

## Effects of halogen atom substitution on luminescent radicals: a case study on tris(2,4,6-trichlorophenyl)methyl radical- carbazole dyads

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## ARTICLE

# Effects of halogen atom substitution on luminescent radical: A case study on *tris*(2,4,6-trichlorophenyl)methyl radical-carbazole dyad

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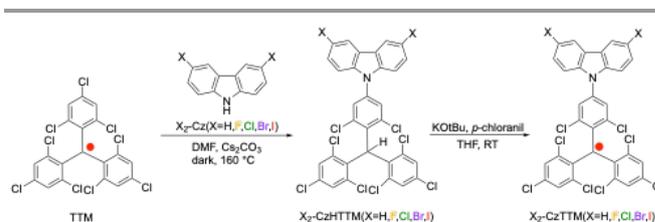
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Series of halogen-substitute carbazole TTM radicals were synthesized. The effect of halogen substituents on radical luminescence was systematically evaluated. It was found that well-known heavy atom effect does not work in the emission of radicals and that halogen substitution of the donor carbazole can change the HOMO and alter the absorption and emission wavelengths. In addition, photostability was found to be improved with respect to TTM but not significantly different from that of closed-shell fluorescent molecules.

## Introduction

Recently, organic radicals have been capturing increasing interest<sup>1</sup> in optics and optoelectronics due to the unique emission properties from the doublet spin state resulting from the open-shell electron configuration.<sup>2,3,4,5,6,7,8,9</sup> Conventional closed-shell fluorescent molecules exhibit fluorescence from the excited singlet (S1) to the ground singlet (S0) and phosphorescence from the excited triplet (T1) to the S0 state after intersystem crossing from S1 to T1 state. The intersystem crossing is well known to be accelerated by intra- or intermolecular heavy atoms due to the large spin-orbital coupling, which reduces the luminescence efficiency of fluorescence (heavy atom effect (HAE)).<sup>10</sup> In general, substituting heavy atoms such as bromine and iodine in fluorescent molecules decreases photoluminescent quantum yield (PLQY) due to HAE.<sup>11,12,13</sup>

Only a few organic radicals show luminescence at room temperature, such as *tris*(2,4,6-trichlorophenyl)methyl (TTM) radicals<sup>14, 15, 16, 17, 18</sup> perchloro triphenylmethyl (PTM) radicals<sup>19, 20, 21, 22, 23</sup>, pyridyl-containing triphenylmethyl (PyBTM) radicals<sup>24, 25, 26, 27, 28</sup> (N-carbazolyl)bis(2,4,6-trichlorophenyl)-methyl (CzBTM) radicals<sup>29, 30</sup>. These trityl radicals are stabilized sterically with bulky chlorine atoms and electronically by spin delocalization over the aromatic ring.



Scheme 1. Synthesis of halogen-modified TTM carbazole dyads.

However, these radicals are known to have (i) low stability under light irradiation<sup>14,19,20</sup> or (ii) low PLQY (TTM = 2.6%<sup>24</sup>, PTM = 1.5%<sup>20</sup>, PyBTM = 2.5%<sup>24</sup>, CzBTM = 2.0%<sup>29</sup>). Among such luminescent organic radicals, TTM radicals have been reported to exhibit high PLQY and photostability when coupled with a carbazole donor (CzTTM)<sup>31</sup>. To date, compounds with Cz derivatives attached to TTM have been synthesized, but only a few halogen-substituted Cz derivatives have been reported<sup>32,33,34,35,36,37</sup>.

Luminescent organic radicals exhibit fluorescence from the excited doublet (D1) to the ground doublet (D0), and since there is no other multiplet state between D1 and D0, the HAE that affects the spin-flipping process can be ignored. The incorporation of heavy atoms into the luminescent organic radical framework is expected to be used as a pure substituent to adjust the luminescence properties without causing a decrease in PLQY due to the absence of intersystem crossing. However, to our knowledge, there are only three reports that have investigated HAE of luminescent radicals<sup>38,39,40</sup>, and a systematic study is not conducted.

In this study, we synthesized (**F2,Cl2,Br2,I2**)-CzTTM radicals (Scheme 1), in which the 3,6 positions of carbazole were replaced by halogen atoms (F, Cl, Br, and I), and investigated the photophysical properties systematically to study HAE in luminescent radical systems. Comparison of photostability

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**Table 1.** Photophysical properties of radicals in cyclohexane(left) and toluene(right).

