Supporting Information

Photostability of luminescent *tris*(2,4,6-trichlorophenyl)methyl radical enhanced by terminal modification of carbazole donor

Kenshiro Matsuda,[a] Rui Xiaotian,[a] Kazuhiro Nakamura,[a] Minori Furukori,[b, c] Takuya Hosokai, [*b, c] Kosuke Anraku, [a] Kohei Nakao,[d] and Ken Albrecht.[*d, e]

a. Interdisciplinary Graduate School of Engineering Sciences, Kyushu University, 6-1 Kasuga-Koen Kasuga-shi Fukuoka 816-8580, Japan.

b. National Institute of Advanced Industrial Science and Technology (AIST), Tsukuba Central 5, 1-1-1 Higashi, Tsukuba, Ibaraki 305-8565, Japan.

c. Department of Pure and Applied Chemistry, Faculty of Science and Technology, Tokyo University of Science, 2641 Yamazaki, Noda, Chiba 278-8510, Japan.

d. Institute for Materials Chemistry and Engineering, Kyushu University, 6-1 Kasuga-Koen Kasuga-shi Fukuoka 816-8580, Japan.

e. JST-PRESTO, 4-1-8 Honcho, Kawaguchi, Saitama 332-0012, Japan.

E-mail: albrecht@cm.kyushu-u.ac.jp

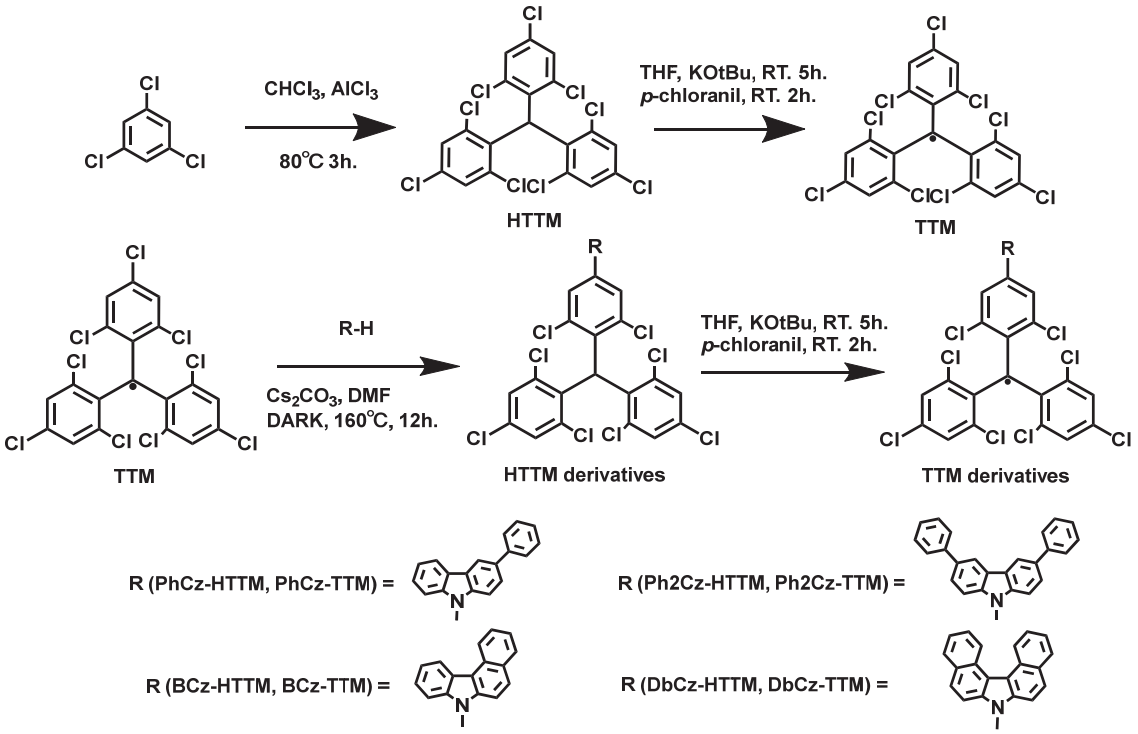
Table of Contents

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. For qNMR, 1,4-Bis(trimethylsilyl)benzene-d_4 (1,4-BTMSB-d_4) was used as an internal standard. FAB-MS spectra were obtained using a JMS-700 plus (JEOL) in FAB^+ ion mode. 3-nitrobenzyl alcohol (3NBA) was used as matrix. 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 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 Bruker Magnettech ESR5000. Microwave synthesis was performed by Biotage Initiator+Microwave System 356700. 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 a 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: 29±4 ps, repetition rate: 10 Hz, laser power: 0.7 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 electrochemical measurements were done using a conventional three-electrode configuration with an electrochemical analyzer (ECstat-302, EC Frontier, JPN). The working, counter and reference electrodes were glassy carbon (7.07mm^2), Pt wire, and Ag/Ag^+, respectively. The solution was not degassed before measurement and the voltage sweep rate was 0.05 V/s. The solvent was dichloromethane and 0.1 M tetrabutylammonium perchlorate (TBAP) was used as the supporting electrolyte.

Synthesis



Scheme S1. Synthesis of modified carbazole substituted TTM radicals.

Synthesis of Tri(2,4,6-trichlorophenyl) methyl (HTTM).

1,3,5-trichlorobenzene (25 g, 138 mmol), $AlCl_3$ (2.39 g, 18 mmol), and dehydrated chloroform (2.65 g, 1.8 mL, 22 mmol) were added to a flask under a nitrogen atmosphere. The mixture was stirred at 80 ºC for 2.5 hours. After the reaction mixture was cooled to room temperature, the reaction mixture was dissolved in chloroform and then poured into an excessive amount of aqueous HCl (1 M). The organic phase was extracted with dichloromethane, combined, and dried with anhydrous sodium sulfate. Sodium sulfate was filtrated, and the filtrate was concentrated. The crude was dried under vacuum at 80 ºC overnight to remove (sublime) the 1,3,5-trichlorobenzene to afford 7.50 g (yield 62%) of a colorless powder (HTTM).

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

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

δ 7.35 (d, J = 2.3 Hz, 3H), 7.22 (d, J = 2.3 Hz, 3H), 6.66 (s, J = 5.5 Hz, 1H).

^{13}C-NMR (101 MHz, $CDCl_3$) δ 138.0, 137.2, 133.9, 133.9, 130.1, 128.5, 49.9.

Synthesis of Tri(2,4,6-trichlorophenyl) methyl radical (TTM).

Tri(2,4,6-trichlorophenyl) methyl (HTTM) (2.07 g, 3.8 mmol), KOtBu (1.22 g, 10.9 mmol) and THF (20 mL) were added in flask under nitrogen atmosphere. The solution was first stirred in the dark for 5 hours at room temperature. Then *p*-Chloranil (1.19 g, 4.8 mmol) was added, and the mixture was stirred for another 2 hours. The resulting mixture was concentrated. The residue was purified with

flash silica gel column chromatography (eluent: n-hexane) to afford 1.86 g (yield 90%) of a deep red powder.

Synthesis of PhCz-HTTM.

TTM radical (0.48 g, 0.9 mmol), 3-Phenyl-9H-carbazole (0.23 g, 1.0 mmol), Cs_2CO_3 (1.18g, 3.6 mmol) and DMF (3 mL) were added in flask under argon atmosphere. The mixture was stirred at 160 ºC (reflux) for 8 hours in the dark. After the reaction mixture was cooled to room temperature, the reaction mixture was poured into an excessive amount of aqueous HCl (1 M). The organic phase was extracted with chloroform, combined, washed with NaCl (aq), and dried with anhydrous sodium sulfate. Sodium sulfate was filtrated and concentrated. The crude was purified with preparative scale GPC (eluent: chloroform). The purified product was vacuum dried at 80 ºC overnight. PhCz-HTTM was obtained as a green powder(70 mg, 30%).

^{1}H-NMR (400 MHz, Methylene-chloride-d2) δ 8.34 (d, J = 1.4 Hz, 1H), 8.17 (d, J = 7.3 Hz, 1H), 7.72-7.65 (m, 5H), 7.52-7.42 (m, 8H), 7.35-7.29 (m, 4H), 6.86 (s, 1H).

