY of the sample, $\Phi_{\Delta,std}$ – SOQY of the standard (AM9 in toluene). m_{std} and m_{sam} – the slope of the absorbance changing at 413nm in standard and the sample. n_{std} and n_{sam} – the refractive index of solution in which the standard and the sample are dissolved. Oxygen was bubbled into the solvents for 30min before sample preparation. All samples in 3.5ml solvents contained diphenylisobenzofuran (DPBF) were irradiated with laser (505nm. 3.16mW ±3%). The concentration of DPBF was fixed to 30mM for preventing from chain reaction. The detailed absorption spectra of mixtures including photosensitizers and the DPBF were included in Figure S15-16.

133 **TTA-UC emission efficiency measurement** The TTA-UC emission efficiency (η_{UC}) of samples was 134 measured relative to the fluorescence quantum yield of AM6 in toluene in response to laser excitation at 135 532 nm (Φ_{std} (AM6) = 2.4%, measured using QE-1100, Otsuka). The calculation of efficiency yield was 136 performed with using eqn 2.

$$\eta_{UC,sam} = 2\Phi_{std} \left(\frac{I_{sam}}{I_{std}}\right) \left(\frac{1-10^{-A_{std}}}{1-10^{-A_{sam}}}\right) \left(\frac{n_{sam}}{n_{std}}\right)^2 \qquad \text{eqn. 2}$$

Where $\eta_{UC,sam}$ – upconversion emission efficiency of the sample, Φ_{std} – fluorescence quantum yield of the standard (AM6 in toluene). I_{std} and I_{sam} – Integrated photoluminescence intensities of the standard and the sample. A_{std} and A_{sam} – Absorbance of standard and sample at excitation wavelength. n_{std} and n_{sam} – the refractive index of solution in which the standard and the sample are dissolved.

142 **Calculation** The ground and excited state geometry was optimized with Gaussian 09 software using the 143 DFT and TDDFT/B3LYP hybrid functional and the 6-31+G(d,p) basis set with toluene as a solvent 144 (IEFPCM). The dihedral angle between donor and acceptor obtained from the optimized geometry at S₀. 145 Overlap integral of S₁ transition was analyzed by multifunctional wavefunction analyzer (Multiwfn) version 146 3.7.[13] Spin orbit coupling matrix element (SUCIVIE) was calculated with the UKCA software based on

147 the optimized ground geometry using B3LYP/G 6-31G(d,p) in toluene (CPCM).

- 148 3. Results and discussion
- 149 3.1 Structural description

150 To investigate the synergistic effect of HAE and PET, three different D-A-H photosensitizers (AM6, AM7, 151 and AM8) were prepared: donor, acceptor, and heavy atom of the D-A-H photosensitizers were selected 152 as triphenylamine (TPA), BODIPY, and bromine, respectively (Scheme 1). AM2 and AM9 were prepared 153 as standards, with their structures containing only a donor-acceptor (D-A) and heavy atoms on BODIPY, 154 respectively. To examine the effect of the number of bromine atoms, AM2(0Br), AM6(1Br), AM7(2Br), 155 and AM8(3Br) were designed. Bromine atoms were introduced at the end of BODIPY to maintain the 156 dihedral angle between D and A. And they were 48-51°, which indicates that the PET of molecules is 157 only affected by the number of bromine atoms and not by the dihedral angles (Figure S13). It is expected 158 that the HAE and the degree of charge separation by PET will increase by increasing the number of 159 bromine atoms in the following order: AM2(0Br) < AM6(1Br) < AM7(2Br) < AM8(3Br)), resulting in an 160 increased SOQY. In contrast, AM9 results in a low SOQY because PET does not occur.

161

3.2 Solvatochromic properties



163 Figure 1 (a) UV-VIS absorption, emission spectra, and (b) Lippert-Iviataga plots of Alviz–Alvis photosen-

sitizers in hexane (HX), toluene (TOL), chloroform (CF), ethyl acetate (EA), dichloromethane (MC), and

165 acetonitrile (ACN) solutions.