Radical	$\lambda_{\text{Abs}}$ (nm)	$\lambda_{\text{PL}}$ (nm)	$\Phi_{\text{F}}$ (%)	PL lifetime (ns)	$k_r$ ( $\times 10^7 \text{ s}^{-1}$ )	$k_{\text{nr}}$ ( $\times 10^7 \text{ s}^{-1}$ )
TTM	541 / 543	564 / 569	1.5 / 2.0	5.4 / 5.7	0.28 / 0.35	18 / 17
CzTTM	603 / 609	628 / 671	91 / 60	41 / 25	2.2 / 2.4	0.22 / 1.6
F2-CzTTM	595 / 603	620 / 664	83 / 49	42 / 21	2.0 / 2.4	0.40 / 2.5
Cl2-CzTTM	592 / 598	617 / 656	64 / 66	42 / 30	1.5 / 2.2	0.87 / 1.1
Br2-CzTTM	594 / 598	614 / 653	68 / 77	41 / 31	1.7 / 2.5	0.79 / 0.74
I2-CzTTM	594 / 601	618 / 660	72 / 66	40 / 29	1.8 / 2.3	0.70 / 1.2

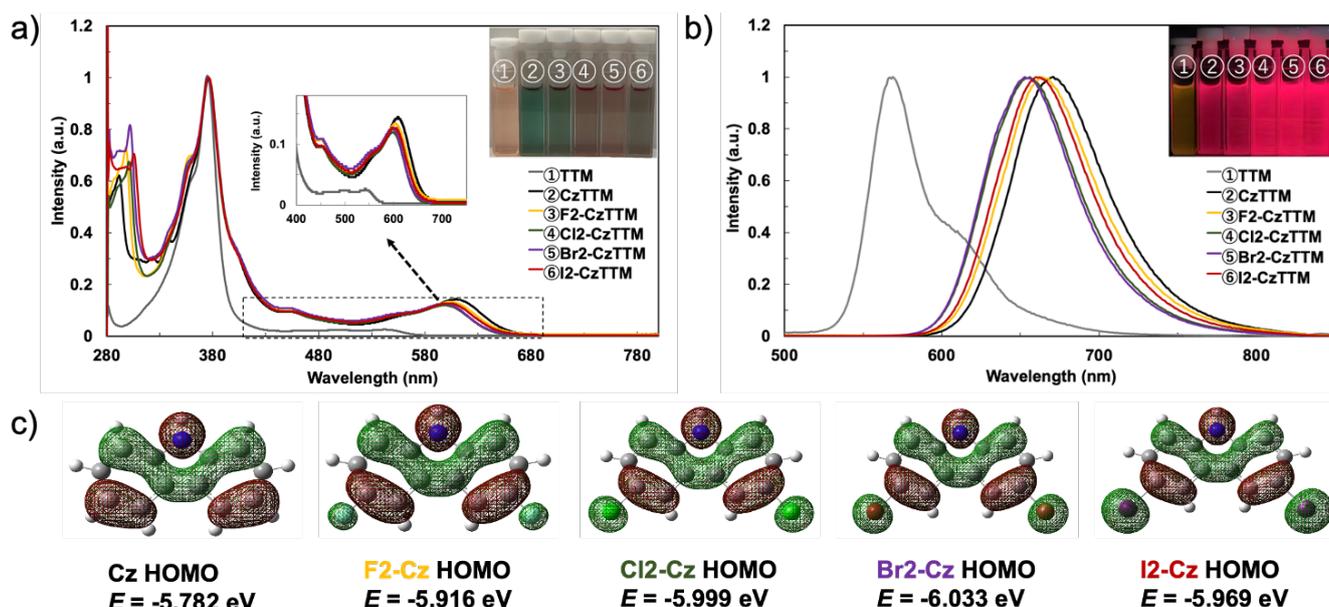
between **CzTTM** and **(F2,Cl2,Br2,I2)-CzTTM** were also investigated. Halogen substitution of luminescent organic radicals can perturbate optical functions while maintaining PLQY and photostability. This is the first systematic report of HAE and halogen substitution in a TTM radical derivative.

