Electronic Supplementary Material (ESI) for Faraday Discussions.

Supporting Information

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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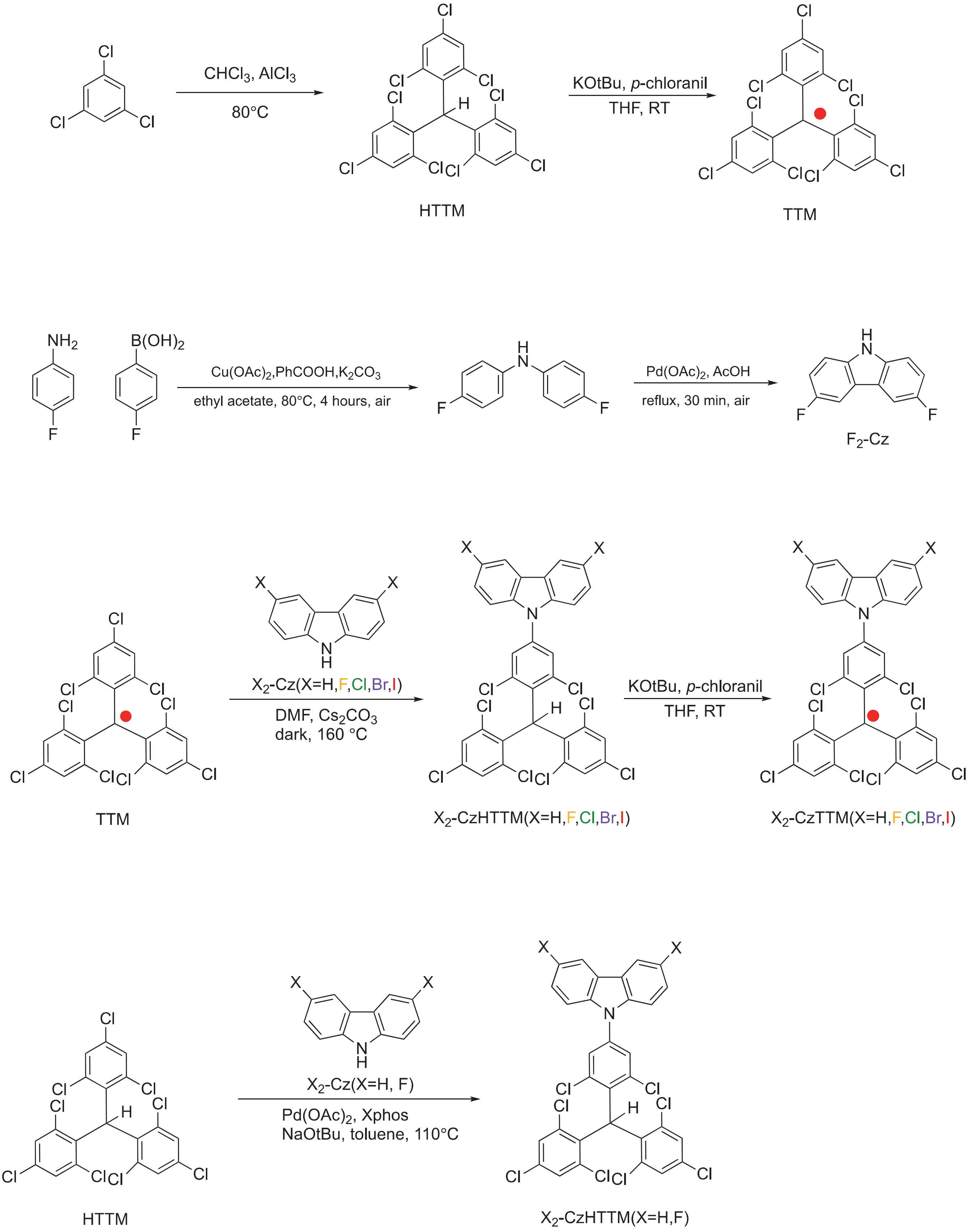
Experimental section

Chemicals. All chemicals were purchased from FUJIFILM Wako Pure Chemical Co., Kanto Kagaku Co., Ltd., TCI chemicals, or Aldrich and used without further purification unless otherwise noted.

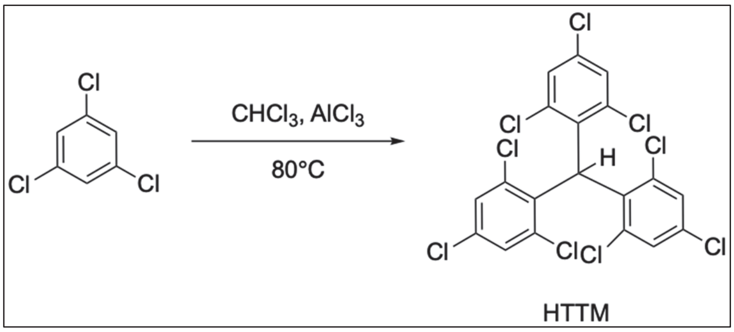
General. The NMR spectra were obtained using a JNM-ECZ400 (400MHz) and JNM-ECA600 (600MHz). ^{1}H NMR and ^{13}C NMR were measured with TMS as the internal standard. ^{19}F NMR was measured with hexafluorobenzene as the internal standard. The elemental analysis was performed at the Service Center of the Elementary Analysis of Organic Compounds, Faculty of Science, Kyushu University. The UV-vis spectra were recorded using a Shimadzu UV-2600 spectrometer with a quartz cell having a 1cm optical length at 25ºC. The PL spectra were measured by HORIBA JOBIN YVON FluoroMax-Plus Model: KUA11 and the fluorescence quantum yields were measured by a Hamamatsu Photonics Quantaurus-QY MODEL C13534-01 absolute PL quantum yield measurement system at room temperature (excitation wavelength: 374nm). A preparative scale gel permeation chromatography, LC-5060 (Japan Analytical Industry Co., Ltd.) with chloroform as the eluent, and an automated flash column chromatography, Biotage Isolera Spektra were used to isolate each compound. Electron Spin Resonance (ESR) spectra were recorded by JEOL JES-FA200. The thin films of the 5 wt% radicals doped PS and PMMA were fabricated in the following method. Radicals toluene solutions (10 mg/mL) and PS and PMMA toluene solutions (10 mg/mL) were prepared and mixed to be 5 wt% of radicals conentration, then spin-coated on a quartz substrate (1,000 rpm). PL spectra of the thin films were recorded in the range of 400 nm to 850 nm; PL spectra were measured at an excitation wavelength of 376 nm. The PL lifetime measurements were performed using Horiba FluoroCube (excitation wavelength of 342 nm, pulse width ~1.0 ns). The photostability tests were conducted using DPSS picosecond pulsed laser (Ekspla, PL2211) and photonic multichannel analyzer (Hamamatsu, PMA-12). The concentration of the samples was controlled to give an absorbance of 0.5 at 355 nm. The measured values were calibrated using the purity and absorption coefficient of the radicals. The excitation light of third harmonics of the Nd:YAG laser (wavelength: 355 nm, pulse width: 28 ps, repetition rate: 100 Hz, laser power: 20 mW) was continuously irradiated to the samples, and the time dependence of the PL intensity at a peak wavelength was detected by the analyzer. All calculations are performed using the Gaussian16 program package.[1] The cyclic voltammetry (CV) measurements were performed using an electrochemical analyzer (ECstat-302, EC Frontier, JPN). A glassy carbon disk was used as the working electrode. A platinum wire acted as the counter electrode, and Ag/Ag^{+} acted as the reference electrode, together with the redox couple ferrocenium/ferrocene as the internal standard. The CV profiles were recorded at the rate of 50 mV·s^{-1}. Tetrabutylammonium hexafluorophosphate (TBAPF$_6$) in dichloromethane (0.2 M) was used as the supporting electrolyte for negative and positive scans.

Synthesis



Scheme S1. Synthesis routes of X2Cz-TTM (X=H, F, Cl, Br, I).

Tris(2,4,6-trichlorophenyl)methyl (HTTM)



HTTM was synthesized similarly to the literature.[2]

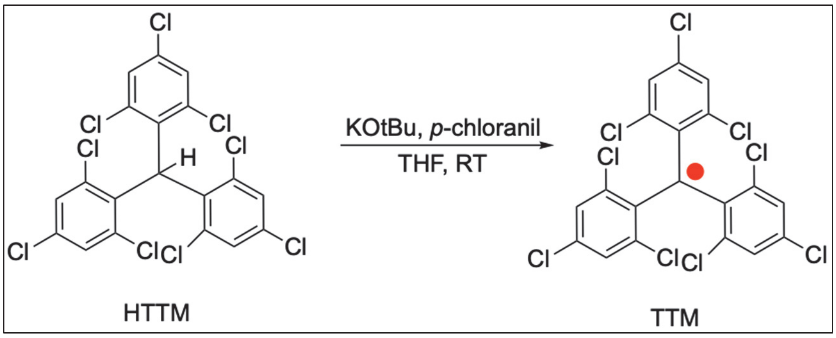
Under nitrogen atmosphere, a mixture of 1,3,5-trichlorobenzene (25.1 g, 0.138 mol), anhydrous chloroform (1.5 mL, 0.0187 mol), and aluminum chloride (2.31 g, 0.0173 mol) was heated at 80°C for 2h in a 500 ml 3-neck flask. After cooling to room temperature, the mixture was dissolved in chloroform and then poured into hydrochloric acid (1M). The mixture was extracted with chloroform (3 × 50 mL) and the combined organic phases were dried over Na_2SO_4. Evaporation of the solvent gave crude product as a colorless solid. The crude product was purified by silica gel column chromatography (hexane) to obtain αHTTM as a colorless powder (8.61 g, 84 %).

The ^{1}H-NMR spectrum was identical to the previous report.[2]

^{1}H-NMR (400 MHz, $CDCl_3$)

δ[ppm] = 7.36 (d, J = 2.2 Hz, 3H), 7.23 (d, J = 2.2 Hz 3H), 6.67 (s, 1H).

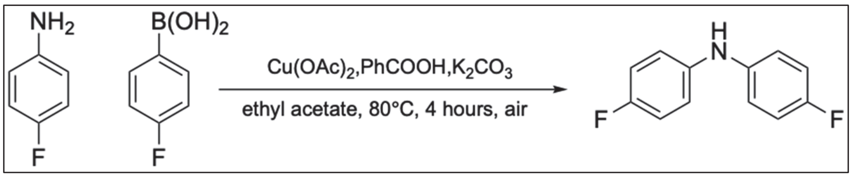
Tris(2,4,6-trichlorophenyl)methyl radical (TTM)



TTM was synthesized similarly to the literature.[2]

Under nitrogen atmosphere and in the dark, αHTTM (200 mg, 0.360 mmol) was dissolved in anhydrous THF (150 mL), then t-BuOK (2.02 g, 18.0 mmol) was added. After the mixture was stirred for 48 h at room temperature, tetrachloro-*p*-benzoquinone (8.81 g, 36.0 mmol) was added to the reaction mixture and allowed to react for another 24 h. After the reaction, the solvent was removed under vacuum. The crude product was purified by silica gel column chromatography (hexane : chloroform = 1:1) to obtain TTM radical as a red powder (65.9 mg, 33 %).

Bis(4-fluorophenyl) amine



Bis(4-fluorophenyl)amine was synthesized similarly to the literature.[3]

A mixture of anhydrous $Cu(OAc)_2$ (418 mg, 2.30 mmol) and benzoic acid (1.30 g, 10.6 mmol), in ethyl acetate was added 4-fluoroaniline (1.19 g, 10.7 mmol) and 4-fluorophenylboronic acid (4.53 g, 32.4 mmol), K_2CO_3 (1.49 g, 10.8 mmol) at room temperature. The resulting mixture was heated to 80 ºC for 4 hours. The solvent was removed with a rotary evaporator. The crude product was purified by silica gel column chromatography (hexane: ethyl acetate= 1:1) to obtain bis(4-fluorophenyl)amine as a sticky black liquid (1.24 g, 57 %).

The ^{1}H-NMR spectrum was identical to the previous report.

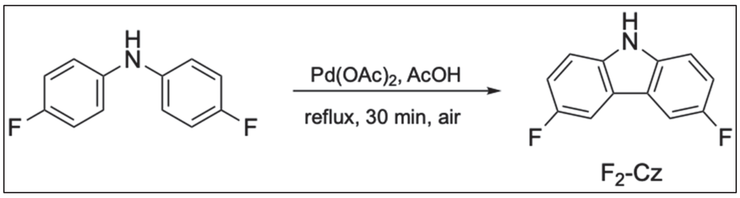
^{1}H-NMR (400 MHz, $CDCl_3$)

δ[ppm] = 6.95-6.97 (m, 8H), 5.37 (br, s, 1H),

^{19}F-NMR (376 MHz, $CDCl_3$)

δ[ppm] = -122.52 (s, 2F).

3,6-difluoro-9*H*-carbazole (F2-Cz)



F_2-Cz was synthesized similarly to the literature.[3]

Bis(4-fluorophenyl)amine (1.18 g, 5.75 mmol) and $Pd(OAc)_2$ (1.18 g, 5.75 mmol) in acetic acid (15 mL) was refluxed for 30 minutes. After cooling, the reaction mixture was filtered through celite, which was subsequently washed with sodium bicarbonate (3 × 10 mL). The mixture was extracted with ethyl acetate (2 × 30 mL) and the combined organic phases were dried over Na_2SO_4. Evaporation of the solvent gave a brown residue. The crude product was purified by silica gel column chromatography (hexane: ethyl acetate= 5:1) to obtain F2-Cz as a light brown precipitate (565 mg, 48 %).

The ^{1}H-NMR spectrum was identical to the previous report.

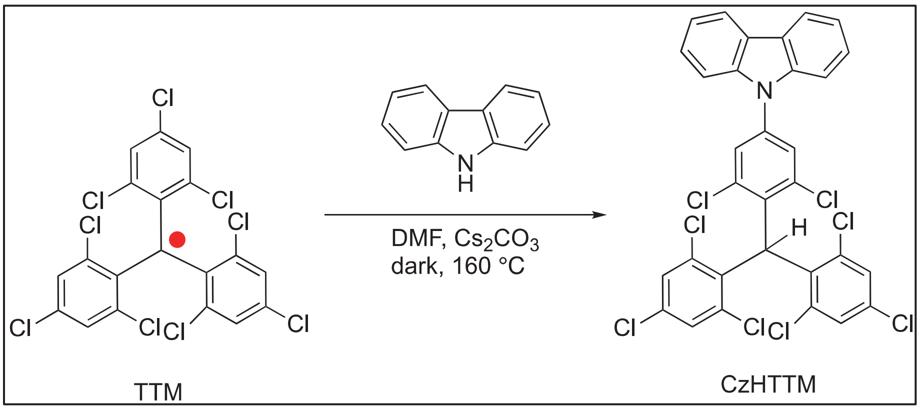
^{1}H-NMR (400 MHz, $CDCl_3$)

δ[ppm]= 8.00 (br s, 1H), 7.66 (dd, Jd = 12 Hz, Jd = 4 Hz, 2H), 7.35 (q, Jq = 4 Hz, 2H), 7.17 (td, Jt = 20 Hz, Jd = 4 Hz, 2H)

^{19}F-NMR (376 MHz, $CDCl_3$)

δ[ppm] = -124.03 (s, 2F).