^{13}C-NMR (101 MHz, Methylene-chloride-d2) δ 141.5, 140.6, 139.6, 138.5, 138.1, 138.0, 137.7, 137.3, 137.2, 134.1, 134.0, 133.9, 130.2, 130.1, 128.9, 128.6, 128.2, 127.2, 126.9, 126.6, 125.7, 124.3, 123.8, 121.0, 120.6, 118.9, 110.0, 109.8, 50.2.

FAB-MS (m/z): $[M]^+$ Calcd for 756.9026; Found 756.9026.

Elem. Anal. Calcd for $C_{37}H_{19}Cl_8N$, C, 58.39; H, 2.52; Cl, 37.26; N, 1.84;

Synthesis of Ph2Cz-HTTM.

TTM radical (0.21 g, 0.4 mmol), 3,6-diphenylcarbazole (0.22 g, 0.7 mmol), Cs_2CO_3 (1.18g, 1.4 mmol) and DMF (3 mL) were added in flask under argon atmosphere. The mixture was stirred at 160 ºC (reflux) for 8 hours in the dark. After the reaction mixture was cooled to room temperature, the reaction mixture was poured into an excessive amount of aqueous HCl (1 M). The organic phase was extracted with chloroform, combined, washed with NaCl (aq), and dried with anhydrous sodium sulfate. Sodium sulfate was filtrated and concentrated. The crude was purified with preparative scale GPC (eluent: chloroform). The purified product was vacuum dried at 80 ºC overnight. Ph2Cz-HTTM was obtained as a green powder (90 mg, 28%).

^{1}H-NMR (400 MHz, Methylene-chloride-d2) δ 8.40 (s, 2H), 7.73-7.68 (m, 8H), 7.55-7.43 (m, 8H), 7.36-7.30 (m, 4H), 6.86 (s, 1H).

^{13}C-NMR (151 MHz, Chloroform-d) δ 141.7, 140.1, 138.7, 138.1, 138.0, 137.8, 137.3, 134.6, 134.1, 133.9, 130.3, 130.2, 129.0, 128.6, 128.1, 127.4, 126.9, 126.5, 126.1, 124.5, 119.2, 110.1, 50.2.

FAB-MS (m/z): $[M]^+$ Calcd for 832.9339.; Found 832.9338.

Elem. Anal. Calcd for $C_{43}H_{23}Cl_8N$, C 61.69, H 2.77, N 1.67; Found C 62.01, H 2.74, N 1.74.

Synthesis of BCz-HTTM.

TTM radical (0.22 g, 0.4 mmol), 7H-benzocarbazole (0.14 g, 0.6 mmol), Cs_2CO_3 (0.62g, 1.9 mmol) and DMF (3 mL) were added in flask under argon atmosphere. The mixture was stirred at 160 ºC (reflux) for 8 hours in the dark. After the reaction mixture was cooled to room temperature, the reaction mixture was poured into an excessive amount of aqueous HCl (1 M). The organic phase was extracted with chloroform, combined, washed with NaCl (aq) and dried with anhydrous sodium sulfate. Sodium sulfate was filtrated and concentrated. The crude was purified with preparative scale GPC (eluent: chloroform). The purified product was vacuum dried at 80 ºC overnight. BCz-HTTM (100 mg, 34%) was obtained as a green powder.

^{1}H-NMR (600 MHz, Methylene-chloride-d2) δ 8.82 (d, J = 8.2 Hz, 1H), 8.62 (dd, J = 6.5, 1.7 Hz, 1H), 8.03 (d, J = 8.2 Hz, 1H), 7.90 (d, J = 8.2 Hz, 1H), 7.75-7.74 (m, 1H), 7.67 (d, J = 2.1 Hz, 1H), 7.60 (d, J = 8.9 Hz, 1H), 7.55-7.45 (m, 7H), 7.36 (d, J = 2.7 Hz, 1H), 7.32 (d, J = 2.1 Hz, 1H), 6.90 (s, 1H).

^{13}C-NMR (151 MHz, Methylene-chloride-d2) δ 140.0, 138.9, 138.4, 138.4, 138.3, 138.1, 138.0, 137.7, 137.6, 135.0, 134.5, 134.5, 134.3, 130.6, 130.5, 130.1, 130.0, 129.7, 129.5, 129.0, 128.9, 128.1, 127.8, 127.7, 125.3, 124.6, 124.0, 123.7, 122.5, 121.8, 116.3, 111.6, 110.5, 50.6.

FAB-MS (m/z): $[M]^+$ Calcd for 730.8869; Found 730.8866.

Elem. Anal. Calcd for $C_{35}H_{17}Cl_8N$, C, 57.19, H, 2.33; N, 1.91, Found C, 57.39; H, 2.38, N,1.93.

Synthesis of DbCz-HTTM.

TTM radical (0.24 g, 0.4 mmol), 7H-Dibenzocarbazole (0.19 g, 0.7 mmol), Cs_2CO_3 (0.57g, 1.8 mmol) and DMF (3 mL) were added in flask under argon atmosphere. The mixture was stirred at 160 ºC (reflux) for 8 hours in the dark. After the reaction mixture was cooled to room temperature, the reaction mixture was poured into an excessive amount of aqueous HCl (1 M). The organic phase was extracted with chloroform, combined, washed with NaCl (aq), and dried with anhydrous sodium sulfate. Sodium sulfate was filtrated and concentrated. The crude was purified with preparative scale GPC (eluent: chloroform). The purified product was vacuum dried at 80 ºC overnight. DbCz-HTTM (100 mg, 30%) was obtained as a green powder.

^{1}H-NMR (600 MHz, Methylene-chloride-d2) δ 9.21 (d, J = 8.2 Hz, 2H), 8.07 (d, J = 7.6 Hz, 2H), 7.91 (d, J = 8.9 Hz, 2H), 7.72 (t, J = 7.2 Hz, 2H), 7.66 (d, J = 2.7 Hz, 1H), 7.60-7.53 (m, 5H), 7.49 (d, J = 2.1 Hz, 1H), 7.46 (d, J = 2.1 Hz, 1H), 7.37 (d, J = 2.1 Hz, 1H), 7.33 (d, J = 2.7 Hz, 1H), 6.92 (s, 1H).

^{13}C-NMR (151 MHz, Methylene-chloride-d2) δ 139.0, 138.4, 138.1, 137.8, 137.7, 137.5, 135.7, 134.4, 134.4, 134.3, 130.8, 130.6, 130.6, 130.1, 129.6, 129.3, 129.0, 128.9, 128.5, 127.6, 126.1, 125.7, 124.2, 118.4, 111.7, 50.6.

FAB-MS (m/z): $[M]^+$ Calcd for 780.9026; Found 780.9028.

Elem. Anal. Calcd for $C_{35}H_{17}Cl_8N$, C 59.66, H 2.44, N 1.78; Found C 59.86, H 2.45, N 1.75.

Synthesis of PhCz-TTM.

PhCz-HTTM (52.30 mg, 0.07 mmol), KOtBu (112.4 mg, 1.00 mmol) and THF (10 mL) were added in a flask under argon atmosphere. The solution was first stirred in the dark for 5 hours at room temperature. Then *p*-Chloranil (131.4 mg, 0.5 mmol) was added, and the mixture was stirred for another 2 hours. The resulting solution was concentrated. The crude was purified by flash silica gel column chromatography (eluent hexane: toluene= 9:1). The purified product was vacuum dried at 80 ºC overnight. PhCz-TTM (30.4 mg, 58%) was obtained as a dark green powder.

FAB-MS (m/z): $[M]^+$ Calcd for 755.8948; Found, 755.8948.

Elem. Anal. Calcd for $C_{37}H_{18}Cl_8N$, C 58.46, H 2.39, N 1.84; Found C 58.36, H 2.59, N 1.70.

Synthesis of Ph2Cz-TTM.