## Results and Discussion

### Synthesis and characterization

**CzTTM** and **(F2,Cl2,Br2,I2)-CzTTM** were synthesized by nucleophilic aromatic substitution between carbazoles and TTM radicals to obtain the precursors and following radicalization process (Scheme 1).<sup>32-33</sup> TTM radical,  $\text{Cs}_2\text{CO}_3$ , and Cz derivatives<sup>41</sup> were heated under a nitrogen atmosphere with DMF as solvent at 160 °C for 24 h. Radical precursors were isolated using preparative scale gel permeation chromatography (GPC). The yields were **CzHTTM**(31%), **F2-CzHTTM** (46%), **Cl2-CzHTTM** (19%), **Br2-CzHTTM** (19%) and **I2-CzHTTM**(17%). These radical precursors contained a trace amount of radicals.<sup>31, 42, 43</sup> The radical existence in the precursor was confirmed by UV-vis absorption spectra (Fig. S10-11). The pure H compounds could be

synthesized by Buckwald-Hartwig reaction of Cz or F2-Cz with HTTM (Scheme S1). The radical precursors were dissolved in THF, t-BuOK was added and stirred in the dark for 48 h to form an anion. *p*-Chloranil was added and stirred for 24h at room temperature to form radicals through a one-electron oxidation process. The final products were purified by flash silica gel column chromatography (eluent: hexane: chloroform=1:1). The yield was **CzTTM**(48%), **F2-CzTTM** (59%), **Cl2-CzTTM** (38%), **Br2-CzTTM** (22%) and **I2-CzTTM** (40%). Note that **CzTTM**, **Cl2-CzTTM** and corresponding precursors have been reported previously.<sup>32,33</sup> The solubility of these radicals in cyclohexane was low. On the other hand, they showed good solubility in toluene. All precursors were characterized with mass spectrometry (MALDI-TOF-MS), <sup>1</sup>H NMR, <sup>13</sup>C NMR, and elemental analysis, and radicals were characterized with mass spectrometry (MALDI-TOF-MS), elemental analysis, and electron spin resonance (ESR). The purity of the radical was determined with ESR to be around 70-95% by comparing the signal strength with reference TEMPOL (Fig. S4, Table S1). The impurities are assumed to be inseparable precursors (HTTM derivatives). The halogen-substituted carbazole-TTM dyads



**Fig. 1.** a) UV-Vis spectra in toluene; b) PL spectra in toluene; c) DFT-calculated HOMO energies and orbital coefficients for the Cz and (F2,Cl2,Br2,I2)-Cz.