166 The absorption and emission spectra of AM2-AM9 were measured using different solvents (Figure 1). 167 All photosensitizers exhibited a constant wavelength of absorption maximum, irrespective of solvent po-168 larity. For AM2–8, an additional weak absorption was observed on the low energy side of the major band. 169 Considering that the weak absorption band increases and the bandwidth broadens with increasing sol-170 vent polarity, it can be deduced that the band corresponds to the charge transfer absorption ($S_0 \rightarrow {}^1CT$ 171 state) (Figure S14). Unlike the absorption spectra, as the solvent polarity increased, the emission maxima 172 of the AM2-8 photosensitizers were bathochromically shifted and their photoluminescence quantum 173 yields were reduced. (Table S1). The emission spectra of the photosensitizers AM2-AM8 in hexane 174 mirrored the respective absorption spectra, corresponding to the local excitation (¹LE) band from the 175 local excited state. The emission spectra of AM2–AM8 in polar solvents, such as toluene, showed shape-176 less and broad emission bands, corresponding to the charge transfer (¹CT) band. The existence of the 177 CT absorption band and solvent-dependent fluorescence quenching indicated that the charge separation 178 in AM2-AM8 was due to PET, as was intended. Normalized emission spectra of AM7, AM8 in dichloro-179 methane (MC) is consisting of two distinct bands: one is corresponding to the singlet local excited (¹LE) 180 band, because their wavelength is same with emission spectrum in hexane (Figure S14). The other band 181 corresponds to the ¹CT band, because it is located over the 700nm with large stokes shift. In high polar 182 solvent, Electrons of ¹LE band should be transferred to the lower ¹CT state, thus ¹LE to S₀ transition 183 probability is theoretically small, but not zero, resulting in low intensity of LE emission. And the ¹CT state 184 in high polar solvent is dark state, resulting in low intensity of CT emission. Thus ¹LE band and ¹CT band 185 can coexist in dichloromethane. The linear dependence of the Stokes shift of the photosensitizers on 186 solvent polarizability (Δf) was demonstrated using the Lippert–Mataga plot (Figure 1b, Tables S2-3). For 187 AM9, a non-linear relationship was observed between the Stokes shift and Δf (R-square = 0.11), indicat-188 ing that the emission of AM9 originated from the ¹LE state. For AM2–AM8, Stokes shift increased signif-189 icantly with increasing Δf . However, the Stokes shift in hexane deviated considerably from the overall 190 trend because the emission in hexane originated from the ¹LE state, unlike those in other solvents that 191 are initiated from the ¹CT state. To evaluate the magnitude of charge separation, the changes in dipole 192 moment ($\Delta \mu_{ae} = \mu_e - \mu_a$) of the ¹CT states were calculated from the slopes of the Lippert-Mataga plots 193 obtained in polar solvents.

- 194 According to the Lippert–Mataga equation (eqn. 3)
- 195

$$\overline{v_a} - \overline{v_f} = S \cdot f(D, n) + \text{constant}$$
 eqn. 3

where \bar{v}_a and \bar{v}_f are the absorption and emission wavenumbers, respectively, and D and n are the dielectric constants and refractive index of the solvents, respectively. The slope (S) obtained from linear 198 regression of the Lippert-Iviataga plot (Equation 4) and the orientation polarizability functions (Equation

199 5) are expressed as

$$S = \frac{2(\Delta \mu_{ge})^2}{a^3 hc} \qquad \qquad \text{eqn. 4}$$

$$f(D,n) = \frac{D-1}{2D+1} - \frac{n^2 - 1}{2n^2 + 1}$$
 eqn. 5

202 where a, h, and c are the Onsager cavity radius, Planck's constant, and the speed of light in vacuum, 203 respectively. A larger cavity radius was obtained from the optimized geometry using DFT/B3LYP(6-204 31G+(d,p)) in toluene as a solvent (IEFPCM). All the calculated parameters are summarized in Tables 205 S2 and S3. AM2, AM6, AM7, and AM8 showed higher $\Delta \mu_{ge}$ values of 12.39 D, 12.82 D, 13.67 D, and 206 15.00 D, respectively, compared to the change in dipole moment of AM9 ($\Delta \mu_{qe} = 1.67$ D). A large value 207 of Δµ_{ge} indicates charge separation through PET; therefore, the electric charge of AM9 may not be sep-208 arated. [14-17] In addition, $\Delta \mu_{ge}$ increased in the order of AM2 < AM6 < AM7 < AM8, indicating that the 209 additional bromine atoms enhanced electron-accepting power and induced a strong PET character.