Ph2Cz-HTTM (55.8 mg, 0.07 mmol), KOtBu (224.6 mg, 2.0 mmol) and THF (10 mL) were added in a flask under argon atmosphere. The solution was first stirred in the dark for 5 hours at room temperature. Then *p*-Chloranil (142.0 mg, 0.6 mmol) was added, and the mixture was stirred for another 2 hours. The resulting solution was concentrated. The crude was purified by flash silica gel column chromatography (eluent hexane: toluene= 9:1). The purified product was vacuum dried at 80 ºC overnight. Ph2Cz-TTM (23.68 mg, 42%) was obtained as a dark green powder.

FAB-MS (m/z): $[M+H]^+$ Calcd for 832.9937; Found 832.9337.

Elem. Anal. Calcd for $C_{43}H_{22}Cl_8N^{\bullet}$, C 61.76, H 2.65, N 1.67 N, 1.84; Found C 62.01, H 2.74, N 1.74.

Synthesis of BCz-TTM.

BCz-HTTM (69.70 mg, 0.10 mmol), KOtBu (90.90 mg, 0.81 mmol) and THF (10 mL) were added in a flask under argon atmosphere. The solution was first stirred in the dark for 5 hours at room temperature. Then *p*-Chloranil (56.35 mg, 0.23 mmol) was added, and the mixture was stirred for another 2 hours. The resulting solution was concentrated. The crude was purified by flash silica gel column chromatography (eluent hexane: toluene= 9:1). The purified product was vacuum dried at 80 ºC overnight. BCz-TTM (38.6 mg, 55%) was obtained as a dark green powder.

FAB-MS (m/z): $[M]^+$ Calcd for 729.8791; Found 729.8791.

Elem. Anal. Calcd for $C_{35}H_{16}Cl_8N^{\bullet}$, C, 57.26 H, 2.20 N, 1.91; Found C 57.21, H 2.39, N 1.79.

Synthesis of DbCz-TTM.

DbCz-HTTM (34.09 mg, 0.04 mmol), KOtBu (38.75 mg, 0.35 mmol) and THF (10 mL) were added in a flask under argon atmosphere. The solution was first stirred in the dark for 5 hours at room

temperature. Then *p*-Chloranil (73.8 mg, 0.30 mmol) was added, and the mixture was stirred for another 2 hours. The resulting solution was concentrated. The crude was purified by flash silica gel column chromatography (eluent hexane: toluene= 9:1). The purified product was vacuum dried at 80 ºC overnight. DbCz-TTM (17.0 mg, 50%) was obtained as dark green powder..

FAB-MS (m/z): $[M+H]^+$ Calcd for 780.9029; Found 780.9029.

Elem. Anal. Calcd for $C_{39}H_{18}Cl_8N^{\bullet}$, C, 59.73, H, 2.31, N, 1.79, 1.84; Found C, 59.52, H, 2.51, N, 1.58.

ESR spectra

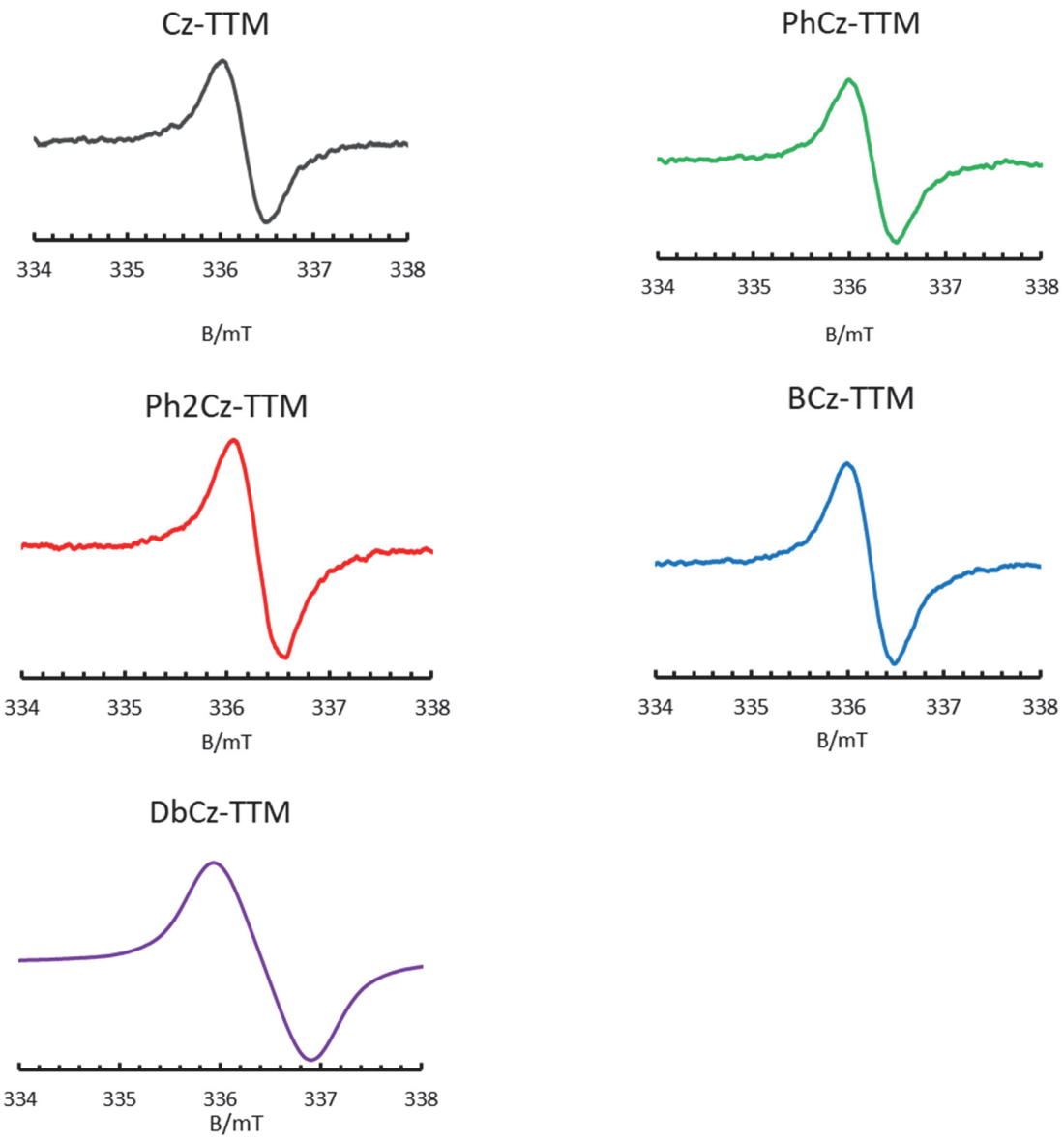


Fig. S1. ESR spectra of Cz-TTM (g = 2.00356, 336.259 mT), PhCz-TTM (g = 2.00360, 336.229 mT), Ph2Cz-TTM (g =2.00353, 336.294 mT), BCz-TTM (g = 2.00353, 336.250 mT), DbCz-TTM (g = 2.00370, 336.413 mT) in toluene (10^{-5} M) at room temperature.