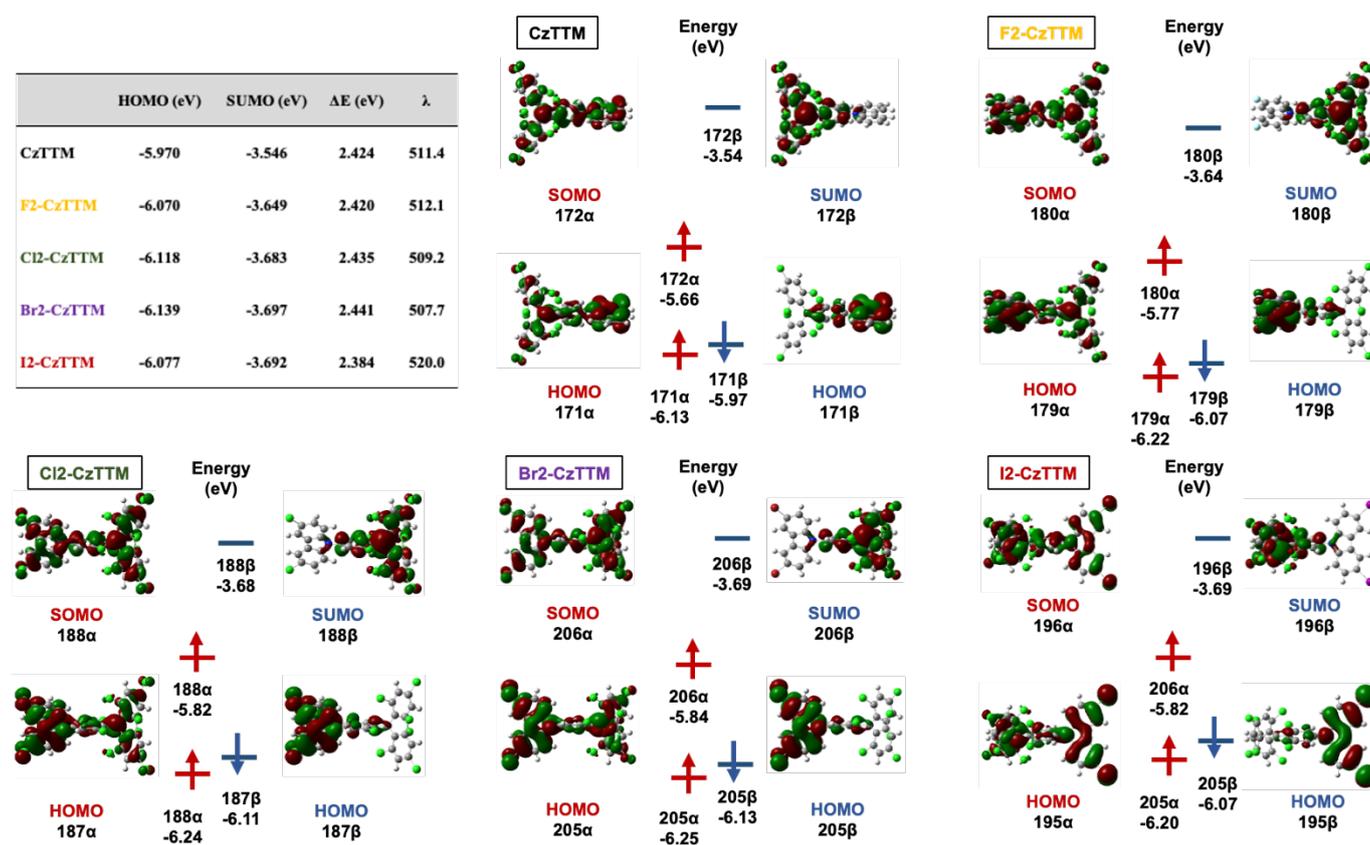


Fig. 2. Molecular orbital and energies of the CzTTM and (F2, Cl2, Br2, I2)-CzTTM radicals calculated by DFT.

were successfully synthesized with sufficient purity to discuss the photophysical property.

### Optical properties

The UV-vis absorption spectra of (F2, Cl2, Br2, I2)-CzTTM were recorded in cyclohexane and toluene solutions (Fig. 1, Fig. S5). Each halogenated-CzTTM radical exhibited absorption bands similar to bare TTM radicals at 373 and 376 nm in cyclohexane and toluene solutions attributed to  $\pi$ - $\pi^*$  transitions of the TTM moiety.<sup>2,44</sup> The absorption around 500-700 nm is attributed to charge transfer (CT) transitions between carbazole (donor) and TTM (acceptor). Note that these two absorptions are not present in the pure H compounds (Fig. S10).<sup>32</sup> In fact, absorption corresponding to the locally excited (LE) state changed little with changing solvent polarity, while the absorption corresponding to CT red shifted with increasing solvent polarity from cyclohexane to toluene (Table 1). The lowest excited state is assumed to be an electronic transition from halogenated Cz HOMO (hCz) to TTM SOMO (sT) with this CT property. The slight difference in absorption wavelength by changing the substituent is attributed to the difference in the energy level of the carbazole donor. Halogen substitution perturbs the energy level (HOMO) of Cz moiety and affects the vertical excitation energy. HOMO energies of carbazole and halogen substituted carbazole were determined by density functional theory (DFT) calculations. HOMO energies were Cz > F2-Cz > I2-Cz > Cl2-Cz > Br2-Cz in ascending order. The order of the blue shift

observed experimentally in toluene solution is CzTTM (609 nm) > F2-CzTTM (603 nm) > I2-CzTTM (601 nm) > Cl2-CzTTM  $\approx$  Br2-CzTTM (598 nm), which is roughly consistent with the HOMO energy order of calculated carbazoles (Fig. 1, Table. 1). From these results, it was found that it is possible to predict the trend in absorption bands by calculating HOMO energy of the Cz derivatives by DFT calculation. Halogen substitution perturbs the energy level of the carbazole donor due to the electron withdrawing character and results in a slight blue shift of the CT absorption band.