9-(4-(bis(2,4,6-trichlorophenyl)methyl)-3,5-dichlorophenyl)-9H-carbazole (CzHTTM)



CzHTTM was synthesized similarly to the literature.[4]

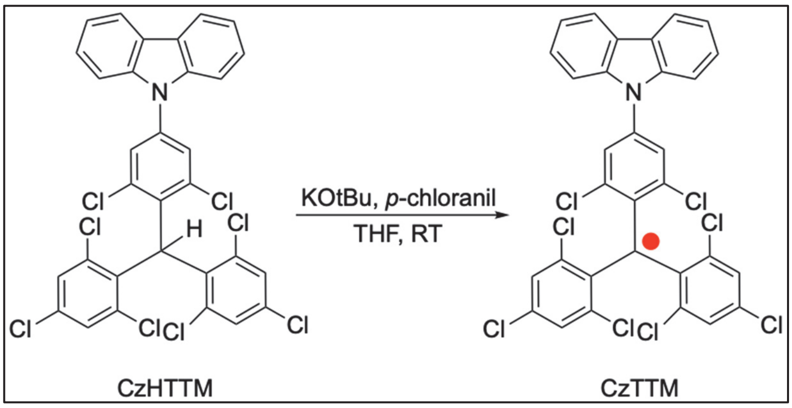
Under nitrogen atmosphere and in the dark, a mixture of TTM (1.29 g, 2.33 mmol), carbazole (467 mg, 2.79 mmol), Cs_2CO_3 (2.24 g, 6.90 mmol), and anhydrous DMF (8 mL) was added into a 100 ml 3-neck flask, and stirred at 160 °C for 24 h. After the solution was cooled to room temperature, the mixture was poured into hydrochloric acid (1M). The mixture was extracted with chloroform (3 × 50 mL) and the combined organic phases were dried over Na_2SO_4. Evaporation of the solvent gave crude product as a dark green solid. The crude product was purified by silica gel column chromatography (hexane) to obtain CzHTTM as a reddish purple powder (491 mg, 31 %).

The ^{1}H-NMR spectrum was identical to the previous report.

^{1}H-NMR (400 MHz, $CDCl_3$)

δ[ppm]= δ 8.13 (d, J = 7.8 Hz, 2H), 7.61 (d, J = 2.3 Hz, 1H), 7.48 (d, J = 2.3 Hz, 1H), 7.44 - 7.47 (m, 4H), 7.43 (d, J = 2.3 Hz, 1H), 7.41 (d, J = 2.3 Hz, 1H), 7.29 - 7.36 (m, 3H), 7.28 (d, J = 2.3 Hz, 1H), 6.85 (s, 1H).

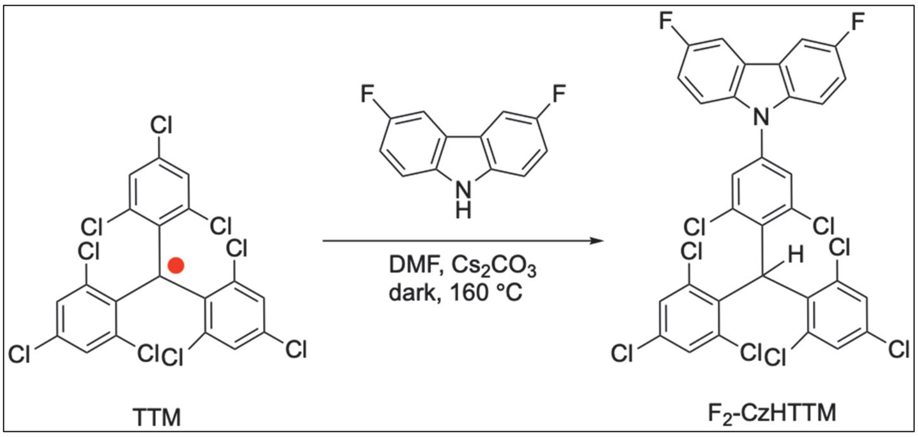
9-(4-(bis(2,4,6-trichlorophenyl)methyl)-3,5-dichlorophenyl)-9*H*-carbazole (CzTTM)



CzTTM was synthesized similarly to the literature.[4]

Under nitrogen atmosphere and in the dark, CzHTTM (215 mg, 0.314 mmol) was dissolved in anhydrous THF (150 mL), then t-BuOK (1.76 g, 15.7 mmol) was added. After the mixture was stirred for 48 h at room temperature, tetrachloro-*p*-benzoquinone (7.72 g, 31.4 mmol) was added to the reaction mixture and allowed to react for another 24 h. After the reaction, the solvent was removed under vacuum. The crude product was purified by silica gel column chromatography (hexane: chloroform = 1:1) to obtain CzTTM radical as a dark red powder (103 mg, 48 %).

9-(4-(bis(2,4,6-trichlorophenyl)methyl)-3,5-dichlorophenyl)-3,6-difluoro-9*H*-carbazole (F2-CzHTTM)



Under nitrogen atmosphere and in the dark, a mixture of TTM (609 mg, 1.10 mmol), 3,6-difluoro-carbazole (112 mg, 0.550 mmol), Cs_2CO_3 (1.08 g, 3.30 mmol), and anhydrous DMF (8 mL) was added into a 100 ml 3-neck flask together, stirring at 160 °C for 24 h. After the solution cooled to room temperature, the mixture was poured into hydrochloric acid (1M). The mixture was extracted with chloroform (3 × 50 mL) and the combined organic phases were dried over Na_2SO_4. Evaporation of the solvent gave crude product as a dark green solid. The crude product was purified by preparative GPC (eluent: chloroform) to obtain F2-CzHTTM as a green powder (181 mg, 46 %).

^{1}H-NMR (400 MHz, $CDCl_3$)

δ[ppm]= δ 7.71 (dd, J = 2.5, 8.5 Hz, 2H), 7.56 (d, J = 2.3 Hz, 1H), 7.42 - 7.45 (m, 2H), 7.41 (d, J = 2.3 Hz, 1H), 7.37 (d, J = 4.1 Hz, 1H), 7.35 (d, J = 4.1 Hz, 1H), 7.30 (d, J = 2.3 Hz, 1H), 7.28 (d, J = 2.3 Hz, 1H), 7.21 (td, J = 2.5, 8.9 Hz, 2H), 6.85 (s, 1H).

^{13}C-NMR (150 MHz, $CDCl_3$)

δ[ppm]= 158.8, 157.3, 138.7, 138.0, 137.9, 137.8, 137.7, 137.3, 137.2, 134.4, 134.0, 133.9, 130.2, 130.2, 128.6, 128.6, 128.0, 126.4, 123.9, 123.9, 123.9, 123.8, 114.9, 114.8, 110.8, 110.8, 110.7, 106.6, 106.4, 50.1.

^{19}F-NMR (376 MHz, $CDCl_3$)

δ[ppm] = -123.46 (s, 2F).

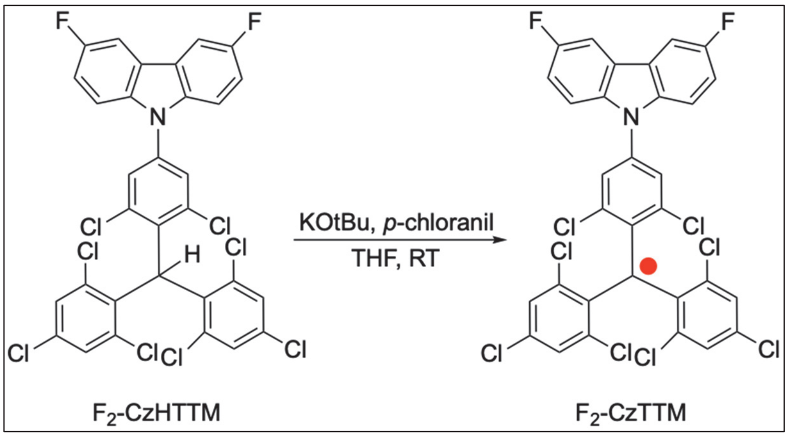
MALDI-TOF-MS (Matrix: 1,8,9-Trihydroxyanthracene)

Calcd : 720.8465($M^{+\cdot}$), Found : 721.0073

Elem. Anal.

Calcd for $C_{31}H_{13}Cl_8F_2N$, C 51.64, H 1.82, N 1.94; Found C 51.68, H 1.81, N 1.89.

9-(4-(bis(2,4,6-trichlorophenyl)methyl)-3,5-dichlorophenyl)-3,6-difluoro-9*H*-carbazole radical (F2-CzTTM)



Under nitrogen atmosphere and in the dark, F2-CzHTTM (102 mg, 0.142 mmol) was dissolved in anhydrous THF (150 mL), then t-BuOK (797 mg, 7.10 mmol) was added. After the mixture was stirred for 48 h at room temperature, tetrachloro-*p*-benzoquinone (3.49 g, 14.2 mmol) was added to the reaction mixture and allowed to react for another 24 h. After the reaction, the solvent was removed under vacuum. The crude product was purified by silica gel column chromatography (hexane: chloroform = 1:1) to obtain F2-CzTTM radical as a green powder (61 mg, 59 %).

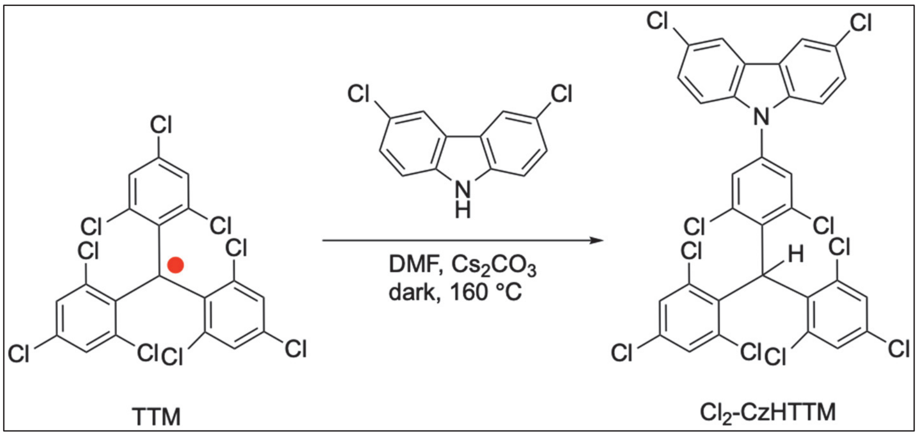
MALDI-TOF-MS (Matrix: 1,8,9-Trihydroxyanthracene)

Calcd : 719.8387($M^{+\cdot}$), Found : 719.9865

Elem. Anal.

Calcd for $C_{31}H_{12}Cl_8F_2N$, C 51.71, H 1.68, N 1.95; Found C 51.60, H 1.77, N 1.94.

9-(4-(bis(2,4,6-trichlorophenyl)methyl)-3,5-dichlorophenyl)-3,6-dichloro-9*H*-carbazole (Cl2-CzHTTM)



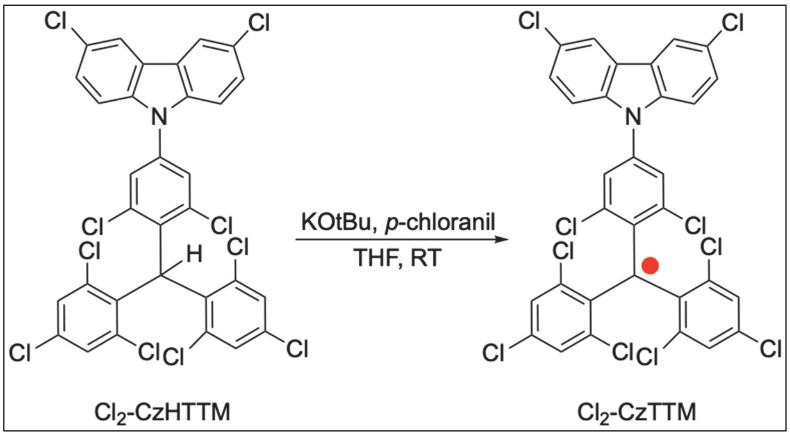
Cl2-CzHTTM was synthesized similarly to the literature.[5]

Under nitrogen atmosphere and in the dark, a mixture of TTM (215 mg, 0.388 mmol), 3,6-dichloro-carbazole (133 mg, 0.561 mmol), Cs_2CO_3 (359 mg, 1.10 mmol), and anhydrous DMF (3 mL) was added into a 100 ml 3-neck flask together, stirring at 160 °C for 12 h. After the solution cooled to room temperature, the mixture was poured into hydrochloric acid (1M). The mixture was extracted with chloroform (3 × 50 mL) and the combined organic phases were dried over Na_2SO_4. Evaporation of the solvent gave crude product as a dark green solid. The crude product was purified by preparative GPC (eluent: chloroform) to obtain Cl2-CzHTTM as a green powder (57 mg, 19 %). The ^{1}H-NMR spectrum was identical to the previous report.

^{1}H-NMR (400 MHz, $CDCl_3$)

δ[ppm]= 6.85 (s, 1H), 7.28 (d, J = 2.1 Hz 1H), 7.30 (d, J = 2.1 Hz, 1H), 7.33 (d, J = 8.8 Hz, 2H),7.40-7.44 (m, 5H),7.54 (d, J = 2.1 Hz, 1H), 8.03 (d, J = 2.1 Hz, 2H).

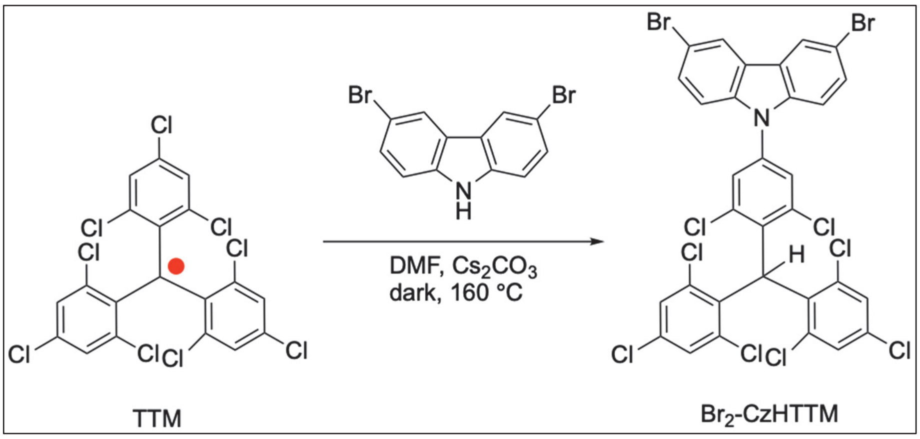
9-(4-(bis(2,4,6-trichlorophenyl)methyl)-3,5-dichlorophenyl)-3,6-dichloro-9*H*-carbazole radical (Cl2-CzTTM)



Cl2-CzTTM was synthesized similarly to the literature.[5]

Under nitrogen atmosphere and in the dark, Cl2-CzHTTM (143 mg, 0.189 mmol) was dissolved in anhydrous THF (150 mL), then, t-BuOK (1.08 g, 9.70 mmol) was added. After the mixture was stirred for 48 h at room temperature, tetrachloro-*p*-benzoquinone (4.76 g, 19.4 mmol) was added to the reaction mixture and allowed to react another 24 h. After the reaction, the solvent was removed under vacuum. The crude product was purified by silica gel column chromatography (hexane : chloroform = 1:1) to obtain Cl2-CzTTM radical as a green powder (55 mg, 38 %).