NMR spectra

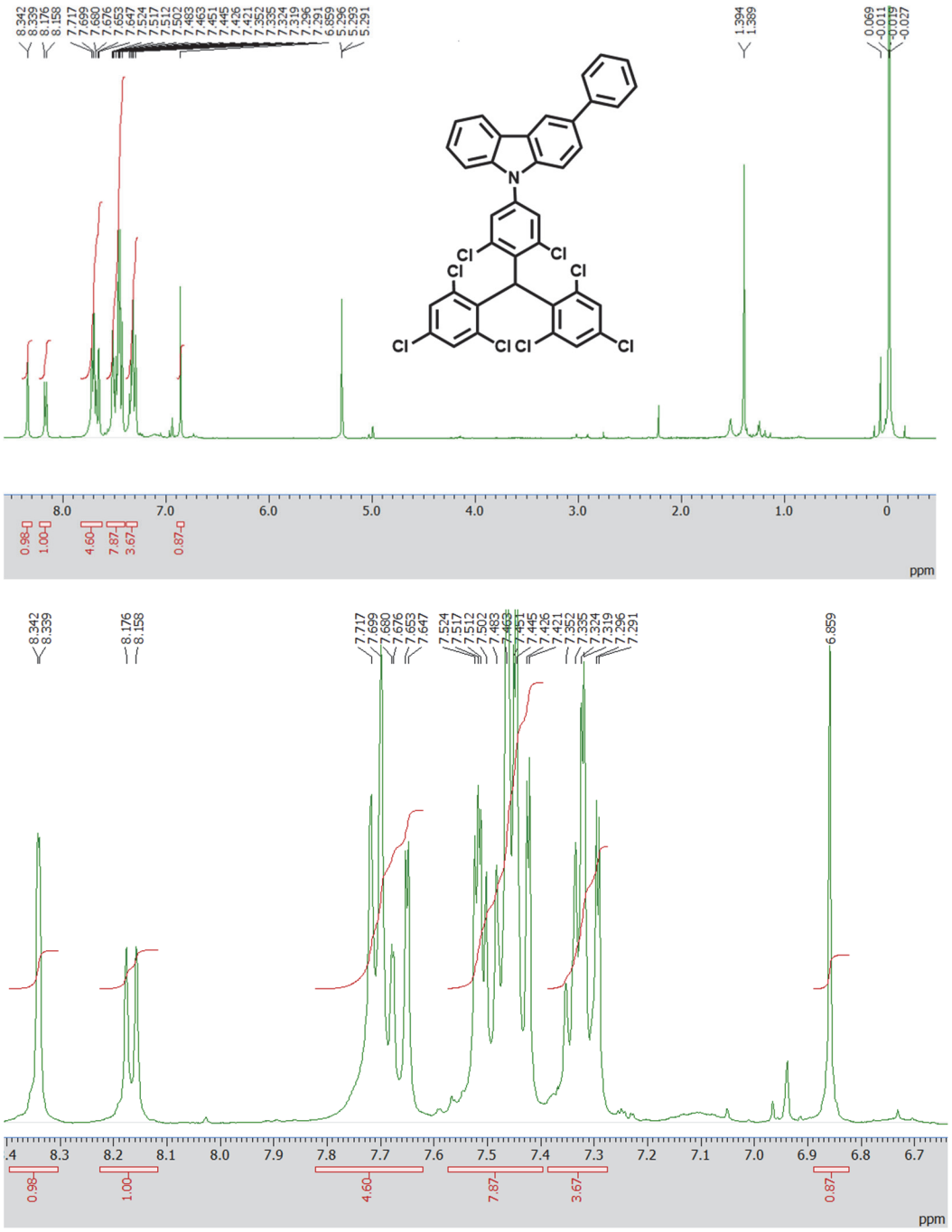


Fig. S2. ^{1}H NMR spectra of PhCz-HTTM.

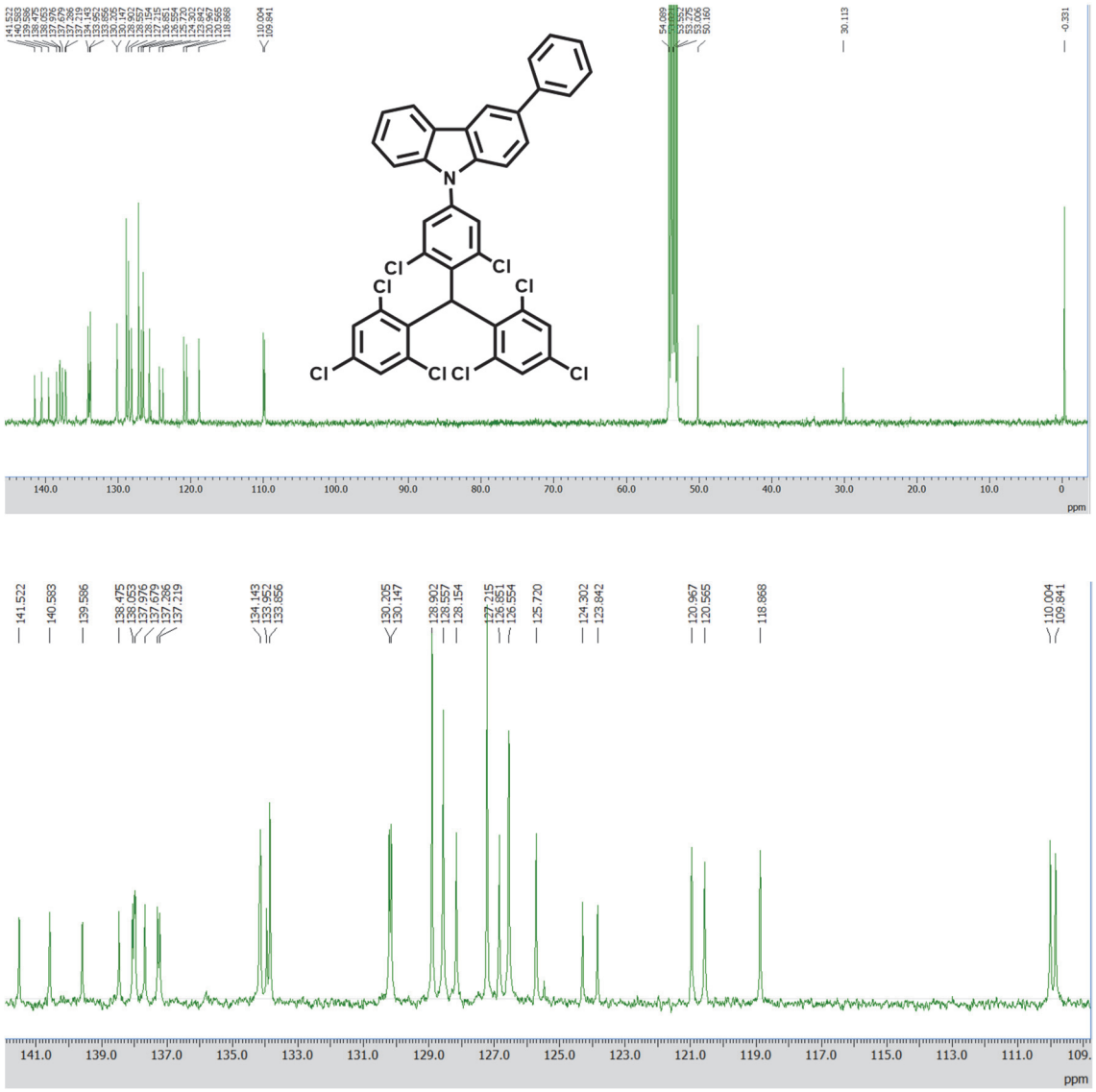


Fig. S3. ^{13}C NMR spectra of PhCz-HTTM.