The PL spectra of (F2, Cl2, Br2, I2)-CzTTM in cyclohexane and toluene solutions were recorded (Fig. 1, Fig. S5). The emission peak wavelength of (F2, Cl2, Br2, I2)-CzTTM in cyclohexane and toluene solutions were red-shifted compared to TTM, but blue shifted compared to CzTTM. The emission wavelength has also slightly changed by the carbazole substitution as well as the absorption wavelength CzTTM (671 nm) > F2-CzTTM (664 nm) > I2-CzTTM (660 nm) > Cl2-CzTTM (656 nm) > Br2-CzTTM (653 nm). Similar to CzTTM<sup>31</sup>, the emission spectra were broad and the peak wavelength of (F2, Cl2, Br2, I2)-CzTTM showed a red shift from cyclohexane to toluene as the polarity of the solvent increased. This behavior suggests that the emission originated from a CT excited state. The excited state CT character was also confirmed by the fact that as the solvent polarity increases, a broader spectrum characteristic of CT emission was observed (Fig. 1, Fig. S5). This emission behavior (energy and CT character) is supported by the HOMO-SUMO gap of CzTTM and (F, Cl, Br, I)2-CzTTM

determined by DFT calculations (Fig. 2). The PL spectra of halogenated carbazole-TTM derivatives showed that halogenation makes small perturbation as well as UV-vis absorption.

PL lifetime and PLQY of **(F2,Cl2,Br2,I2)-CzTTM** were measured with and without degassing after solution preparation in the dark, and kinetic rate constants in cyclohexane and toluene were determined (Table 1). The PL lifetimes of each compound could be fitted with a single exponential decay function (Fig. S18-21). The lifetime has only shown little change before and after degassing process: around 1 ns increases after degassing. Observed PLQYs measured without degassing process were **(F2,Cl2,Br2,I2)-CzTTM** (64-83%) compared to **CzTTM**(91%) in cyclohexane solution, **(F2,Cl2,Br2,I2)-CzTTM** (49-77%) compared to **CzTTM**(60%) in toluene solution (Table 1). Note that the 91 % PLQY of **CzTTM** is higher than the reported value with a relative method.<sup>32</sup> However, our measurement was conducted with following points, (i) during the sample preparation to the measurement process, the irradiation of room light to the samples was avoided as much as possible because we found the PLQY can decrease rapidly under the light irradiation, and (ii) measurement was done with an integrating sphere, and the absolute PLQY was determined (the result was also confirmed with 2 independent absolute PLQY apparatus). Similar to PL lifetime, PLQY changed little after degassing process; After the degassing PLQY of most of compounds increased only 1~2 %. These results suggest that PL lifetime and PLQY are hardly affected by oxygen, probably due to the relatively short emission lifetime and doublet spin character. **(F2,Cl2,Br2,I2)-CzTTM** and **CzTTM** showed no clear change in terms of PLQY in each solvent. This is the exact opposite of the closed-shell fluorescent molecules mentioned earlier.<sup>11,12,13</sup> For further discussion, rate constants for radiative ( $k_r$ ) and non-radiative ( $k_{nr}$ ) decay constants were determined from PLQY and PL lifetimes (Table 1). The  $k_r$  and  $k_{nr}$  of **CzTTM** and **(F2, Cl2, Br2, I2)-CzTTM** were compared in cyclohexane and toluene solutions, but there was no clear difference between **CzTTM** and **(F2, Cl2, Br2, I2)-CzTTM** in each solvent (Table 1). In comparing two solvents, the PLQY and PL lifetime of **CzTTM** and **(F, I)2-CzTTM** was clearly lower in toluene, and the main reason is an increase of  $k_{nr}$  probably due to the energy gap law (see Table 1). On the other hand, **(Cl,Br)2-CzTTM** has improved PLQY in toluene (see Table 1). The reason is unclear but may be due to the presence of barriers to conical intersections that are very sensitive to solvent polarity.<sup>45</sup> The PLQY and PL lifetime of **(F2, Cl2, Br2, I2)-Cz** (carbazoles without TTM) were also measured (Fig. S16-17). The results showed that PLQY clearly decreases and  $k_{nr}$  increases from light to heavy halogen atoms due to the HAE (Table. S3). The PLQY and rate constants of halogenated CzTTM dyads indicate that HAE does not work in radical emission.