9-(4-(bis(2,4,6-trichlorophenyl)methyl)-3,5-dichlorophenyl)-3,6-dibromo-9*H*-carbazole (Br2-CzHTTM)



Br2-CzHTTM was synthesized similarly to the literature.[5]

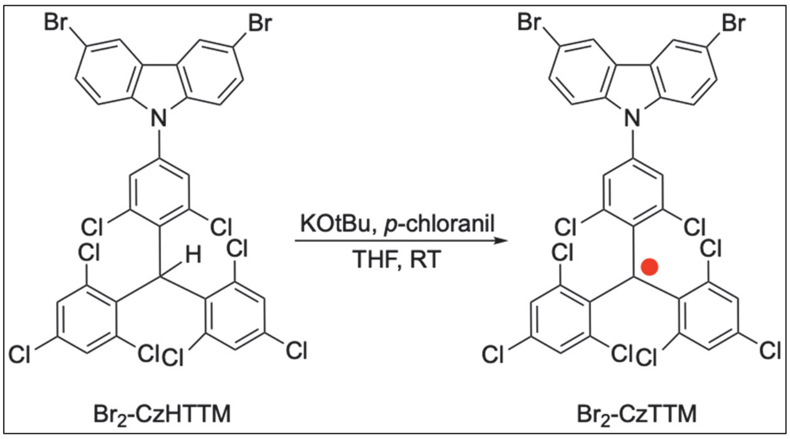
Under nitrogen atmosphere and in the dark, a mixture of TTM (217 mg, 0.392 mmol), 3,6-dibromo-carbazole (153 mg, 0.470 mmol), Cs_2CO_3 (371.3 mg, 1.14 mmol), and anhydrous DMF (3 mL) were added into a 100 ml 3-neck flask together, stirring at 160 °C for 12 h. After the solution cooled to room temperature, the mixture was poured into hydrochloric acid (1M). The mixture was extracted with chloroform (3 × 50 mL) and the combined organic phases were dried over Na_2SO_4. Evaporation of the solvent gave crude product as a dark green solid. The crude product was purified by preparative GPC (eluent: chloroform) to obtain Br2-CzHTTM as a green powder (29 mg, 9 %).

The ^{1}H-NMR spectrum was identical to the previous report.

^{1}H-NMR (400 MHz, $CDCl_3$)

δ[ppm]= 6.85 (s, 1H), 7.27-7.30 (m, 4H), 7.40-7.41 (m, 2H), 7.43 (d, 1H, J = 2.4 Hz), 7.54 (d, 2H, J = 1.8 Hz), 7.56 (d, 1H, J = 2.1 Hz), 8.18 (d, 2H, J = 1.8 Hz).

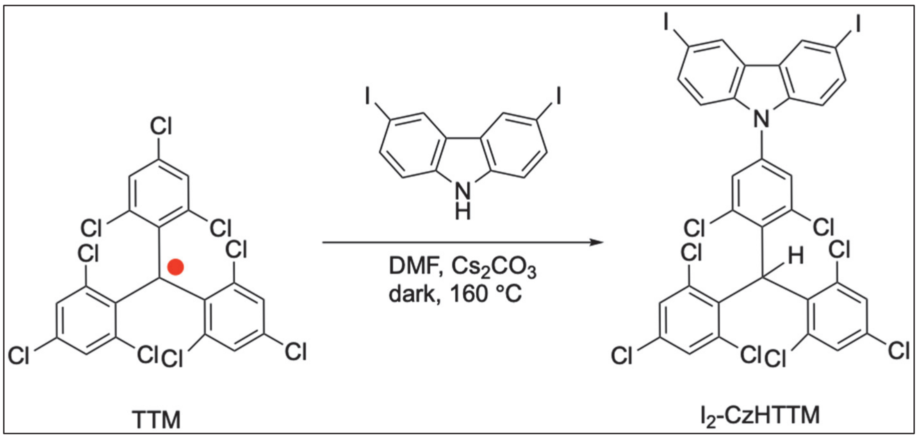
9-(4-(bis(2,4,6-trichlorophenyl)methyl)-3,5-dichlorophenyl)-3,6-dibromo-9*H*-carbazole radical (Br2-CzTTM)



Br2-CzTTM was synthesized similarly to the literature.[5]

Under nitrogen atmosphere and in the dark, Br2-CzHTTM (135 mg, 0.159 mmol) was dissolved in anhydrous THF (150 mL), then, t-BuOK (892 mg, 7.95 mmol) was added. After the mixture was stirred for 48 h at room temperature, tetrachloro-*p*-benzoquinone (3.90 g, 15.9 mmol) was added to the reaction mixture and allowed to react for another 24 h. After the reaction, the solvent was removed under vacuum. The crude product was purified by silica gel column chromatography (hexane: chloroform = 1:1) to obtain Br2-CzTTM radical as a green powder (31 mg, 22 %).

9-(4-(bis(2,4,6-trichlorophenyl)methyl)-3,5-dichlorophenyl)-3,6-diiodo-9*H*-carbazole (I2-CzHTTM)



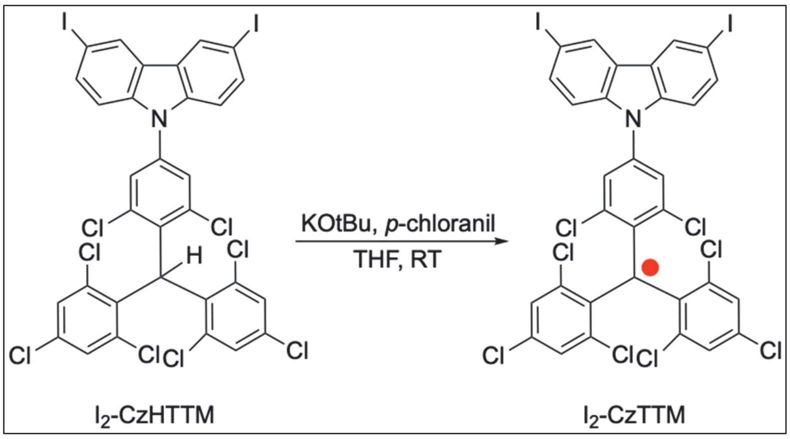
I2-CzHTTM was synthesized similarly to the literature.[6]

Under nitrogen atmosphere and in the dark, a mixture of TTM (219 mg, 0.396 mmol), 3,6-diiode-carbazole (206 mg, 0.492 mmol), Cs_2CO_3 (359 mg, 1.10 mmol), and anhydrous DMF (3 mL) was added into a 100 ml 3-neck flask together, stirring at 160 °C for 12 h. After the solution cooled to room temperature, the mixture was poured into hydrochloric acid (1M). The mixture was extracted with chloroform (3 × 50 mL), and the combined organic phases were dried over Na_2SO_4. Evaporation of the solvent gave crude product as a dark green solid. The crude product was purified by preparative GPC (eluent: chloroform) to obtain l2-CzHTTM as a green powder (45 mg, 12 %).
The ^{1}H-NMR spectrum was identical to the previous report.

^{1}H-NMR (400 MHz, $CDCl_3$)

δ[ppm]=6.84 (s, 1H), 7.19 (d, J = 8.69 Hz 2H), 7.28 (d, J = 2.29 Hz, 1H), 7.30 (d, J = 2.29 Hz, 1H),7.39 (d, J = 2.29 Hz 1H),7.40 (d, J = 2.29 Hz, 1H), 7.52 (d, J = 2.29 Hz, 1H), 7.70 (d, J =1.68 Hz, 1H), 7.72 (d, J = 1.68 Hz, 1H) 8.38 (d, J = 1.68 Hz, 2H).

9-(4-(bis(2,4,6-trichlorophenyl)methyl)-3,5-dichlorophenyl)-3,6-diiodo-9*H*-carbazole radical (I2-CzTTM)



Under nitrogen atmosphere and in the dark, I2-CzHTTM (150 mg, 0.160 mmol) was dissolved in anhydrous THF (150 mL), then, t-BuOK (900 mg, 8.01 mmol) was added. After the mixture was stirred for 48 h at room temperature, tetrachloro-*p*-benzoquinone (3.93 g, 16.0 mmol) was added to the reaction mixture and allowed to react for another 24 h. After the reaction, the solvent was removed under vacuum. The crude product was purified by silica gel column chromatography (hexane: chloroform = 1:1) to obtain I2-CzTTM radical as a green powder (61 mg, 40 %).

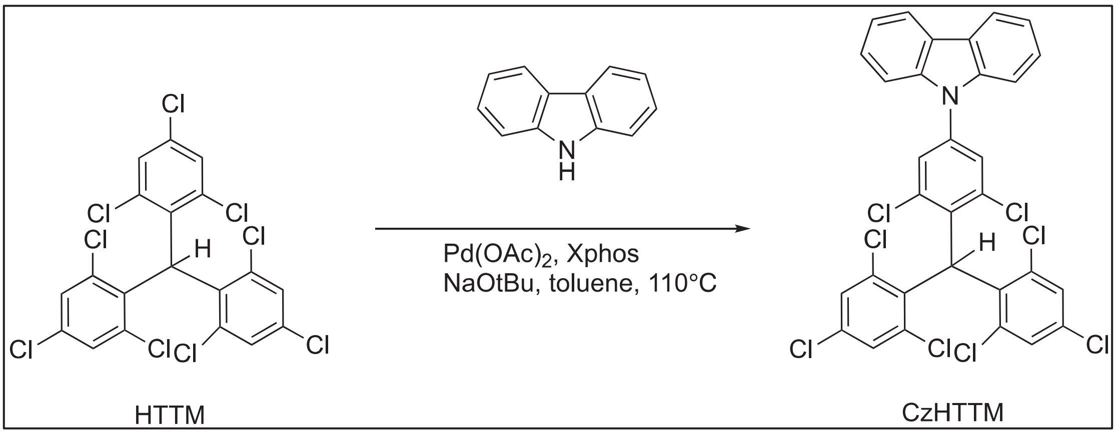
MALDI-TOF-MS (Matrix: 1,8,9-Trihydroxyanthracene)

Calcd : 935.6508($M^{+\cdot}$), Found : 935.8395

Elem. Anal.

Calcd for $C_{31}H_{12}Cl_8I_2N$, C 39.79, H 1.29, N 1.50; Found C 40.02, H 1.41, N 1.33.

9-(4-(bis(2,4,6-trichlorophenyl)methyl)-3,5-dichlorophenyl)-9H-carbazole (CzHTTM)



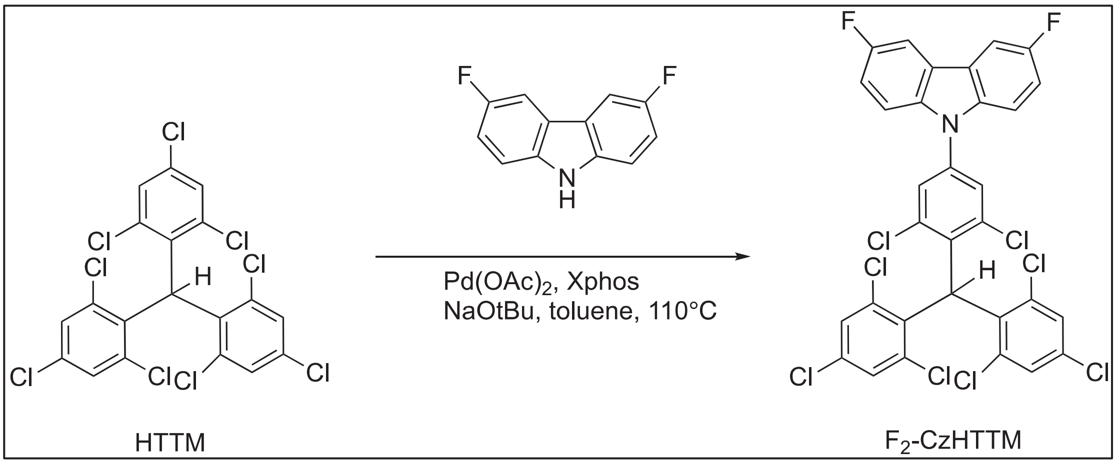
Under nitrogen atmosphere, a mixture of HTTM (1.00 g, 1.80 mmol), carbazole (534 mg, 3.19 mmol), $Pd(OAc)_2$ (121 mg, 0.538 mmol), XPhos (515 mg, 1.08 mmol), NaOtBu (691 mg, 7.20 mmol) and toluene (40 mL) were added into a 300 ml round-bottom flask together, stirring at 110 °C for 24 h. After the solution cooled to room temperature, the mixture was poured into hydrochloric acid (1M). The mixture was extracted with chloroform (3 × 50 mL) and the combined organic phases were dried over Na_2SO_4. Evaporation of the solvent gave crude product. The crude product was purified by silica gel column chromatography (hexane) to obtain CzHTTM as a colorless powder (81 mg, 6 %).

The ^{1}H-NMR spectrum was identical to the previous report.

^{1}H-NMR (400 MHz, $CDCl_3$)

δ[ppm]= δ 8.13 (d, J = 7.8 Hz, 2H), 7.61 (d, J = 2.3 Hz, 1H), 7.48 (d, J = 2.3 Hz, 1H), 7.44 - 7.47 (m, 4H), 7.43 (d, J = 2.3 Hz, 1H), 7.41 (d, J = 2.3 Hz, 1H), 7.29 - 7.36 (m, 3H), 7.28 (d, J = 2.3 Hz, 1H), 6.85 (s, 1H).

9-(4-(bis(2,4,6-trichlorophenyl)methyl)-3,5-dichlorophenyl)-3,6-difluoro-9*H*-carbazole (F2-CzHTTM)



Under nitrogen atmosphere, a mixture of HTTM (1.05 g, 1.90 mmol), F2-Cz (194 mg, 0.954 mmol), Pd(OAc)$_2$ (43 mg, 0.19 mmol), XPhos (272 mg, 0.570 mmol), NaOtBu (730 mg, 7.59 mmol) and toluene (60 mL) were added into a 200 ml round-bottom flask together, stirring at 110 °C for 24 h. After the solution cooled to room temperature, the mixture was poured into hydrochloric acid (1M). The mixture was extracted with chloroform (3 × 50 mL) and the combined organic phases were dried over Na$_2$SO$_4$. Evaporation of the solvent gave crude product. The crude product was purified by silica gel column chromatography (hexane) to obtain F2-CzHTTM as a colorless powder (39 mg, 5 %).