210

211

3.3 Singlet oxygen quantum yield (SOQY)



Figure 2 Time dependence of ln([DPBF]₁/[DPBF]₀) in mixtures with Photosensitizers and DPBF under
toluene (505nm laser excitation).

212

216 The triplet generation of the photosensitizers was assessed through the generation of singlet oxygen 217 (SOQY). The SOQYs of AM2, AM6, AM7, AM8, and AM9 in toluene were 0.32, 0.66, 0.70, 0.74, and 218 0.49, respectively (Figure 2 and Table 3). AM2 does not have any heavy atoms; therefore, the generation 219 of singlet oxygen is only attributed to PET, and because AM9 is not a D-A structure, the generation of 220 singlet oxygen is attributed to the HAE. The SOQYs of AM6–8 were higher than those of AM2 and AM9, 221 as we proposed. Notably, the SOQYs of AM6-8 were significantly higher than those of AM9, even though 222 the number of bromine atoms in AM6–8 was less than that in AM9. These results may indicate the syn-223 ergistic effect of PET and HAE. In addition, SOQY tends to increase with an increase in the number of 224 bromine atoms, which could be because the introduction of additional bromine atoms increases the HAE 225 as well as the PET. On the other hand, the SOQYs of AM2, AM6, AM7, and AM8 in dichloromethane 226 (MC) were 0.05, 0.16, 0.20, and 0.05, respectively, which were lower than those of the SOQYs in toluene. 227 This might be because charge recombination from the ¹CT to the S₀ state was favorable in highly polar 228 solvents. The ¹CT state can become highly stabilized in polar solvents, leading to increased rates of 229 charge recombination [18, 19]. For AM9, the SOQYs in MC were almost similar to those in toluene be-230 cause PET was not allowed.

231

233

- 232
- 3.4 Electrochemical properties



Figure 3 Cyclic voltammograms of Alviz–Alvi9 (0.1 mivi) in dichloromethane containing 0.10 IVI Bu₄IV[PF₆] as the supporting electrolyte, and Ag/AgCl as the reference electrode. Scan rates: 50 mV/s. Ferrocene (Fc) was used as the external reference [E_{1/2} = +0.38 V (Fc+/Fc)].

237 The redox potentials of the photosensitizers AM2-AM9, triphenylamine (TPA), and BODIPY (BDP) in 238 dichloromethane were obtained by cyclic voltammetry (Figure 3), and the results are summarized in 239 Table 1. The photosensitizers AM2-AM8 exhibited a one-electron reversible oxidation process on the 240 positive potential side, which was attributed to the TPA molety in comparison with the oxidation wave of 241 the pristine TPA. On the other hand, irreversible reduction waves were observed for all the photosensi-242 tizers on the negative potential sides. For AM2, the first electron reduction potential was observed at 243 -0.77 V, which may be attributed to the reduction of the pristine BDP unit, supported by the CV curve of 244 the reference BDP moiety (Figure S17a). In addition, the first reduction potentials increased in the fol-245 lowing order: AM2 (-0.77 V) < AM6 (-0.74 V) < AM7 (-0.69 V) < AM8 (-0.59 V) < AM9 (-0.48 V) (Figures 246 3 and S17b-c). This trend was attributed to bromine atoms acting on the BODIPY core as electron-247 withdrawing groups, and thus inducing conjugated molecules to accept an electron more readily.

248

Table 1 Oxidation (E_{OX}) and reduction (E_{RED}) potential, charge separation driving force (ΔG_{CS}), reorganization energy (λ), and Franck–Condon weighted density of states (FCWD)

	E _{OX} (V) ^a	E _{RED} (V) ^b	ΔG _{CS} (eV) ^c		λ (eV)		FCWD	
			TOL	MC	TOL	MC	TOL	MC
AM2	0.98	-0.77	-0.21	-0.87	0.29	0.63	3.00	1.60
AM6	0.98	-0.74	-0.23	-0.86	0.29	0.62	3.73	1.66
AM7	0.99	-0.69	-0.24	-0.84	0.29	0.65	3.86	1.92
AM8	1.02	-0.60	-0.26	-0.85	0.27	0.59	3.94	0.91
AM9	1.56	-0.48		-	-			

^a The first oxidation onset potential and ^b the first reduction onset potential determined by the cyclic-

volatmmetry in dichloromethane.