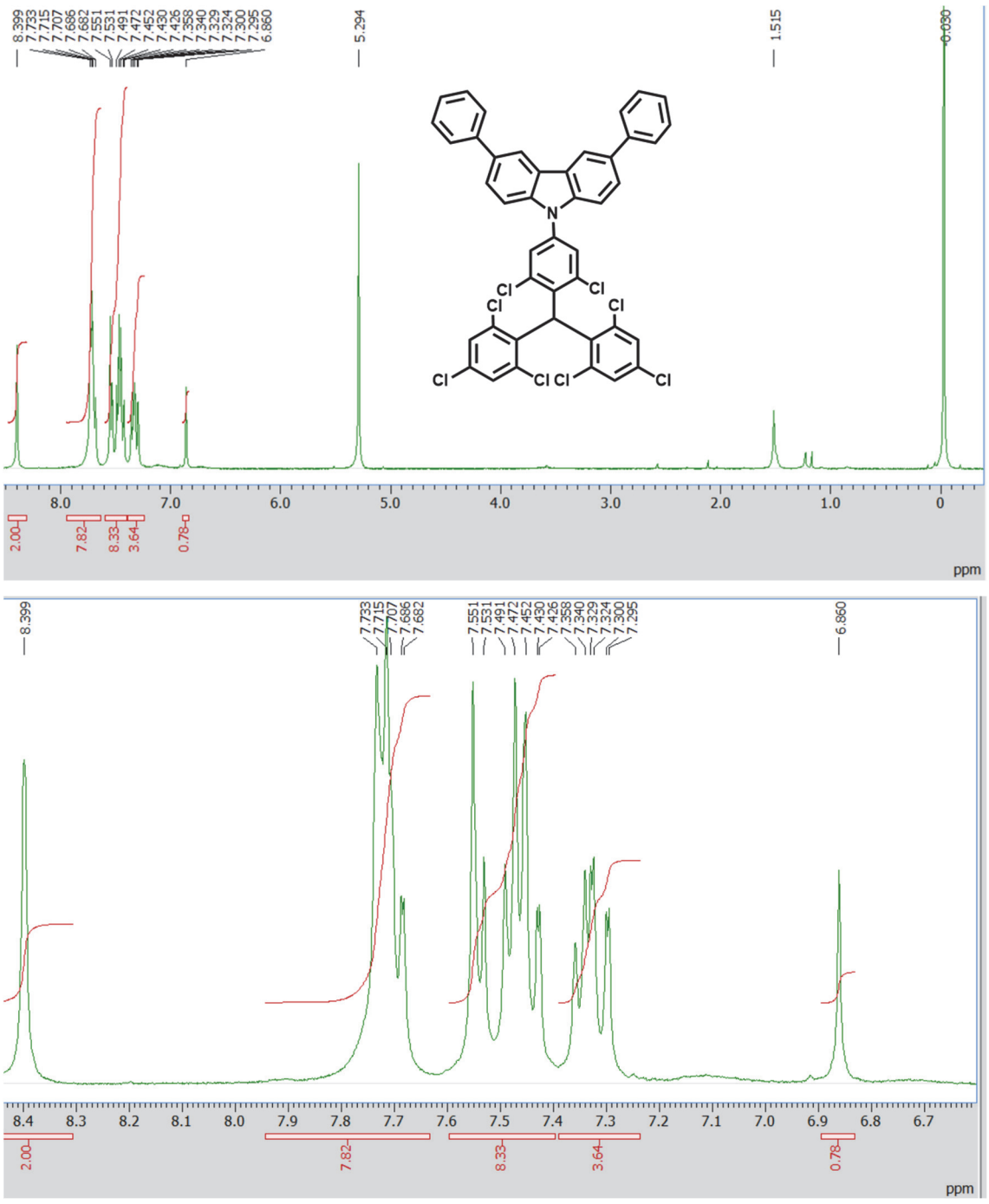


Fig. S4. ^{1}H NMR spectra of Ph2Cz-HTTM.

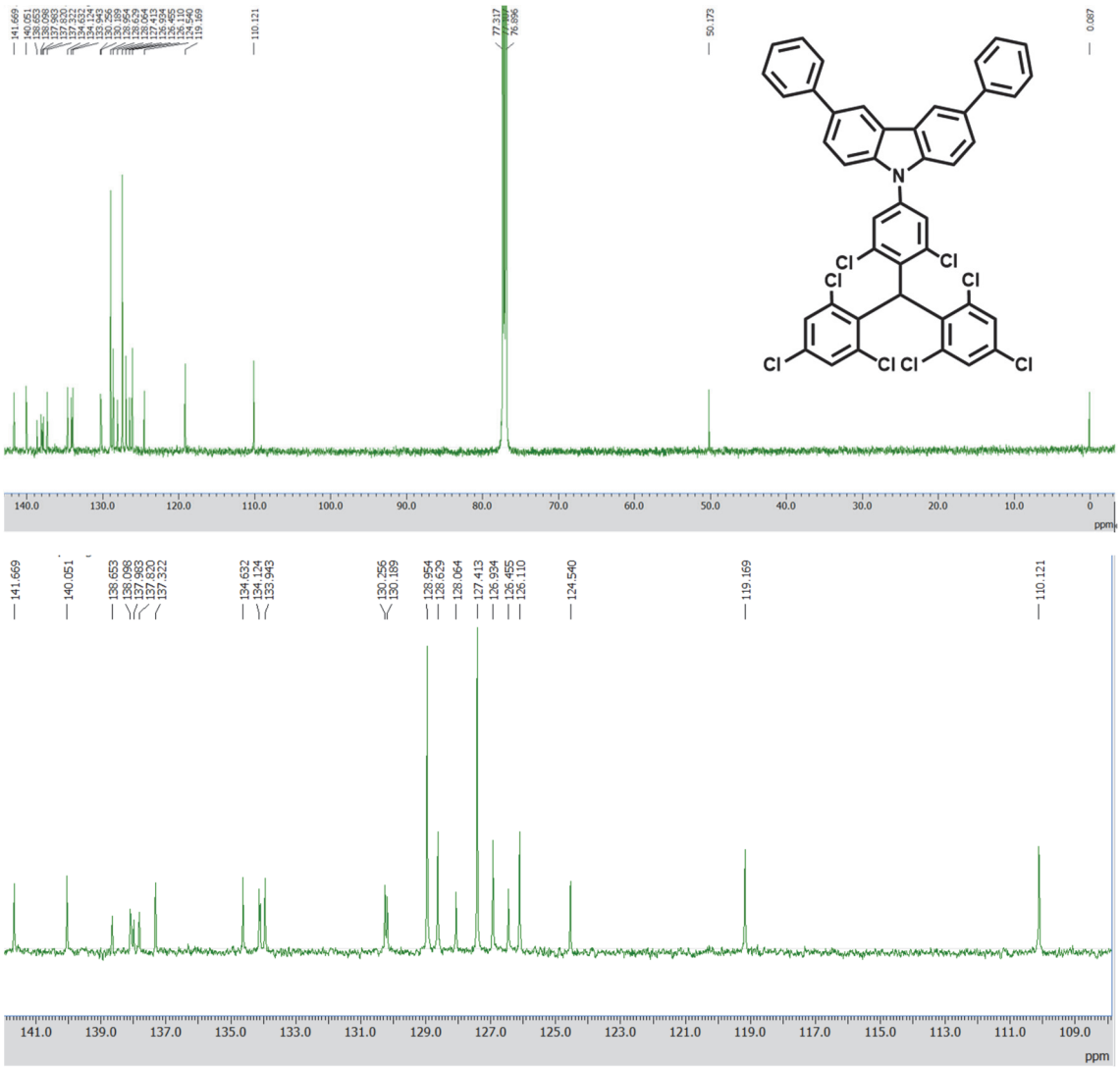


Fig. S5. ^{13}C NMR spectra of Ph2Cz-HTTM.