^{1}H-NMR (400 MHz, CDCl$_3$)

δ[ppm]= δ 7.71 (dd, J = 2.5, 8.5 Hz, 2H), 7.56 (d, J = 2.3 Hz, 1H), 7.42 - 7.45 (m, 2H), 7.41 (d, J = 2.3 Hz, 1H), 7.37 (d, J = 4.1 Hz, 1H), 7.35 (d, J = 4.1 Hz, 1H), 7.30 (d, J = 2.3 Hz, 1H), 7.28 (d, J = 2.3 Hz, 1H), 7.21 (td, J = 2.5, 8.9 Hz, 2H), 6.85 (s, 1H).

^{13}C-NMR (150 MHz, CDCl$_3$)

δ[ppm]= 158.8, 157.3, 138.7, 138.0, 137.9, 137.8, 137.7, 137.3, 137.2, 134.4, 134.0, 133.9, 130.2, 130.2, 128.6, 128.6, 128.0, 126.4, 123.9, 123.9, 123.9, 123.8, 114.9, 114.8, 110.8, 110.8, 110.7, 106.6, 106.4, 50.1.

^{19}F-NMR (376 MHz, CDCl$_3$)

δ[ppm] = -123.46 (s, 2F).

NMR spectra

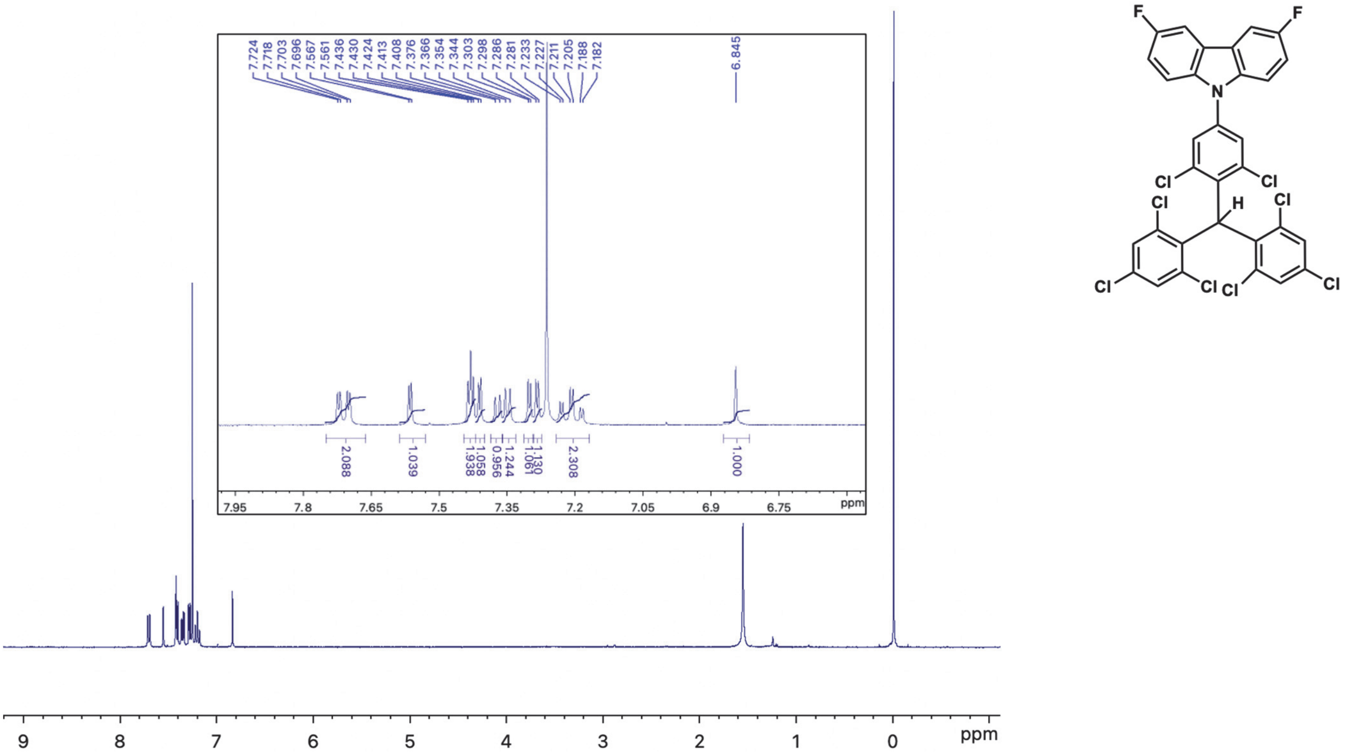


Fig. S1. ^{1}HNMR spectra of F2-CzHTTM.

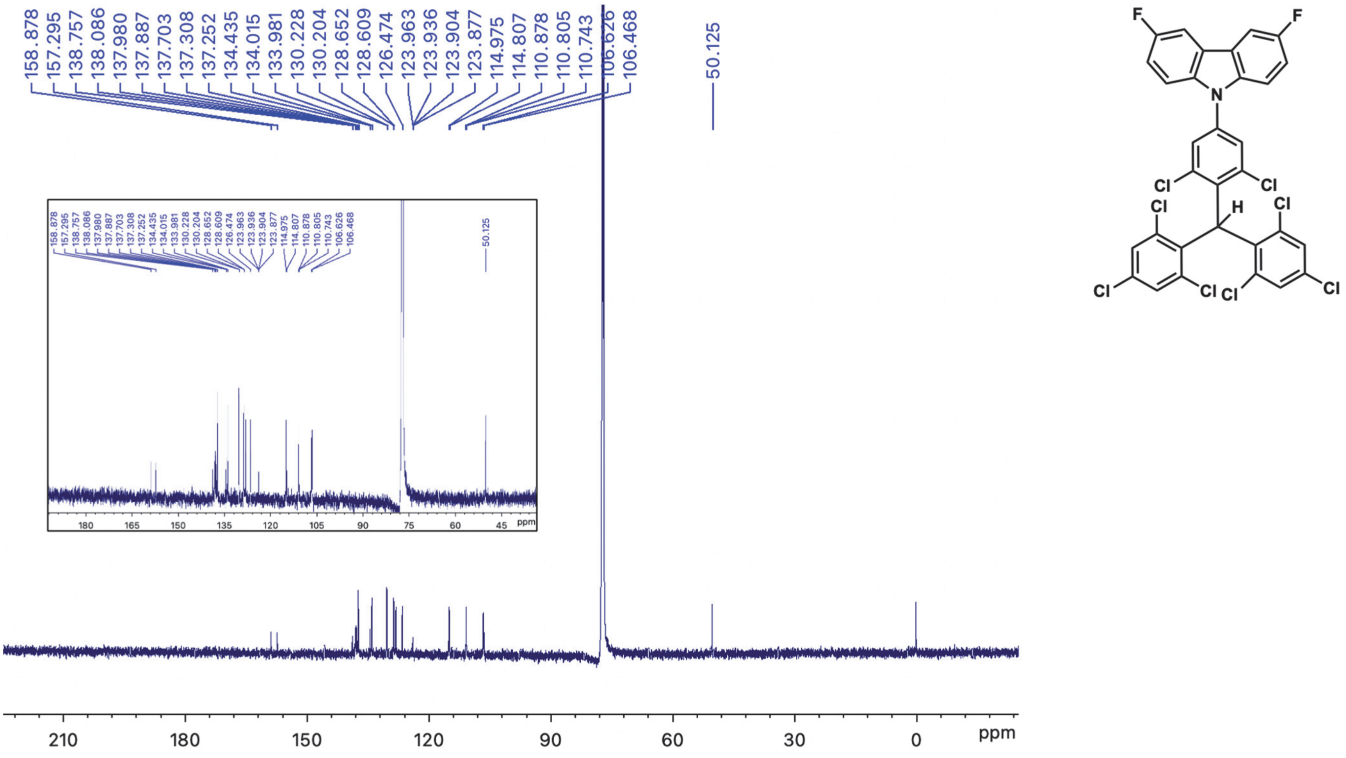


Fig. S2. ^{13}CNMR spectra of F2-CzHTTM.

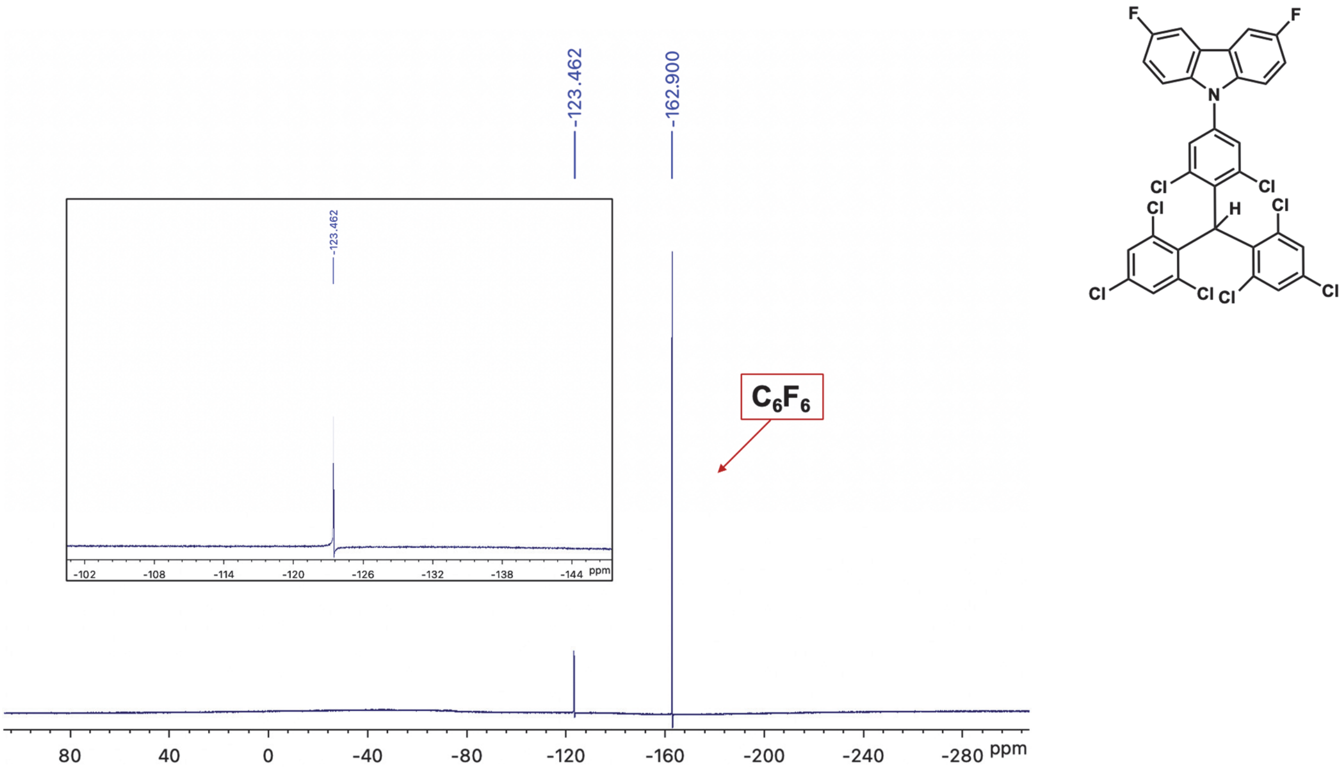


Fig. S3. ^{19}FNMR spectra of F2-CzHTTM.

ESR spectra

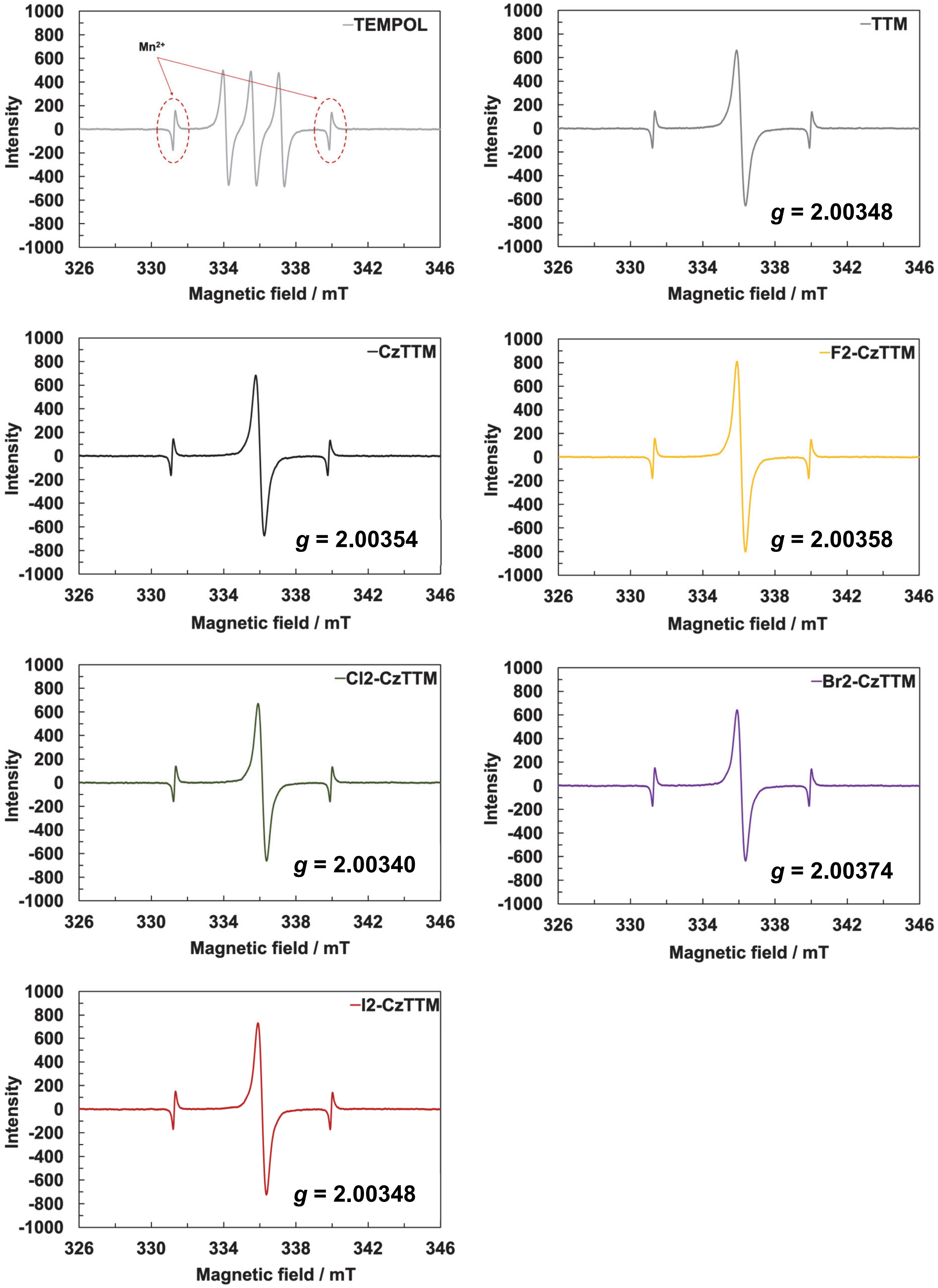


Fig. S4. ESR spectra of TEMPOL, TTM, CzTTM, F2-CzTTM, Cl2-CzTTM, Br2-CzTTM, and I2-CzTTM in toluene (10^{-5} M) at room temperature.