To explore its potential as a luminescent material, the PL and PLQY of 5 wt% **CzTTM** and **(F2, Cl2, Br2, I2)-CzTTM** doped polystyrene (PS) and poly methyl methacrylate (PMMA) thin films were measured (Table S2, Fig. 13-14). The PL spectra of each compound showed red shift and PLQYs were significantly

lower compared to cyclohexane solution described earlier (Table 1, Table S2). PMMA film showed the most red-shifted emission and lowest PLQY. This trend follows the polarity of the environment, i.e., cyclohexane has the lowest polarity, PS is next, and PMMA has the highest polarity. Higher polarity shifts the CT emission to a longer wavelength and typically, the PLQY decreases due to the energy gap law. This indicates that the doping matrix strongly affects the photophysical properties. For future applications in an OLED device, the matrix and doping concentration have to be considered<sup>46</sup>.

### Quantum mechanical calculations

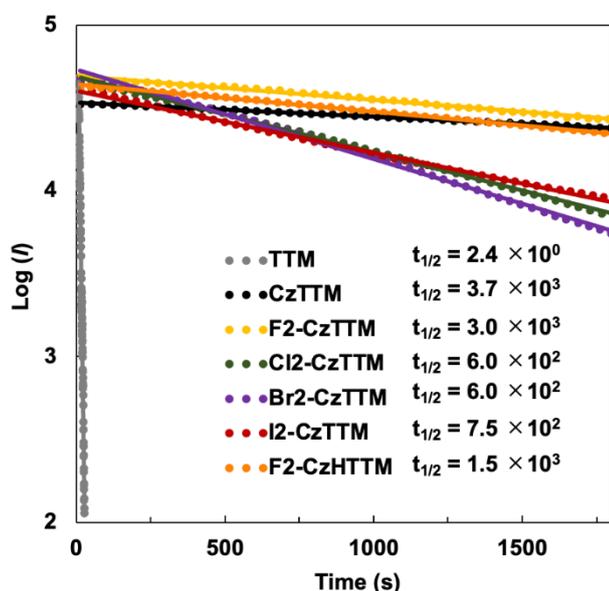
The unrestricted Kohn-Sham density functional theory (UKS-DFT) calculations using Gaussian 16 with UB3LYP functional and def2TVZPP basis sets were performed in a vacuum to understand the electronic structure of carbazole-TTM dyads.<sup>39,47</sup> The HOMO-SUMO energies were obtained to give an orbital description of the lowest energy absorption band. The energy difference between HOMO-SUMO was 2.424 eV (**CzTTM** 171 $\beta$ -172 $\beta$ ), 2.420 eV (**F2-CzTTM** 179 $\beta$ -180 $\beta$ ), 2.435 eV (**Cl2-CzTTM** 187 $\beta$ -188 $\beta$ ), 2.441 eV (**Br2-CzTTM** 205 $\beta$ -206 $\beta$ ), and 2.384 eV (**I2-CzTTM** 195 $\beta$ -196 $\beta$ ), respectively (Fig. 2). DFT calculations show that the lowest absorption band is likely the CT absorption from the Cz derivative to TTM. As mentioned in the UV-vis absorption section, calculations show that the HOMO level of Cz and (F, Cl, Br, I)2-Cz change depending on the substituents. The calculated HOMO energies of **CzTTM** (-5.97 eV) > **F2-CzTTM** (-6.07 eV)  $\approx$  **I2-CzTTM** (-6.07 eV) > **Cl2-CzTTM** (-6.11 eV) > **Br2-CzTTM** (-6.13 eV), were consistent with the aforementioned Cz and (F, Cl, Br, I)2-Cz. DFT calculation has confirmed the CT character of the lowest excited state and correlation with donor HOMO level.