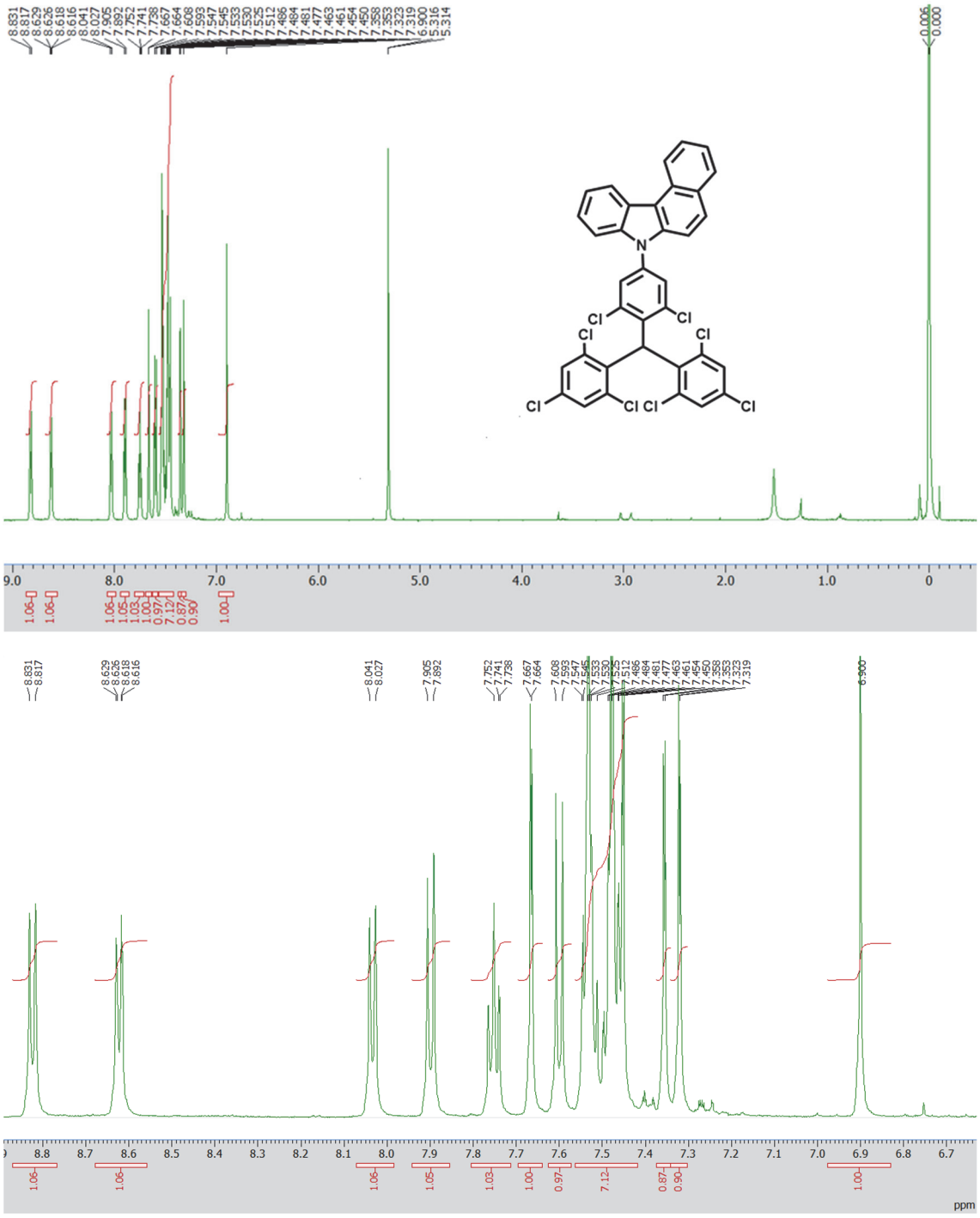


Fig. S6. ^{1}H NMR spectra of BCz-HTTM.

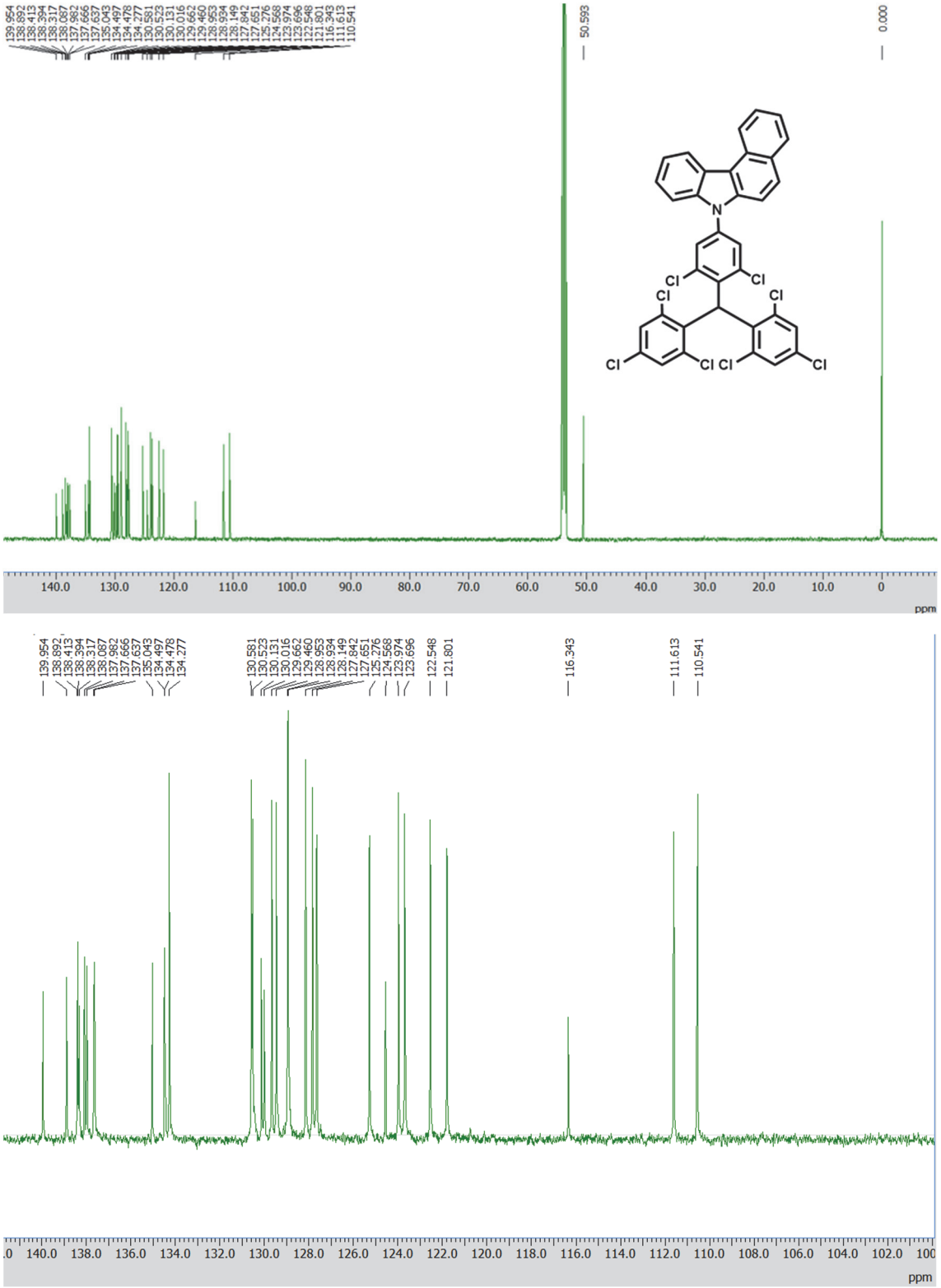


Fig. S7. ^{13}C NMR spectra of BCz-HTTM.