The following formula was used to determine radical purity by ESR. TEMPOL was used as the standard sample, and variations in sensitivity from measurement to measurement were corrected using the integral area of the Mn^{2+} marker.

$$Sx = \frac{Ix\,J0}{I0\,Jx} S0$$

S_x : Amount of spin in TTM, CzTTM, (F,Cl,Br,I)2-CzTTM
S_0 : Amount of spin in TEMPOL
I_x : Integral value of TTM, CzTTM, (F,Cl,Br,I)2-CzTTM
I_0 : Integral value of TEMPOL
J_x : Integral value of Mn^{2+} marker during TTM, CzTTM, (F,Cl,Br,I)2-CzTTM measurement
J_0 : Integral value of Mn^{2+} marker during TEMPOL measurement

Table S1. Integral values of radicals and Mn^{2+}.

	Integral value (I_0)	**Integral value (J_0)**
TEMPOL	**36.206**	**-0.60591**

	Integral value (I_x)	**Integral value (J_x)**	**Radical purities (%)**
TTM	**34.1566**	**-0.630637**	**91**
CzTTM	**31.0371**	**-0.545967**	**95**
F2-CzTTM	**36.5125**	**-0.65173**	**94**
Cl2-CzTTM	**29.5393**	**-0.626046**	**79**
Br2-CzTTM	**28.3463**	**-0.678546**	**70**
I2-CzTTM	**32.5873**	**-0.593748**	**92**

Uv-vis and PL spectra

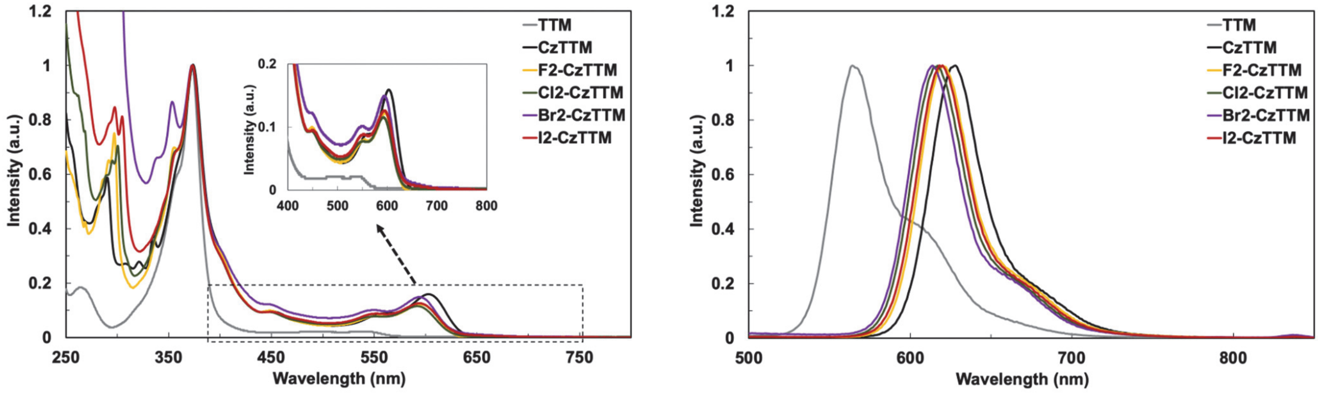


Fig. S5. Normalized absorption(left) and photoluminescence(right) spectra of TTM, CzTTM, and (F2,Cl2,Br2,I2)-CzTTM in cyclohexane.

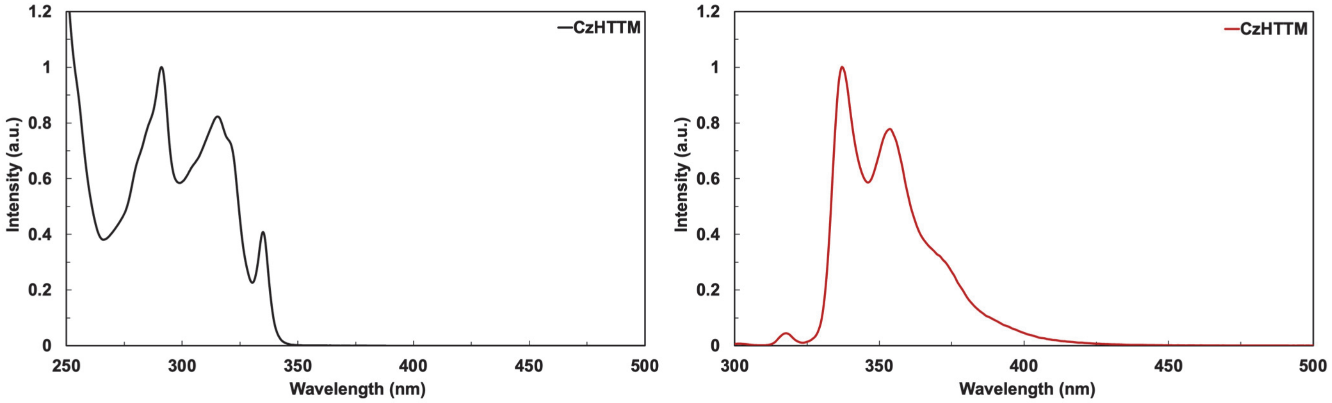


Fig. S6. Normalized absorption(left) and photoluminescence(right) spectra of CzHTTM in cyclohexane.

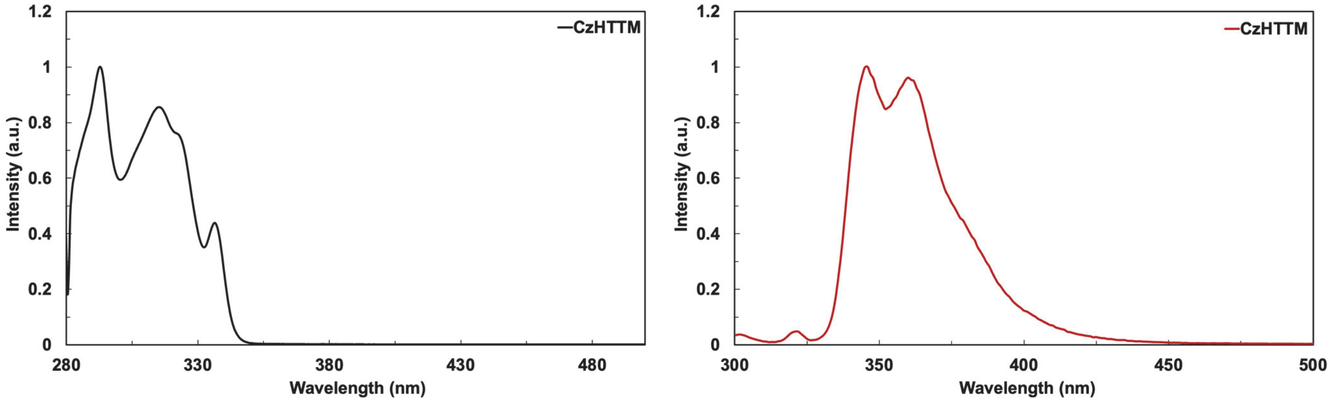


Fig. S7. Normalized absorption(left) and photoluminescence(right) spectra of CzHTTM in toluene.

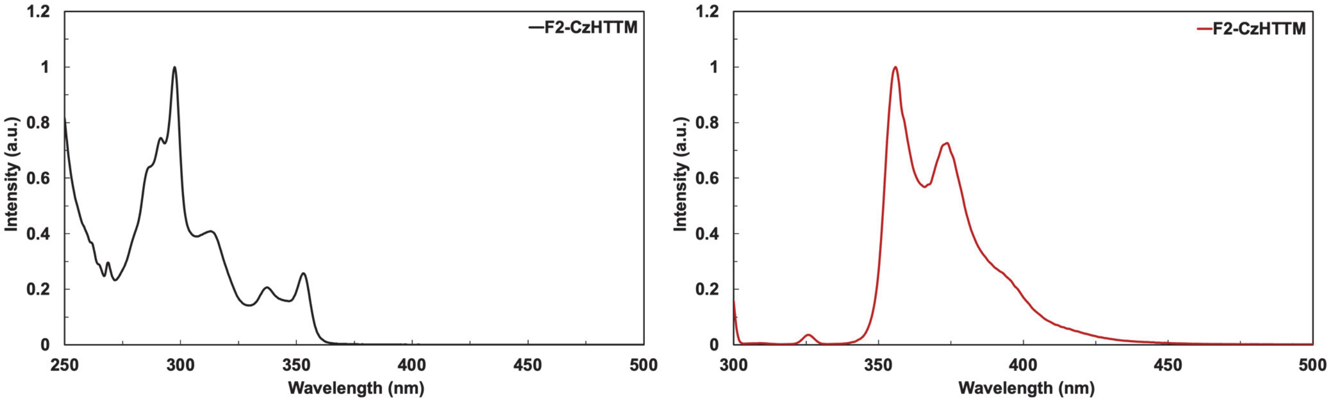


Fig. S8. Normalized absorption(left) and photoluminescence(right) spectra of F2-CzHTTM in cyclohexane.

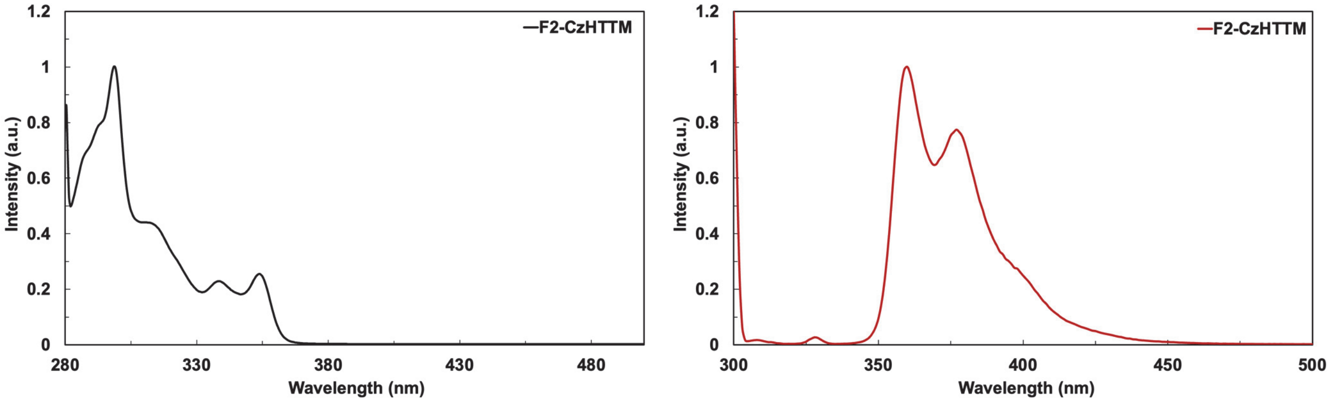


Fig. S9. Normalized absorption(left) and photoluminescence(right) spectra of F2-CzHTTM in toluene.

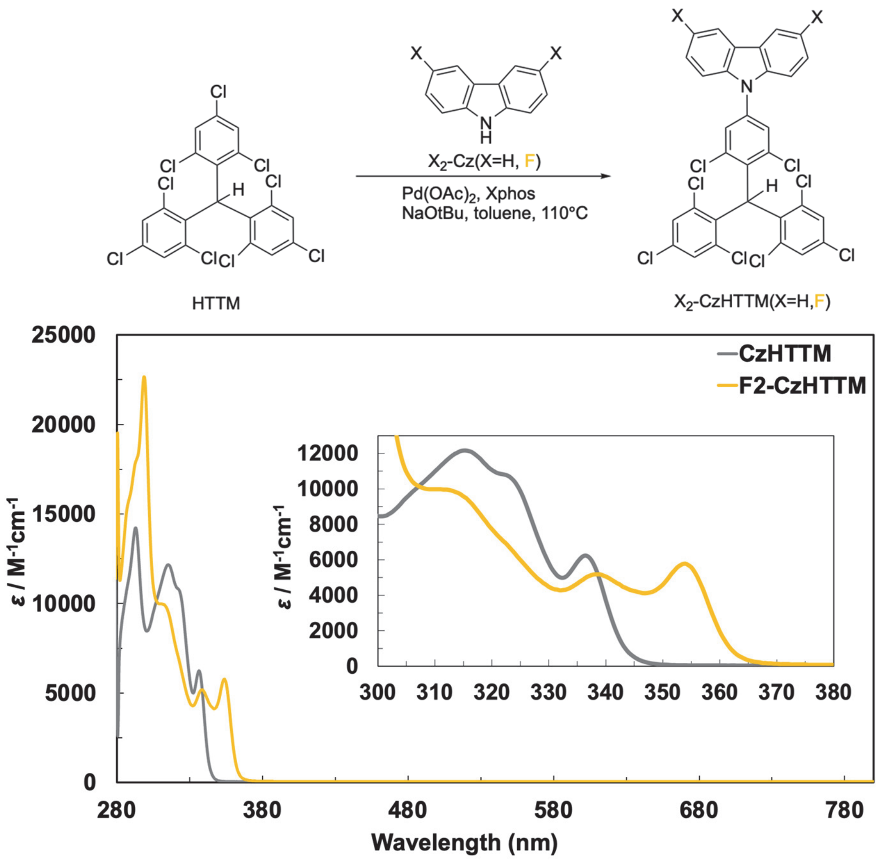


Fig. S10. UV-vis spectra of pure CzHTTM and F2-CzHTTM (without radicals) in toluene. These compounds were synthesized by Buckwald-Hartwig coupling reaction.