253 The rate of photoinduced electron transfer is proportional to the Franck–Condon weighted density of

254 states (FCWD), which is expressed by

255 Journal Pre-proof

$$FCWD = \frac{1}{\sqrt{4\pi\lambda k_B T}} \times exp\left[-\frac{(\lambda + \Delta G_{CS})^2}{4\pi\lambda k_B T}\right] \qquad \text{eqn. 6}$$

where λ and ΔG_{CS} are reorganization energy and Gibbs free energy changes of charge separation. The ΔG_{CS} was obtained through the Rehm-Weller equation (Equation 7).

$$\Delta G_{CS} = e[E_{OX} - E_{RED}] - E_{00} + \Delta G_S \qquad \text{eqn. 7}$$

259
$$\Delta G_S = -\frac{e^2}{4\pi\varepsilon_s\varepsilon_0R_{cc}} - \frac{e^2}{8\pi\varepsilon_0} \left(\frac{1}{R_D} + \frac{1}{R_A}\right) \left(\frac{1}{\varepsilon_{REF}} + \frac{1}{\varepsilon_s}\right)$$
eqn. 8

260 where E_{OX} and E_{RED} are the first oxidation and reduction onset potentials, respectively, determined by 261 cyclic voltammetry, E_{00} is the energy of the lowest excited state, ΔG_S is the static coulombic energy, e is the elementary charge, ε_s is the static dielectric constant of the solvent, ε_0 is the vacuum permittivity, and 262 263 R_{CC} is the center-to-center distance between the electron donor (TPA) and the electron acceptor (BDP 264 including bromine). R_D and R_A are the radii of the electron donor (TPA) and the acceptor unit (BDP 265 including bromine), respectively, obtained from DFT optimization (DFT/B3LYP/6-31+G(d,p)). The R_{cc} 266 values of AM2, AM6, AM7, and AM8 were 7.57, 7.59, 7.62, and 7.61 Å, respectively. The reorganization 267 energy (λ) of charge separation was evaluated by the arithmetic average of the forward (λ_1) and back-268 ward (λ_2) reorganization energy using DFT calculation, which was expressed by the Equation 9

269
$$\lambda_1 = E(D^+|D) - E(D^+|D^+) + E(A^-|A^*) - E(A^-|A^-)$$
270
$$\lambda_2 = E(D|D^+) - E(D|D) + E(A^*|A^-) - E(A^*|A^*)$$
eqn. 9

where the symbolization E(X|Y) denotes that the single point energy of the X state at the Y geometry. The λ_1 and λ_2 were determined by the sum of the reorganization energy of the donor and the acceptor independently. [20-25] A detailed calculation procedure is described in Supplementary materials.



274

Scheme 2 Schematic representation of photoinduced electron transfer in toluene (TOL) and dichloro-methane (MC)

277 In toluene, the $-\Delta G_{CS}$ increased in the order AM2 < AM6 < AM7 < AM8, representing that the ability of 278 charge separation tentatively increased from AM2 to AM8. The λ of AM2, AM6, AM7, and AM8 were 0.29 eV and 0.27eV which was higher than the $-\Delta G_{CS}$. This indicates that the chare separation occurs in the 279 280 Marcus normal regime (Scheme 2). In addition, the value of ($\lambda + \Delta G_{CS}$) became close to zero with in-281 creasing the number of bromines, resulting in the increased the FCWD. This clearly shows that the de-282 gree of charge separation increased with increasing the number of bromine atoms. On the other hand, 283 in MC, no significant correlation was observed between the $-\Delta G_{CS}$ and the number of bromine atoms, 284 and the charge separation occurs in the Marcus inverted regime, because $-\Delta G_{CS}$ was higher than the λ . 285 In addition, the value of ($\lambda + \Delta G_{CS}$) in AM2-AM8 was large, so the FCWD in MC was low compared to 286 that in toluene. this result means that the charge separation is relatively unfavorable in the MC, and as a 287 result, the SOQY appears to be small. Although the driving force of all the photosensitizers in MC was 288 higher than that in toluene, the charge separation in toluene may be more favorable than that in MC. This 289 is because the charge separation state in MC was located in the Marcus inverted region owing to the 290 large charge separation driving force. Thus, this may be another factor that reduced the SOQY in di-291 chloromethane along with charge recombination.