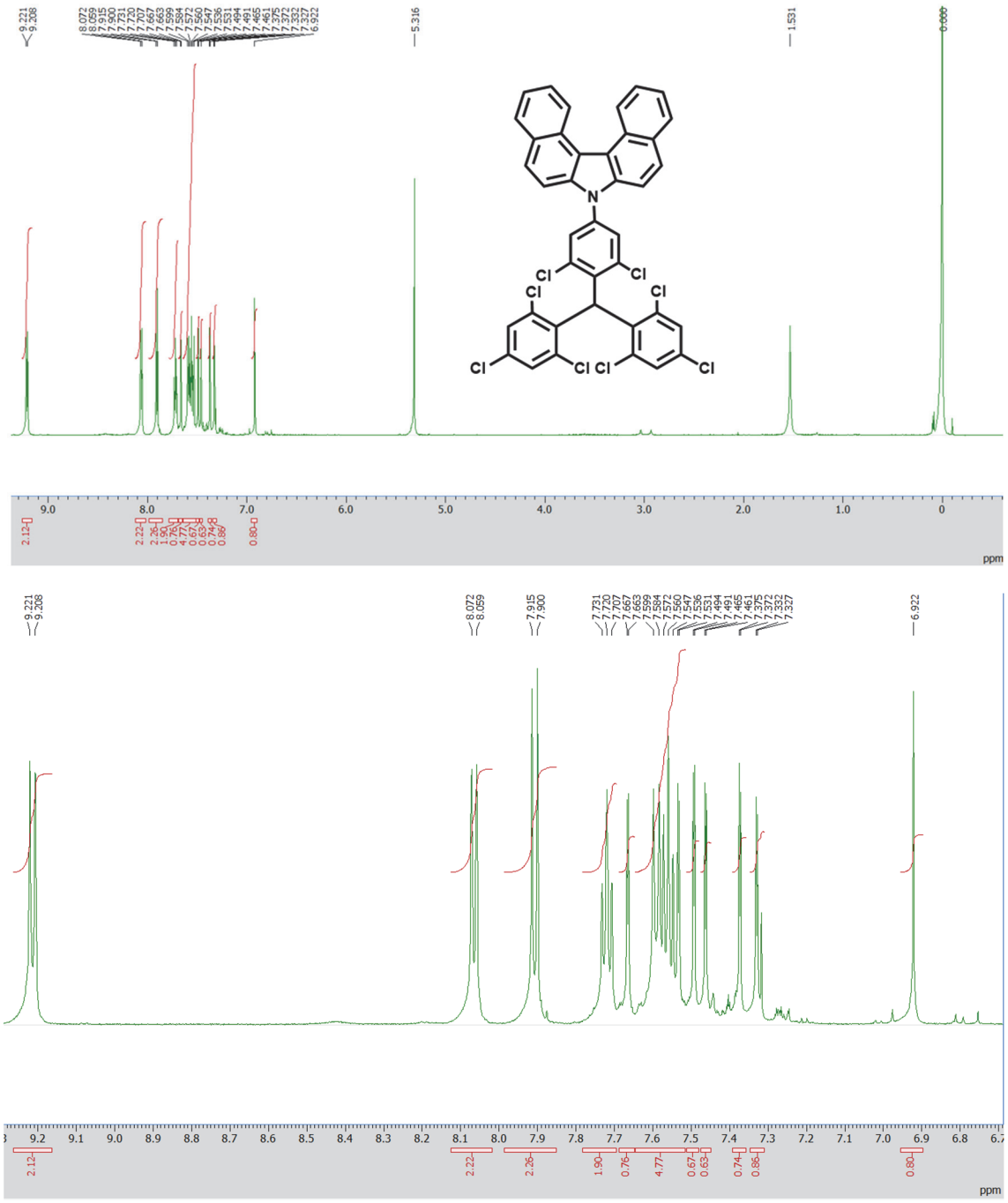


Fig. S8. ^{1}H NMR spectra of DbCz-HTTM.

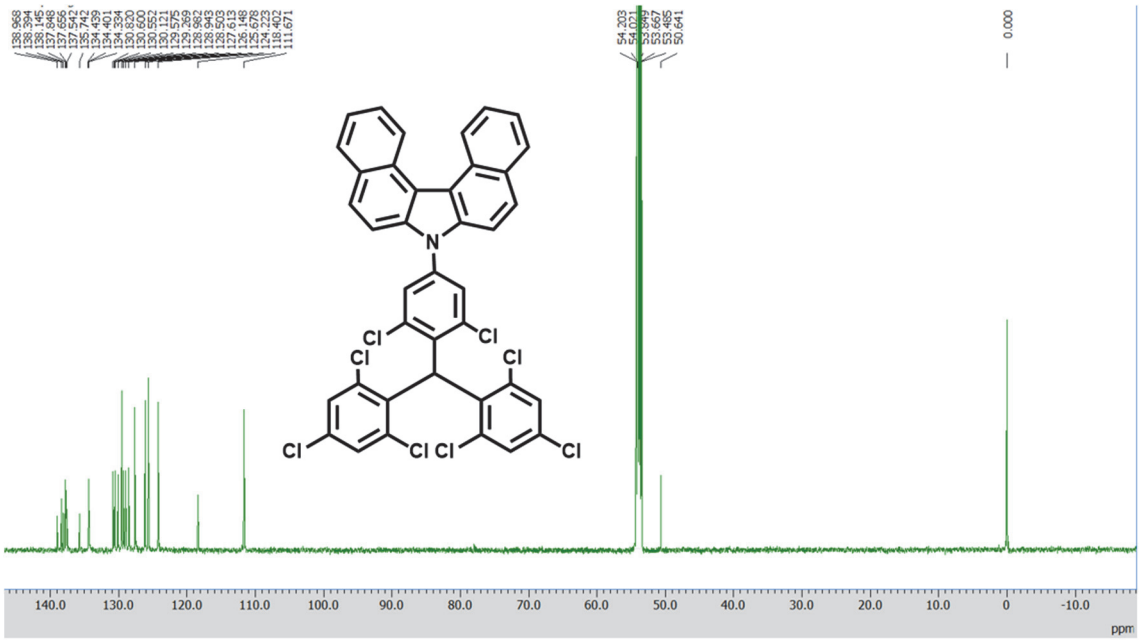


Fig. S9. ^{13}C NMR spectra of DbCz-HTTM.

qNMR

The determination of radical purity by qNMR was performed using the following equation. 1,4-Bis(trimethylsilyl)benzene-d_4 (1, 4-BTMSB-d_4, Purity 99.9+%, FUJIFILM Wako Chemicals) was used as an internal standard[3].

$$P_a = \frac{S_a}{S_S} \times \frac{N_s}{N_a} \times \frac{M_a}{M_S} \times \frac{m_s}{m_a} \times P_s$$

P_a : Purity or content of the analyzed species.

P_s : Purity of reference material for qNMR.

S_a : Signal area of analyzed species

S_s : Signal area of reference material for qNMR

N_a : Number of protons of analyzed species

N_s : Number of protons of reference material for qNMR

M_a : Molar mass of analyzed species

M_s : Molar mass of reference material for qNMR

m_a : Mass of material

m_s : Mass of reference material for qNMR

Table S1. Radical and 1,4-BTMSB-d_4 weighed values used for qNMR.

	Weight of Radicals (mg)	Weight of 1,4-BTMSB-d_4 (mg)	Molar mass of radical precursors	Radical precursor content (wt%)	Radical purities (%)
Cz-TTM	1.09	0.97	685.07	17	83
PhCz-TTM	2.59	1.02	761.17	<1	99
Ph2Cz-TTM	1.02	1.07	837.26	<1	99
BCz-TTM	2.24	2.01	735.13	<1	99
DbCz-TTM	2.91	1.22	785.19	<1	99

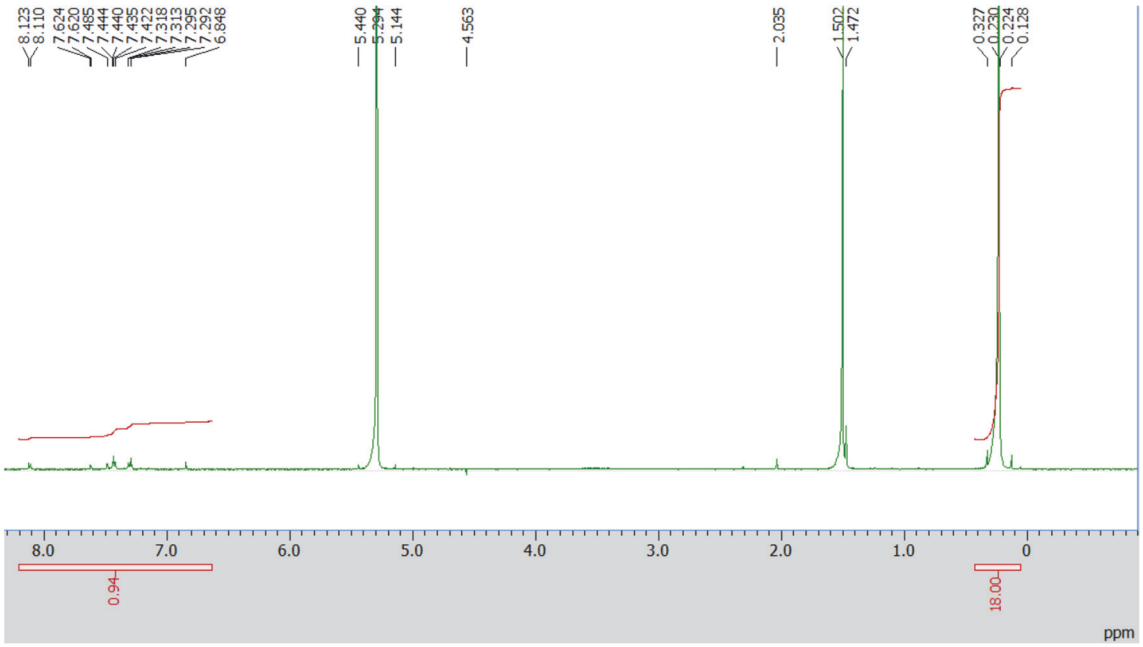


Fig. S10. [1]H NMR spectrum of Cz-TTM with 1,4-BTMSB-d4 as internal standard. The peaks at 6.5-8.5 ppm are assigned to Cz-HTTM (impurity).