### Electrochemical Properties

The electrochemical behavior of the radicals in the solution was measured to further study the energy level (Fig. S22). The cyclic voltammetry (CV) measurements were performed using a conventional 3 electrode system. A glassy carbon disk was used as the working electrode, platinum wire as a counter electrode, and Ag/Ag<sup>+</sup> as the reference electrode. The redox couple ferrocenium/ferrocene was added as the internal standard. Tetrabutylammonium hexafluorophosphate (TBAPF<sub>6</sub>) in dichloromethane (0.2 M) was used as the supporting electrolyte. All radicals showed two reversible redox couples at -1.04 / +0.83 V (TTM), -1.07 / +0.57 V (**CzTTM**), -1.04 / +0.60 V (**F2-CzTTM**), -1.02 / +0.64 V (**Cl2-CzTTM**), -1.02 / +0.67 V (**Br2-CzTTM**), and -1.01 / +0.64 V (**I2-CzTTM**). The redox around -1 V corresponds to the reduction (SUMO) and the redox around +0.5~+0.8 V corresponds to the oxidation (SOMO) of TTM radical.<sup>48, 49, 50, 51</sup> These results are mostly consistent with the calculated energy ordering of SUMO and SOMO. The redox potential of the radicals shows that the halogen substitution gives a small perturbation to the energy level of TTM radical.

### Photostability of radicals

The photostability of each halogenated carbazole-TTM dyad was observed by continuously irradiating a 355 nm pulsed laser to toluene solution and monitoring the PL intensity (Fig. 3, Fig. S23).<sup>50,52</sup> Note that the absorbance of all compounds was controlled to be 0.5 at 355 nm, measured with and without degassing, and the solution was stirred under all the measurements. **F2-CzHTTM**, a closed-shell fluorescence molecule, was also measured under the same conditions for comparison with radicals.<sup>53,54,55</sup> Without degassing, the half-life ( $t_{1/2}$ ) of bare TTM radical was shown to be 2.4 s. The  $t_{1/2}$  of halogenated carbazole TTM radicals were **F2-CzTTM** ( $3.0 \times 10^3$  s), **Cl2-CzTTM** ( $6.0 \times 10^2$  s), **Br2-CzTTM** ( $6.0 \times 10^2$  s) and **I2-CzTTM** ( $7.5 \times 10^2$  s), respectively. Compared to **CzTTM** ( $3.7 \times 10^3$  s), a slight decrease due to halogen substitution was observed, but the stability was still much higher than the bare TTM radical. Interestingly, the slope of the emission intensity of **F2-CzTTM** and **F2-CzHTTM** (Fig. 3) is similar, suggesting a similar degradation mechanism. Both **F2-CzTTM** and **F2-CzHTTM** have the same neutral F2-Cz moiety. This result seems to suggest that the donor unit stability dominates the radical photostability, but further investigation is necessary. In addition, the  $t_{1/2}$  was extended by up to a factor of 2 after degassing (Fig. S23). The photostability study revealed that 1) halogen substitution decreases the photostability, 2) the photostability of radicals is affected by the existence of oxygen, but this is not dominant, and 3) The photostability of the radical is comparable to corresponding closed shell molecule (**F2-CzHTTM**) and might be dominated with the stability of the donor unit rather than the radical in some CT stabilized radicals (Fig. 3).



**Fig. 3.** The emission intensity ( $I$ ) of radicals during 355 nm pulsed laser radiation in without degassed toluene (power : 20.0 mW, beam diameter (Gaussian beam,  $1/e^2$  level, FWHM) :  $\sim 3$  mm, pulse width : 28 ps, repetition rate : 100 Hz). The unit of  $t_{1/2}$  in the inset is second.

### Conclusion

We synthesized (**F, Cl, Br, I**)-**CzTTM** and **CzTTM** radicals and systematically evaluated the effect of halogen substitution on radical luminescence. Halogen substitution on the donor carbazole changes HOMO energy and alters absorption and luminescence properties. PLQY measurements in cyclohexane and toluene with and without degassing showed that HAE does not work in radical luminescence and is not affected by oxygen. The photostability of (**F, Cl, Br, I**)-**CzTTM** and **CzTTM** radicals were found to be improved relative to TTM and comparable to that of closed-shell fluorescence molecules. This study clearly shows that HAE does not work in radical luminescence. To seek the possibility of applications of the halogenated radicals, we are planning to utilize them for OLEDs and their application to bioimaging, which will be presented in near future.

### Conflicts of interest

There are no conflicts to declare.

### Acknowledgements

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