292 3.5 Triplet lifetime (TT)

Time-resolved photoluminescence experiments at emission maxima wavelength were carried out to investigate the triplet lifetime of AM2–9 (Figure S18). All the samples showed a biexponential decay profile. 295 A fast component was assigned to a snortened decay by \cup_2 because the decay curve of a tast compo-296 nent in a deaerated environment coincides with that in an aerated environment (Figure S19). The triplet 297 lifetimes of the slow components of AM2, AM6, AM7, AM8, and AM9 were 132, 122, 175, 199, and 57 298 us, respectively. AM9, which contains only heavy atoms, showed a short lifetime similar to the reported 299 one (36 µs). This supported the findings of previous studies that the electrons of heavy atoms decay 300 rapidly from T_1 to S_0 along the nonradiative pathway.[7] In contrast, D-A-H photosensitizers showed long 301 triplet lifetimes. It is quite interesting that the triplet lifetimes of AM6, AM7, and AM8 were long despite 302 the presence of heavy atoms. Although the triplet lifetime of AM6 was relatively short, those of AM7 and 303 AM8, which contained heavy atoms, were longer than that of AM2, which did not contain heavy atoms. 304 In addition, the triplet lifetime of the D-A-H photosensitizers increased with increasing number of bromine 305 atoms. This is contrary to the results from previous studies, which showed an increase in SOQY and a 306 decrease in triplet lifetime with increasing number of heavy atoms.[7] Therefore, this result indicated that 307 increasing the number of heavy atoms in a D-A-H photosensitizer is a good strategy for improving its ISC 308 vield as well as triplet lifetime.

309 3.6 Quantum chemical calculation

310 For a detailed understanding of the relationship between PET and SOQY, the orbital overlap between 311 the HOMO and LUMO of the optimized S₁ state was calculated using the overlap integral (Sr) by Multiwfn. 312 Sr is occasionally used in the field of OLED research as a parameter for quantifying the size of charge 313 separation.[26, 27] The Sr values of AM2, AM6, AM7, and AM8 were 0.08328, 0.08158, 0.08133, and 314 0.07889, respectively, and gradually decreased as the number of bromine atoms increased (Table 3). 315 Although there was no significant difference in the values of Sr of the photosensitizers, this trend is 316 consistent with the results of the $\Delta \mu_{ae}$ and the ΔG_{CS} in the previous section. Overall, these results repre-317 sent that an increase in the number of bromine enhances the charge separation. Notably, the Sr of AM9 318 was 0.64344, which is considerably higher than that of the other molecules. This significant difference in 319 the orbital overlap can be intuitively confirmed by the visualized image (Figure S20), suggesting that PET 320 does not occur in AM9.



322 Figure 4 Spin density of AM2, AM7, and AM9 photosensitizers (optimized T₁ state)

323 To obtain deeper insights into the synergistic effect, the spin density distribution (SDD) in the optimized 324 T₁ state of AM2, AM7, and AM9 was calculated by UDFT/B3LYP/6-31+G(d,p). For AM2 and AM7, the spin was localized mainly in BODIPY, and for AM9, it was spread over the entire molecule (Figure S21). 325 326 Zhao et al. reported that higher the spin density of the carbon atom at the meso position in BODIPY. 327 larger the ISC because of PET (Figure 4).[3] The spin density of carbon in AM2 and AM7 was 0.36 each. 328 Although these are not consistent with the result of the $\Delta \mu_{qe}$ and the ΔG_{CS} , it indicates that the extent of 329 PET in AM7 is similar to that in AM2. In addition, the spin density of bromine located at the end of BODIPY 330 was 0.07 for AM7, which is similar to that for AM9. The spin density of a heavy atom is considered a 331 parameter that determines HAE; therefore, this may indicate that HAE may have almost the same effect 332 as that in case of AM9.[28] Therefore, based on the SDD results, it can be confirmed that AM7 showed 333 HAE and PET simultaneously, which is a synergistic effect.



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321

Figure 5. Schematic of the mechanism of intersystem crossing between the excited singlet and triplet states. ¹LE and ¹CT states were determined by spectroscopic and cyclic voltammetric analyses. The

triplet excited states were calculated by IDDFI/B3LYP/0-31+G(d,p). Natural transition orbitals (NTO) 337 338 and their transition probabilities corresponding to the excited states are included.