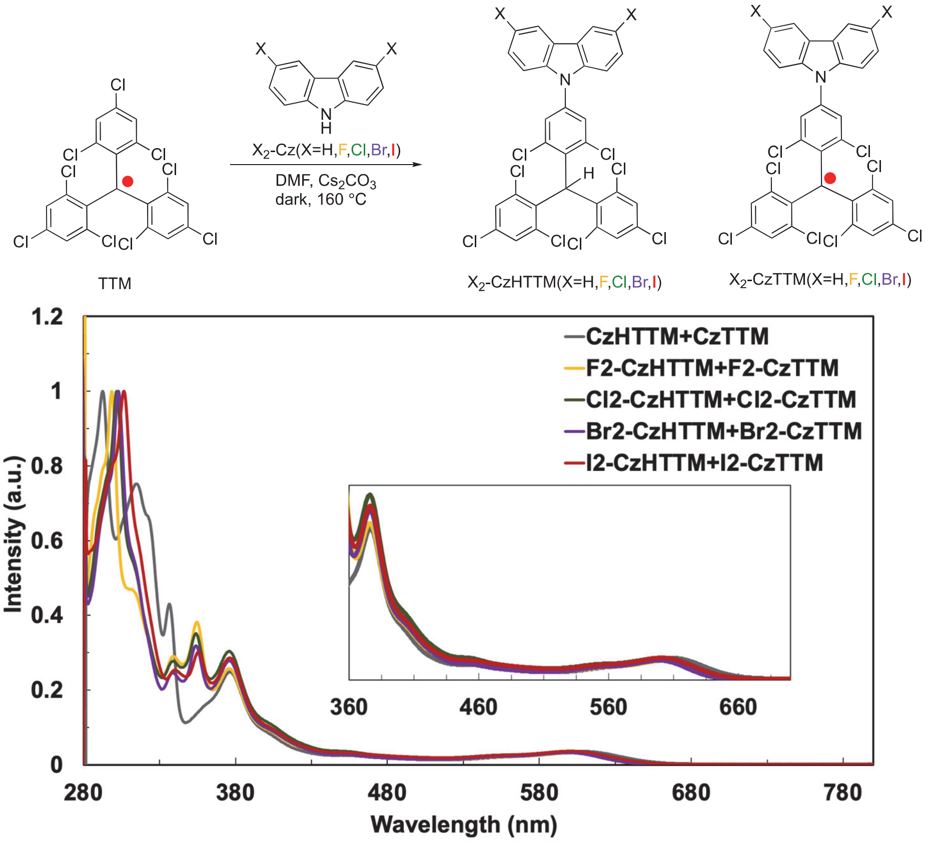


Fig. S11. UV-vis spectra of TTM radicals with some HTTM precursors as impurities in toluene (normalized at largest absorption around 300 nm). These Radicals were synthesized by SN_{Ar} reaction.

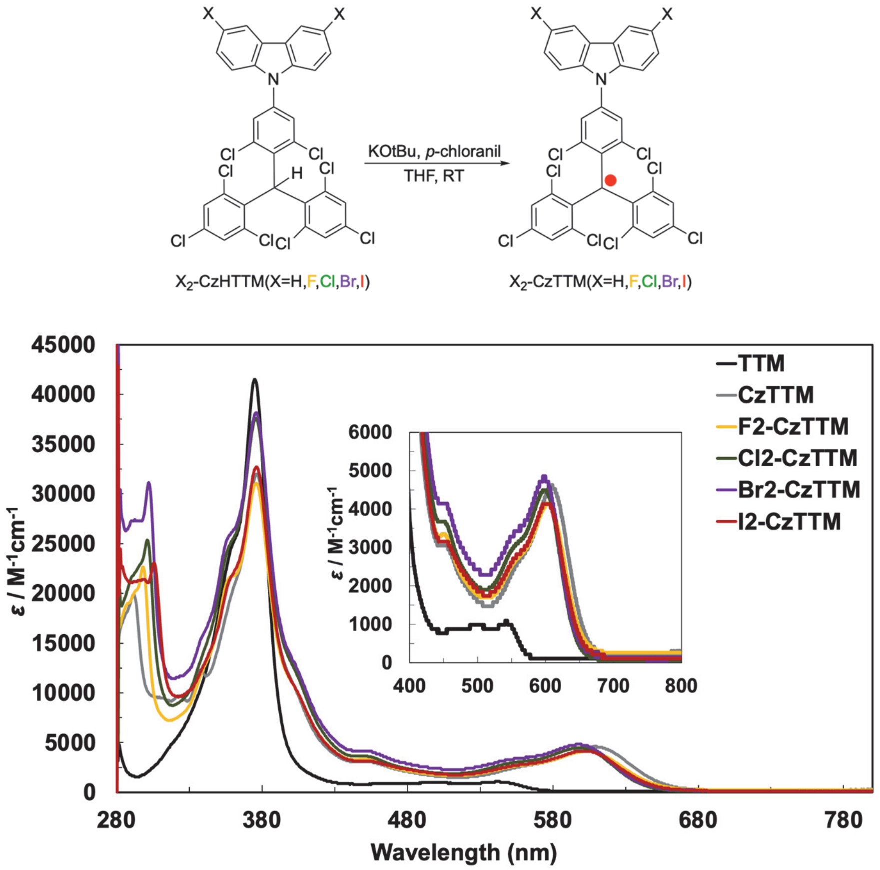


Fig. S12. UV-vis spectra of CzTTM and (F2, Cl2, Br2, I2)-CzTTM in toluene. The molar extinction coefficient of the radicals was corrected with the purity in the range of 280-800nm; Note that the absorption of H compounds is also included below 370nm. Therefore, the accurate region is over 370 nm.

Table S2. Photophysical parameters of cyclohexane solution (left), PS (middle)) and PMMA (right) thin film doped with 5 wt% of CzTTM and (F2,Cl2,Br2,I2)-CzTTM.

	λ_{PL}	Φ_F (%)
	Cyclohexane/PS/PMMA	Cyclohexane/PS/PMMA
CzTTM	**628 / 661 / 678**	**91 / 19 / 11**
F2-CzTTM	**620 / 654 / 667**	**83 / 27 / 11**
Cl2-CzTTM	**617 / 644 / 655**	**64 / 37 / 26**
Br2-CzTTM	**614 / 637 / 654**	**68 / 32 / 23**
I2-CzTTM	**618 / 651 / 658**	**72 / 25 / 20**

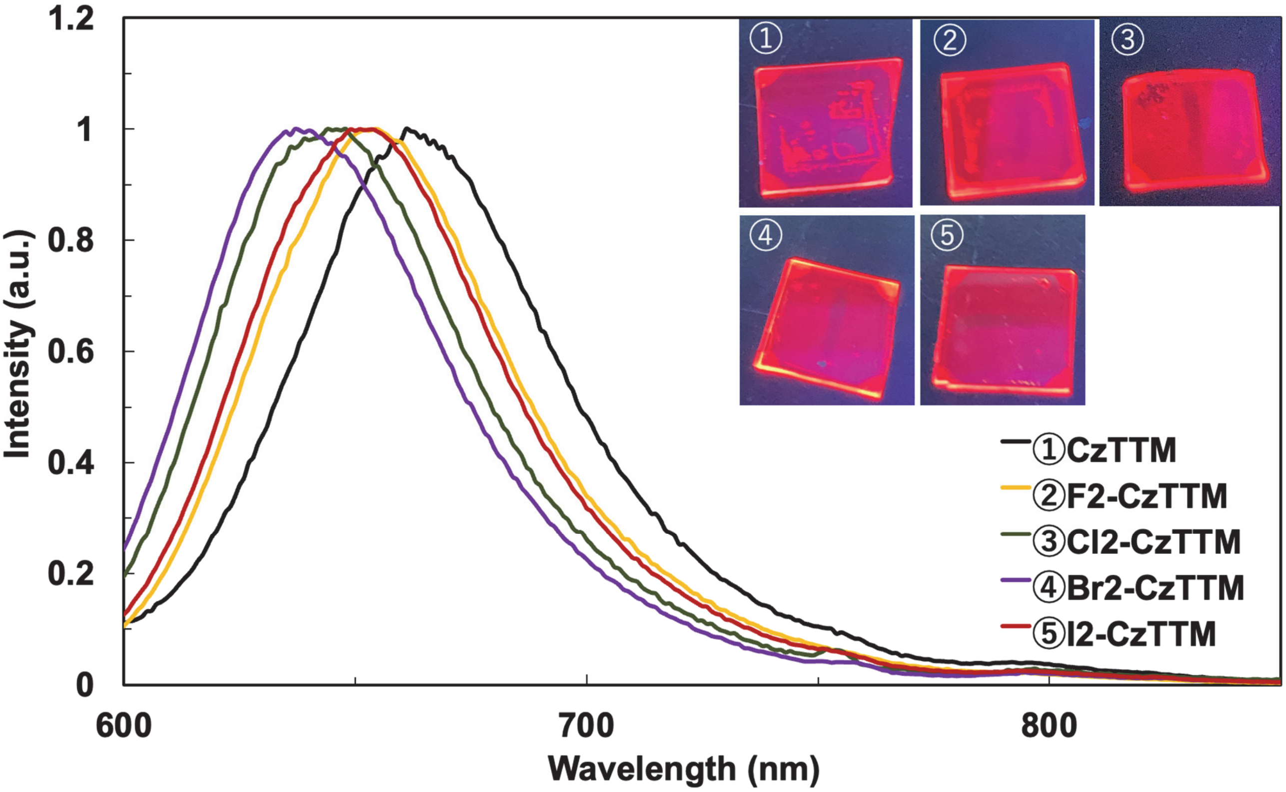


Fig. S13. PL spectra of PS thin films doped with 5 wt% CzTTM and (F2, Cl2, Br2, I2)-CzTTM.

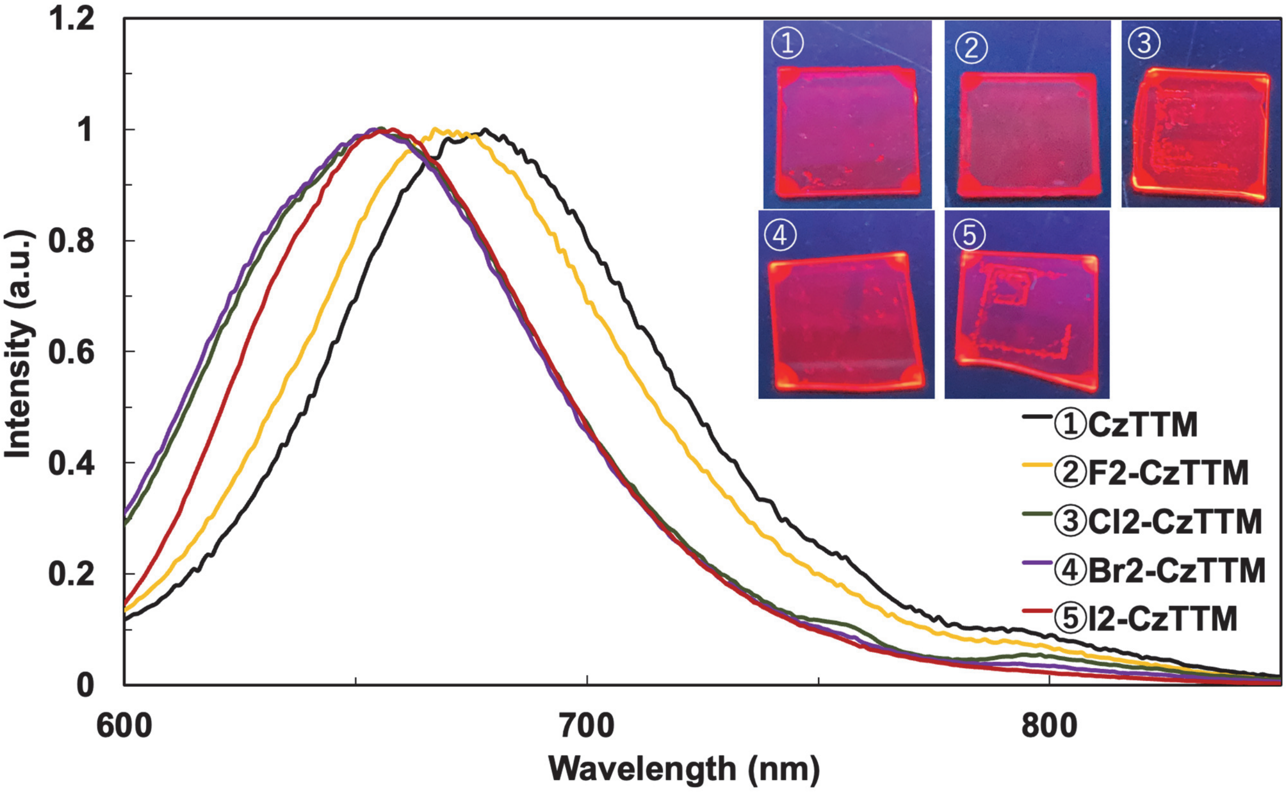


Fig. S14. PL spectra of PMMA thin films doped with 5 wt% CzTTM and (F2, Cl2, Br2, I2)-CzTTM.

Photophysical Parameters of Cz and (F2,Cl2,Br2,I2)-Cz

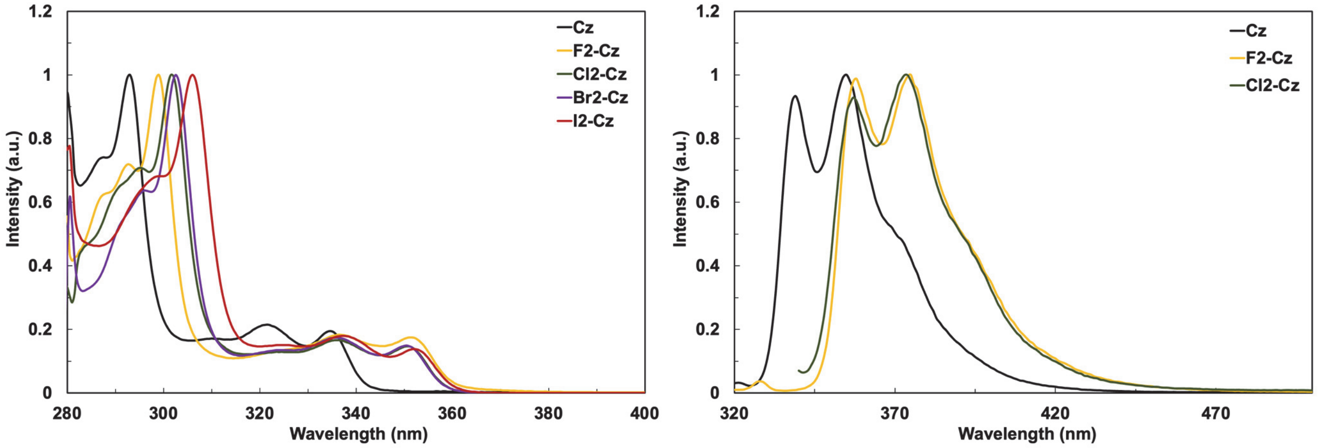


Fig. S15. Normalized absorption(left) and photoluminescence(right) spectra of Cz and (F2, Cl2, Br2, I2)-Cz in toluene.