339

340 In order to evaluate the transition characteristics of the singlet and triplet excited states, the natural tran-341 sition orbitals (NTO) and the energy levels of all the excited states participating in photochemical kinetics 342 were also investigated. For all the photosensitizers, except AM9, the S₁ and T₂ states exhibited CT char-343 acteristics, and the S₂ and T₁ states exhibited LE characteristics (Figure 5 and S22). The AM9 photosen-344 sitizer showed LE character in all the calculated states because PET did not occur in AM9. The excited-345 state energy levels of AM7 appeared in the order T_1 (1.68 eV) < T_2 (1.88 eV) < S_1 (2.09 eV) < T_3 (2.75 346 eV); AM2–AM8 also showed a similar order of energy levels. ISC from the S₁ state to the T₃ state was 347 thermodynamically not allowed because the T₃ state had higher energy than the S₁ state. The SOCT-348 induced ISC (SOCT-ISC) would occur between the S_1 and T_1 states because the S_1 and T_1 states are 349 assigned to the ¹CT and ³LE states, respectively. According to Fermi's golden rule, the SOCT-ISC pro-350 cess is governed by the energy gap (ΔE_{S1-T1}) between the S₁ and T₁ states, and ΔE_{S1-T1} was determined 351 to slightly decrease from AM2 to AM8, which enhanced the SOCT-ISC.

352 In addition, the HFC-induced ISC (HFC-ISC) between the S₁ and T₂ states is valid, because both the S₁ 353 and T₂ states have CT characteristics. Similar to SOCT-ISC, HFC-ISC was determined by the energy 354 gap (ΔE_{S1-T2}) between the S₁ and T₂ states. The ΔE_{S1-T2} values of AM2–AM8 decreased marginally with 355 increasing number of bromine atoms. Therefore, it is believed that HFC-ISC might increase from AM2 to 356 AM8. However, the HFC may rarely contribute to the total ISC because an extremely small ΔE_{ST} (20 357 μ eV) is required to generate HFC-ISC [29]. On the other hand, ΔE_{S1-T2} is identical to twice the electron 358 exchange energy (J), which is the constant of exchange interaction. The extent of J is influenced by of 359 the overlap integral between orbitals with spin [9]. Thus, the J value can be compared with Sr in the 360 previous section. J gradually decreased with increasing Sr, indicating that the increased PET by bromine 361 decreased the overlap integral and therefore decreased J (Table 3). For AM9, the excited energy level 362 was in the order T_1 (1.48 eV) < S_1 (2.20 eV) < T_2 (2.61 eV); thus, ISC is only favorable between the S_1 363 and 11 states. Although Alvis does not have PET characteristics, the SOC induced by HAE can encour-

364 age ISC. The ΔE_{S1-T1} of AM9 was 0.72 eV, considerably larger than those of the other photosensitizers,

365 and may lower ISC from the S₁ to the T₁ state.

366

367



Figure 6 Spin-orbit coupling matrix element (SOCME) and energy gap (ΔE_{S1-T1}) between the S₁ and T₁ states of AM2–AM9.

The spin-orbit coupling matrix element (SOCME), calculated using ORCA software based on the opti-370 371 mized ground geometry (Figure 6 and Table 2) [30], is a key parameter that determines the magnitude 372 of spin-orbit coupling, and thus provides important information on the dynamics of SOCT-ISC and HAE. 373 The SOCME between S₁ and T₁ states was 0.44 cm⁻¹ for AM9, indicating that the ISC of AM9 originated 374 from the HAE induced SOC. On the other hand, AM2 exhibited an SOCME of 0.57 cm⁻¹, indicating that 375 ISC was induced by spin-orbit charge transfer in AM2. The SOCME values of AM6, AM7, and AM8 were 376 5.18, 8.93, and 8.74 cm⁻¹ respectively, significantly higher than those of AM2 and AM9. Since this was 377 identical to the trend of SOQY, it was postulated that ISC was mainly influenced by SOC, and not HFC. 378 SOCME values between the S_1 and T_2 states for AM2–AM8 were relatively small, in the range from 0.00 379 to 0.16, which indicated that SOC did not occur properly because both the S₁ and T₂ states have CT 380 characteristics. The SOCME between S_0 and T_1 correlated well with the triplet lifetime. In general, with 381 increasing SOCME, the nonradiative decay from T_1 to S_0 became dominant, and as a result, the triplet 382 lifetime decreased. The SOCME values of AM2, AM6, AM7, AM8, and AM9 were 0.76, 0.91, 0.56, 0.15, 17