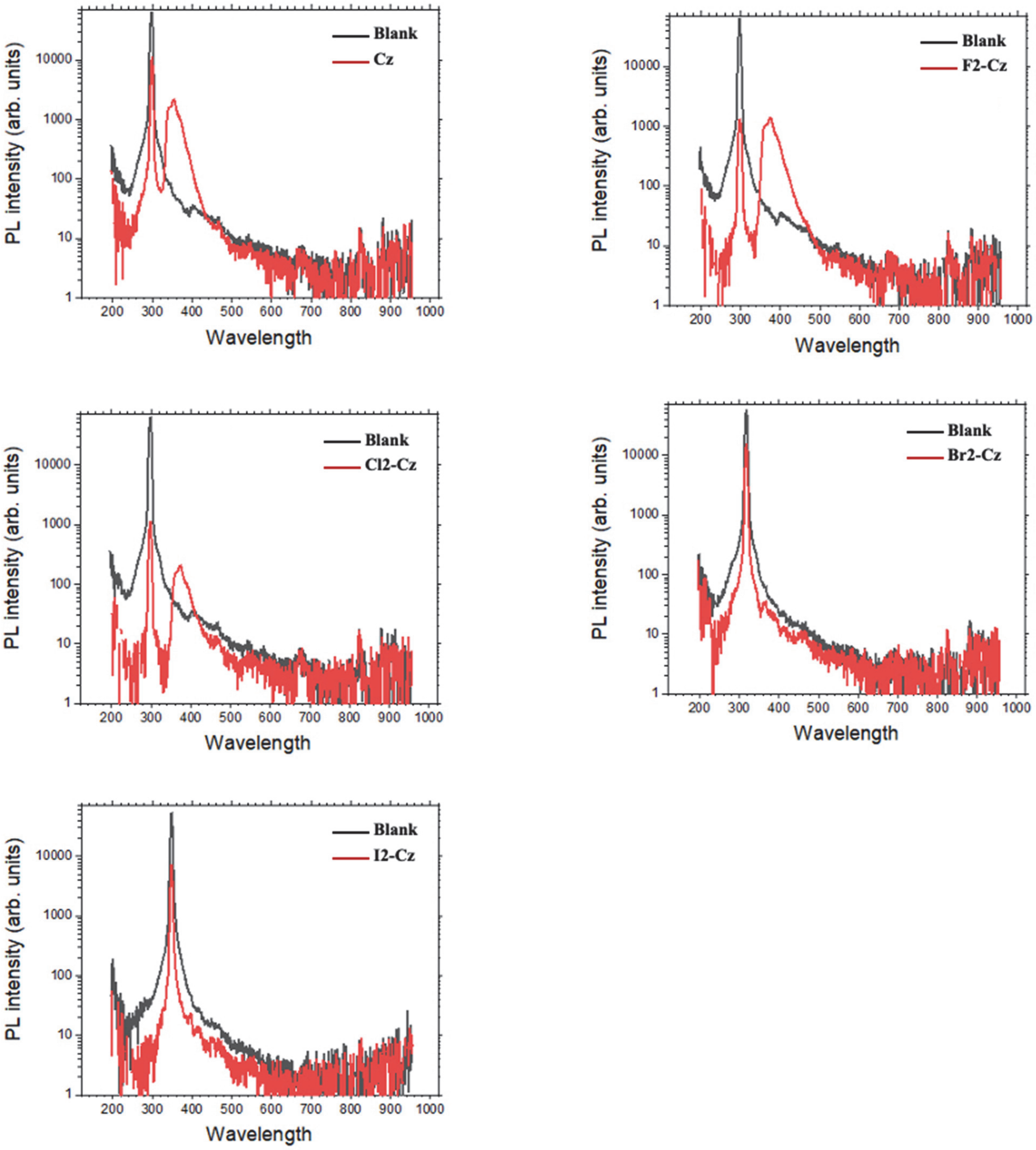


Fig. S16. Absolute photoluminescence quantum yield measurement of Cz and (F2,Cl2,Br2,I2)-Cz in toluene.

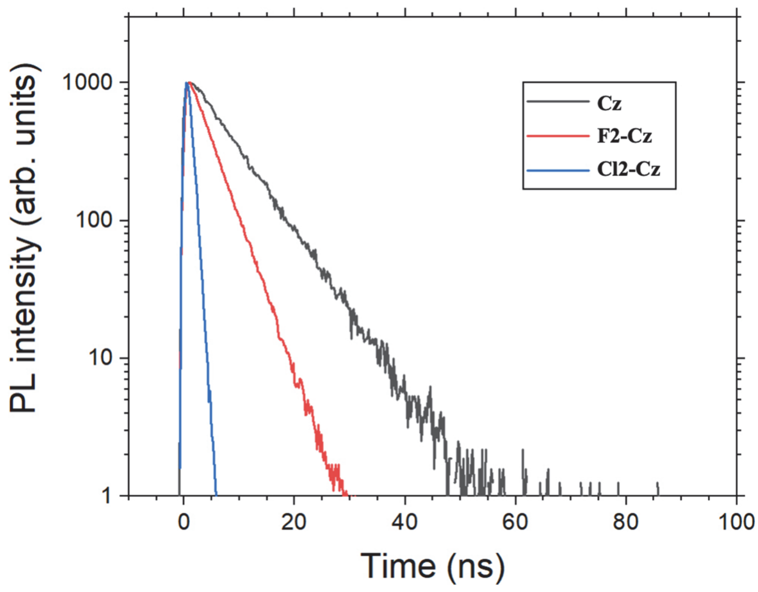


Fig. S17. PL lifetime (room temperature) of Cz, F2-Cz and Cl2-Cz in toluene.

Table S3. Photophysical parameters of Cz and (F,Cl,Br,I)2-Cz in toluene.

	λ_{Abs}	Φ_F (%)	PL lifetime (ns)	k_r ($\times 10^7 s^{-1}$)	k_{nr} ($\times 10^7 s^{-1}$)
Cz	**293**	**21**	**7.7**	**2.7**	**10.2**
F2-Cz	**299**	**14**	**4.0**	**3.5**	**21.5**
Cl2-Cz	**302**	**1.8**	**0.8**	**2.5**	**122.7**
Br2-Cz	**303**	**N.D.***	**N.D.***	**N.D.***	**N.D.***
I2-Cz	**306**	**N.D.***	**N.D.***	**N.D.***	**N.D.***

* Could not be calculated due to low PLQY and PL lifetime.

PL lifetime

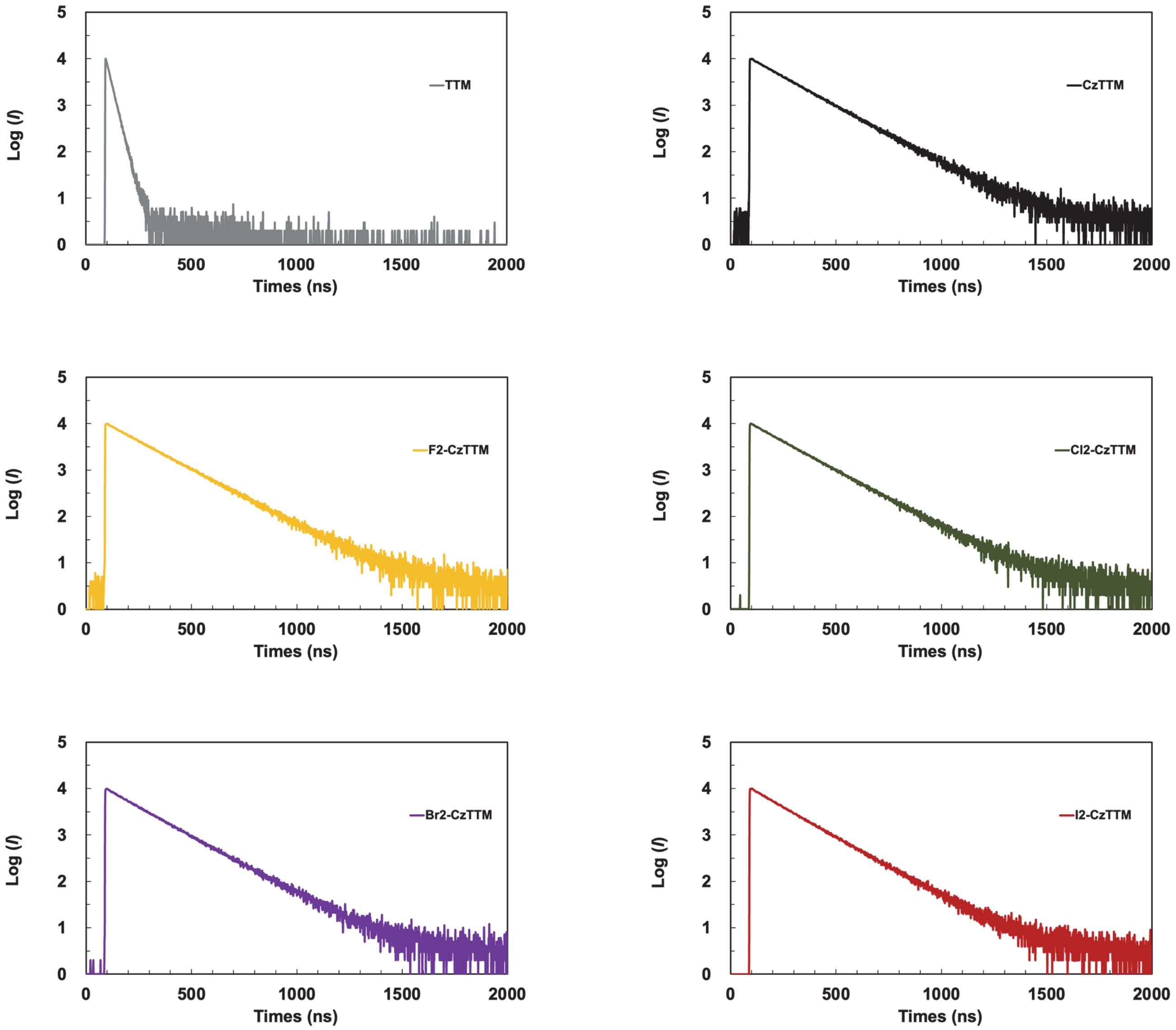


Fig. S18. PL lifetime (room temperature) of TTM (5.4 ns), CzTTM (41 ns) and (F2,Cl2,Br2,I2)-CzTTM (42, 42, 41, 40 ns) in cyclohexane without degassing.

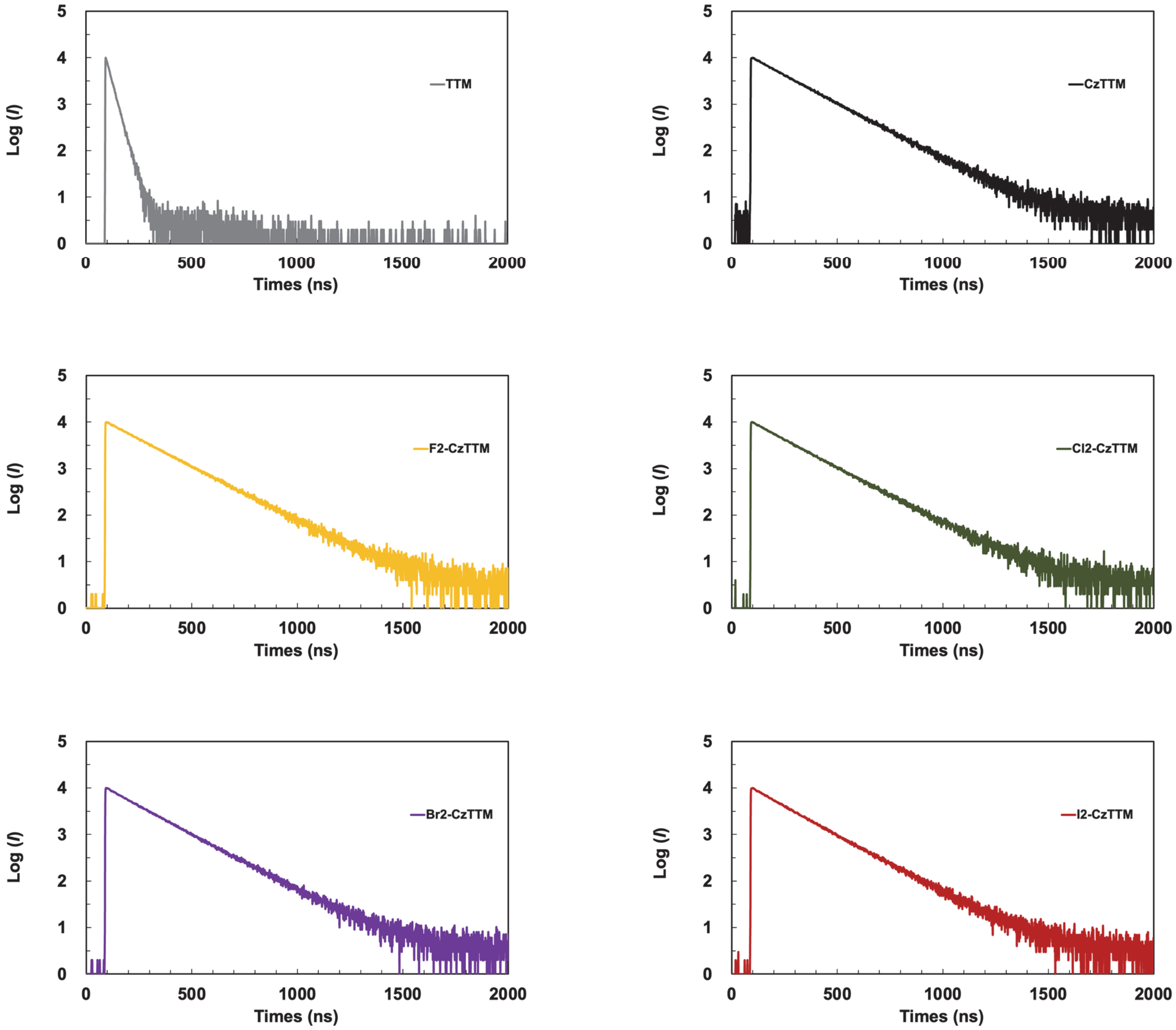


Fig. S19. PL lifetime (room temperature) of TTM (6.0 ns), CzTTM (41 ns) and (F2,Cl2,Br2,I2)-CzTTM (44, 43, 42, 41 ns) in cyclohexane under degassing.