- and 2.80 cm⁻, respectively, and this trend was inversely correlated with the triplet lifetime. In particular, AM9 showed the highest SOCME, which resulted in the shortest triplet lifetime. On the other hand, the SOCME (S_0 -T₁) values of AM6–AM8 were reduced, even though they contained heavy atoms. The synergistic effect of PET and HAE lowered SOCME (S_0 -T₁) and selectively increased only SOCME (S_1 -T₁), which may result in shortened triplet lifetime and increased ISC yield.
- 388
- 389 Table 2 Spin orbit coupling matrix element (SOCME) and the energy gap between the excited singlet
- 390 (S_n) and triplet (T_m) states.

		SOCME	ΔE_{Sn-Tm}
		(cm ⁻¹)	(eV)
	$S_0 \leftrightarrow T_1$	0.76	1.68
AM2	$S_1 \leftrightarrow T_1$	0.57	0.52
	$S_1 \leftrightarrow T_2$	0.03	0.33
	$S_0 \leftrightarrow T_1$	0.91	1.64
AM6	$S_1 \leftrightarrow T_1$	5.18	0.49
	$S_1 \leftrightarrow T_2$	0.16	0.28
	$S_0 \leftrightarrow T_1$	0.56	1.60
AM7	$S_1 \leftrightarrow T_1$	8.93	0.49
	$S_1 \leftrightarrow T_2$	0.00	0.28
	$S_0 \leftrightarrow T_1$	0.15	1.59
AM8	$S_1 \leftrightarrow T_1$	8.74	0.36
	$S_1 \leftrightarrow T_2$	0.10	0.21
A M 0	$S_0 \leftrightarrow T_1$	2.80	1.48
AIVI9	$S_1 \leftrightarrow T_1$	0.44	0.72

- 391
- 392
- 393 3.7 Triplet-triplet annihilation upconversion (TTA-UC)



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Figure 7 (a) TTA-UC photoluminescence spectra of AM2–9 (inset) photographs of emission in upconversion system. (b) Upconversion intensity (log scale) and (c) upconversion emission efficiencies of AM2–
9 (sensitizers: 20µM, annihilator: 32µM) as a function of incident laser power density (mW/cm²)

398

399 TTA-UC, which generates anti-Stokes emission, is generally achieved by molecular energy transfer be-400 tween two different organic molecules, a sensitizer and an annihilator. Here, the triplet sensitizer plays 401 an important role in generating the triplet annihilator by absorbing photons, being excited, and transfer-402 ring energy to the annihilator. Therefore, the triplet feature of the sensitizer largely affects the overall UC 403 emission efficiency of TTA-UC. Although porphyrin-based photosensitizers have been widely studied in 404 TTA-UC, we employed AM2-9 photosensitizers as triplet sensitizers in TTA-UC and investigated their 405 photochemical properties. Perylene was selected as a triplet annihilator because of its superior fluores-406 cence quantum yield, and all measurements were performed in deaerated toluene using a 532 nm laser 407 as a light source to achieve typical green-to-blue upconversion. The sensitizer and pervlene concentra-

tions were optimized to 20 µivi and 32 µivi, respectively, based on the preliminary 00 intensity measure-408 409 ments (Figure S23) using AM8. When a 532 nm laser (4.9 W/cm²) was irradiated onto the UC solution, 410 upconverted blue emission (430-500 nm), attributed to delayed fluorescence of perylene, was clearly 411 visible in all samples, along with spectral measurement, although there was a clear difference in UC 412 intensity according to the type of sensitizer (Figure 7a). Note that the AM8 solution, not including perylene 413 (the leftmost picture in Figure 7a), shows down-shifted red fluorescence. Moreover, UC intensity ap-414 peared in the order of AM8>AM7>AM6>AM9>AM2, which is consistent with the result of SOQY, demon-415 strating the triplet synergistic effect of AM6–8 photosensitizers. (Table 3)

416

417 Table 3 Overlap integral (Sr), electron exchange energy (J), singlet oxygen quantum yield (Φ_{Δ}), and 418 triplet lifetime (τ_{T}), upconversion emission efficiency (η_{UC}), and threshold intensity (I_{th}) of AM2–9 photo-

419 sensitizers under excitation at 532nm

	Sr ^a	J (eV) ^b	ΦΔ	τ _τ ϲ (μs)	η _{υc} e	I _{th} (mW/cm²) ^c
AM2	0.08328	0.17	0.32 ^c , 0.05 ^d	132	0.015	179
AM6	0.08158	0.14	0.66 ^c , 0.16 ^d	122	0.039	465
AM7	0.08133	0.14	0.70 ^c , 0.20 ^d	175	0.062	176
AM8	0.07889	0.11	0.74 ^c , 0.05 ^d	199	0.065	179
AM9	0.64344	<u> </u>	0.49 ^c , 0.55 ^d	57	0.017	1,916

^a Overlap integral was obtained from the natural transition orbital of S1 state. ^b Electron exchange integral was determined by the energy difference between ¹CT and ³CT states. In ^c toluene and ^d dichloromethane. ^e Upconversion emission efficiency was determined in toluene using a 532 nm laser (4.9 W/cm²)

424

To further characterize TTA-UC properties, UC emission efficiency (η_{UC}) and UC intensities were measured by varying the laser excitation power (Figure 7b and c). As the laser power increased, the UC emission efficiency of all the solutions increased and then plateaued. The highest UC emission efficiency (6.5%) was obtained for the AM8 solution. Although higher levels of UC emission efficiency have been reported in porphyrin-based TTA-UC,[31, 32] this is close to the UC emission efficiency of iodine BODIPY

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- 430 photosensitizers, which showed high UC emission efficiency in toluene among BODIPY-based sensitiz 431 ers.[33]

432 In the plot of UC intensity versus laser power density (Figure 7b), clear quadratic (at low power density, 433 slope=2) to linear (at high power density, slope=1) power dependency was observed for all UC solutions, 434 which is a typical feature of TTA-UC.[34, 35] Meanwhile, the effectiveness of TTA-UC is also evaluated 435 by the threshold intensity (I_{th}), which is the laser power density at the point where these quadratic-to-436 linear correlations intersect. That is, for lower values of I_{th} value, the triplet annihilator is more rapidly 437 generated, and the generated excited triplet annihilators are consumed by TTA, not by unimolecular 438 decay. The Ith values of UC solutions containing AM2, AM6, AM7, AM8, and AM9 were 179, 465, 176, 179, and 1.916 mW/cm², respectively. Interestingly, the Ith values of the UC solutions containing D-A 439 440 sensitizers (AM2, AM6, AM7, and AM8) were low, whereas that of the UC solution without the D-A sen-441 sitizer (AM9) was exceptionally high. Because the I_{th} is mainly determined by the triplet energy transfer 442 efficiency from the sensitizer to the annihilator, [36] this difference is attributed to the increased triplet 443 lifetime of the sensitizer because of the introduction of a donor molecule. These results clearly indicate 444 that D-A coupled with heavy atoms reduces the high I_{th} of heavy atom photosensitizers.

445

446 **Conclusions**

447 In summary, we reported a novel approach for triplet photosensitizers comprising triphenylamine (D)-448 BODIPY (A)-bromine (H), and demonstrated that merging D-A molecules with heavy atoms drove the 449 synergistic effect of PET and HAE, contributing to enhanced triplet characteristics such as SOQY and 450 triplet lifetime. Moreover, the TTA-UC study showed that D-A-H photosensitizers achieved high upcon-451 version emission efficiency and low Ith compared with standards (D-A and heavy atom photosensitizers). 452 However, it was not possible to obtain excellent triplet characteristics because the study was only fo-453 cused on photosensitizers consisting of triphenylamine-BODIPY-bromine. This might be overcome by 454 several strategies such as enhancing the PET or introducing a heavier atom. Therefore, D-A-H photo-455 sensitizers with various donors, acceptor, and heavy atoms may achieve more improved triplet quantum 456 yield, triplet lifetime, and upconversion properties.

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- D-A-H compounds exhibit better triplet properties than conventional strategies
- Synergistic effect of photoinduced electron transfer and heavy atom effect
- D-A-H compounds overcome the limitation of heavy atom effect

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Declaration of interests: The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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