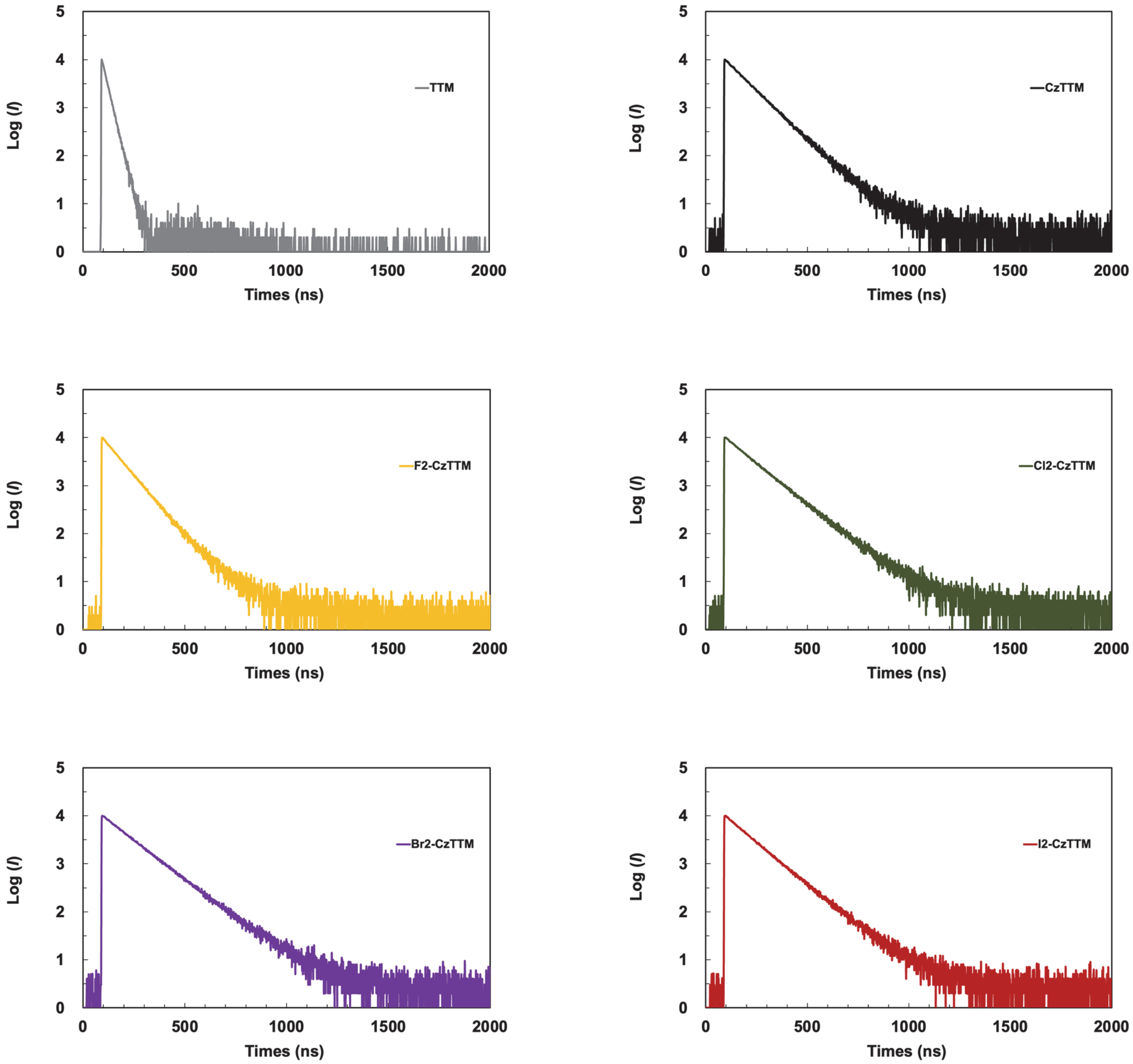


Fig. S20. PL lifetime (room temperature) of TTM (5.7 ns), CzTTM (25 ns) and (F2,Cl2,Br2,I2)-CzTTM (21, 30, 31, 29 ns) in toluene without degassing.

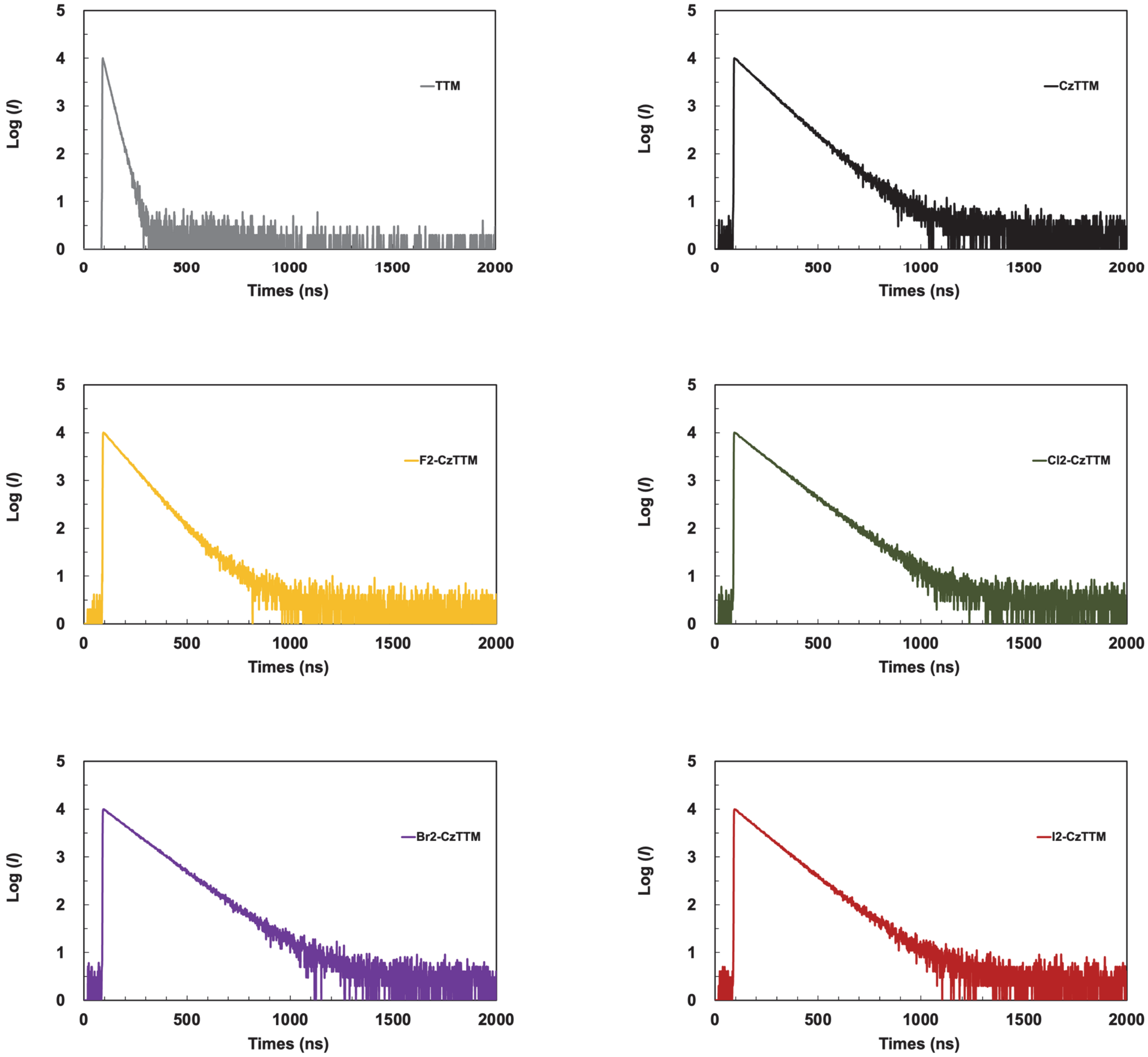


Fig. S21. PL lifetime (room temperature) of TTM (5.8 ns), CzTTM (26 ns) and (F2,Cl2,Br2,I2)-CzTTM (21, 30, 32, 29 ns) in toluene under degassing.

Cyclic voltammetry

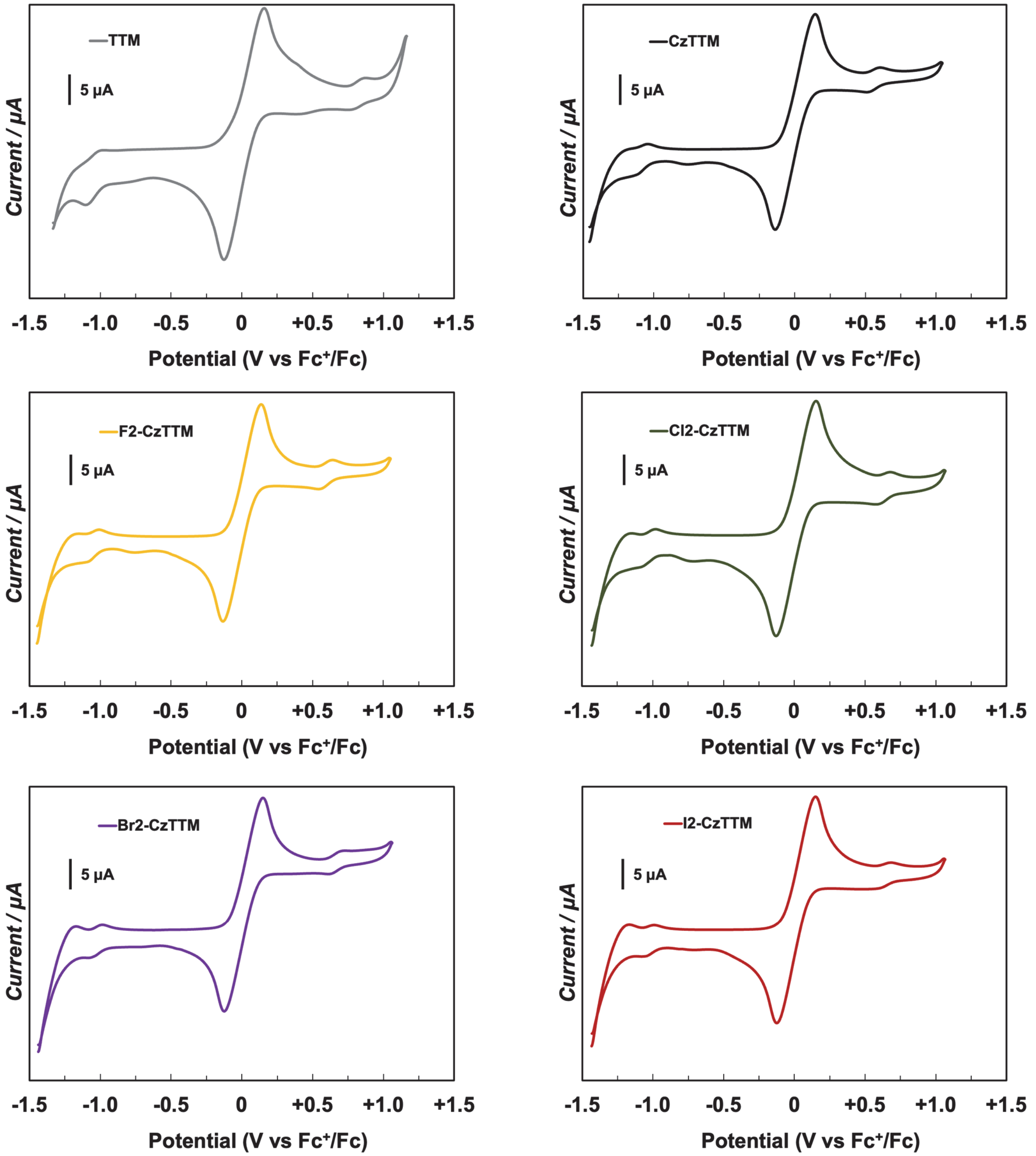


Fig. S22. Cyclicvoltammogram of 0.1 mM TTM, (F2, Cl2, Br2, I2)-CzTTM and CzTTM radicals in toluene. The redox couple at 0 V is the redox of 1 mM toluene solution ferrocene (Fc/Fc^+) added as internal standard (X axis is calibrated). The redox potential ($E_{1/2}$) was -1.04 V (TTM), -1.07 V (CzTTM), -1.04 V (F2-CzTTM), -1.02 V (Cl2-CzTTM), -1.02 V (Br2-CzTTM), and -1.01 V (I2-CzTTM) respectively. The oxydation potential ($E_{1/2}$) was +0.83 V (TTM), +0.57 V (CzTTM), +0.60 V (F2-CzTTM), +0.64 V (Cl2-CzTTM), +0.67 V (Br2-CzTTM), and. +0.64 V (I2-CzTTM) respectively.

Photostability

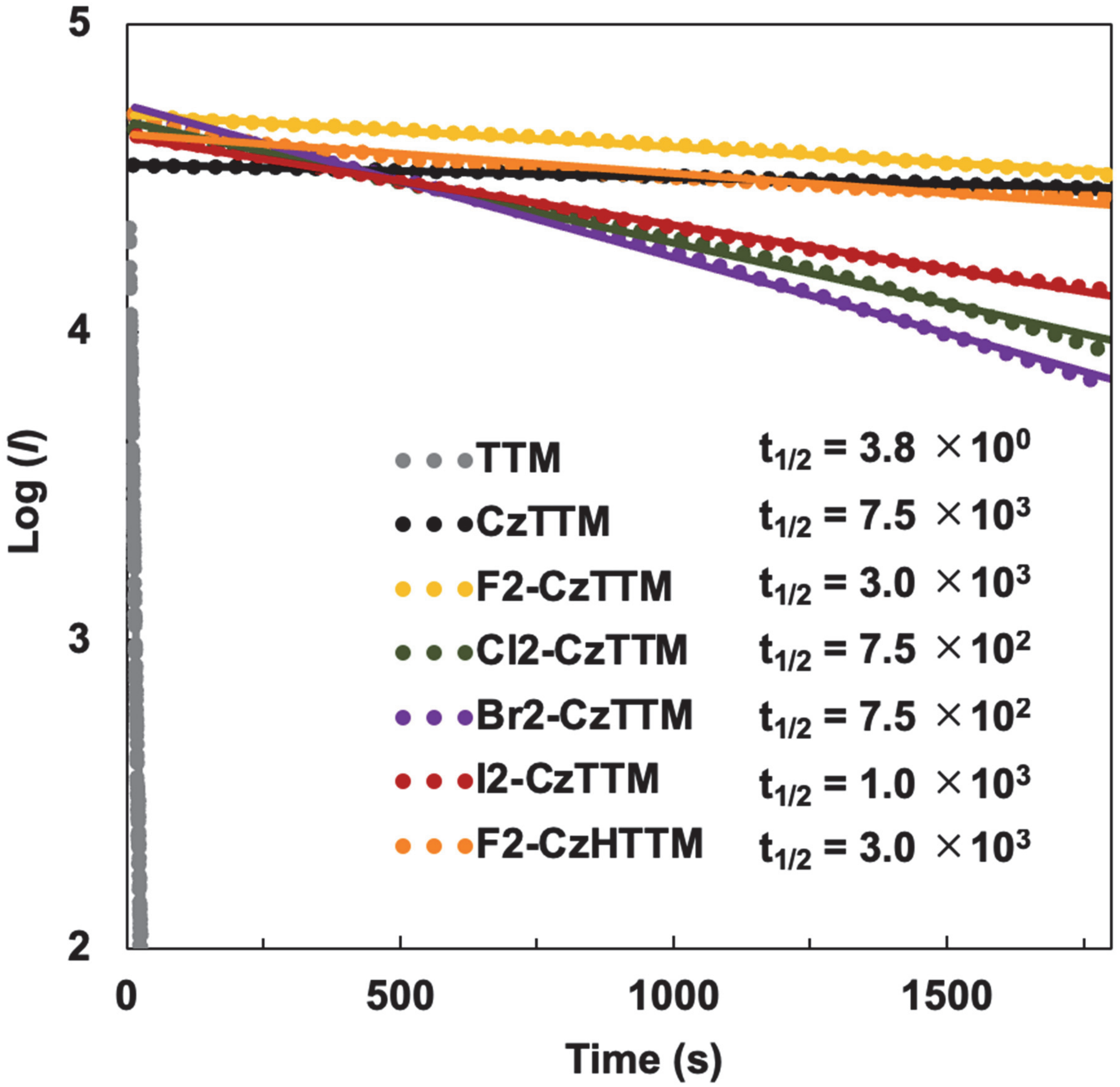


Fig. S23. The emission intensity (I) of radicals during 355 nm pulsed laser radiation in degassed toluene (power : 20.0 mW, beam diameter (Gaussian beam, 1/e^2 level, FHWM) : ~ 3 mm, pulse width : 28 ps, repetition rate : 100 Hz).

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