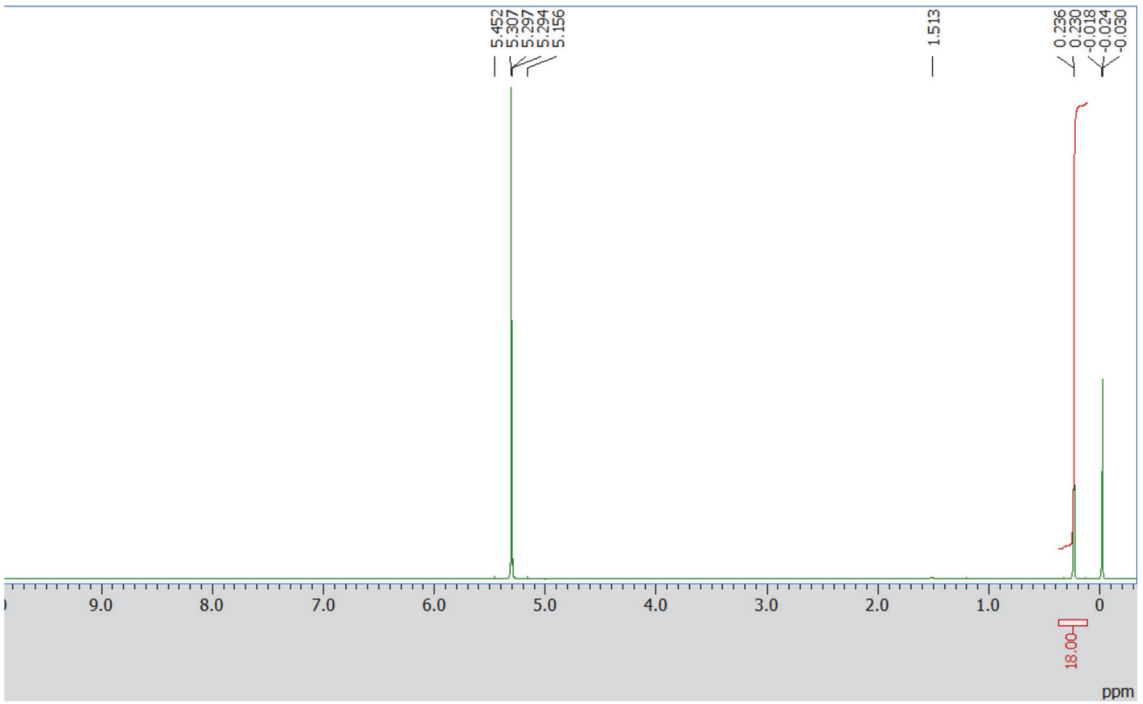


Fig. S11. [1]H NMR spectrum of PhCz-TTM with 1,4-BTMSB-d4 as internal standard.

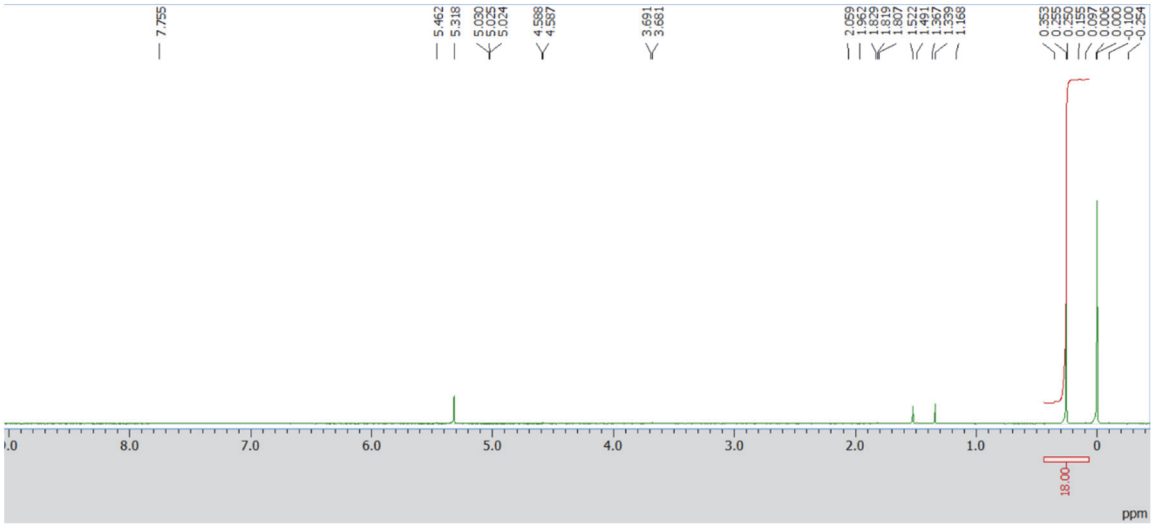


Fig. S12. [1]H NMR spectrum of Ph2Cz-TTM with 1,4-BTMSB-d4 as internal standard.

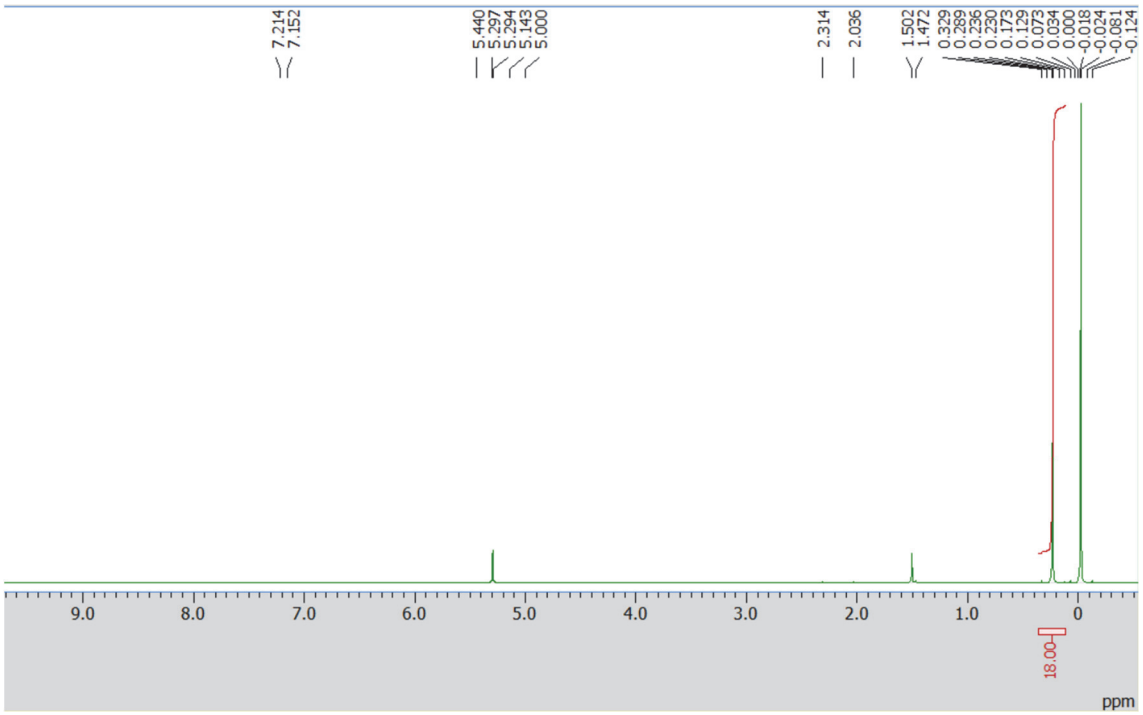


Fig. S13. [1]H NMR spectrum of BCz-TTM with 1,4-BTMSB-d4 as internal standard.

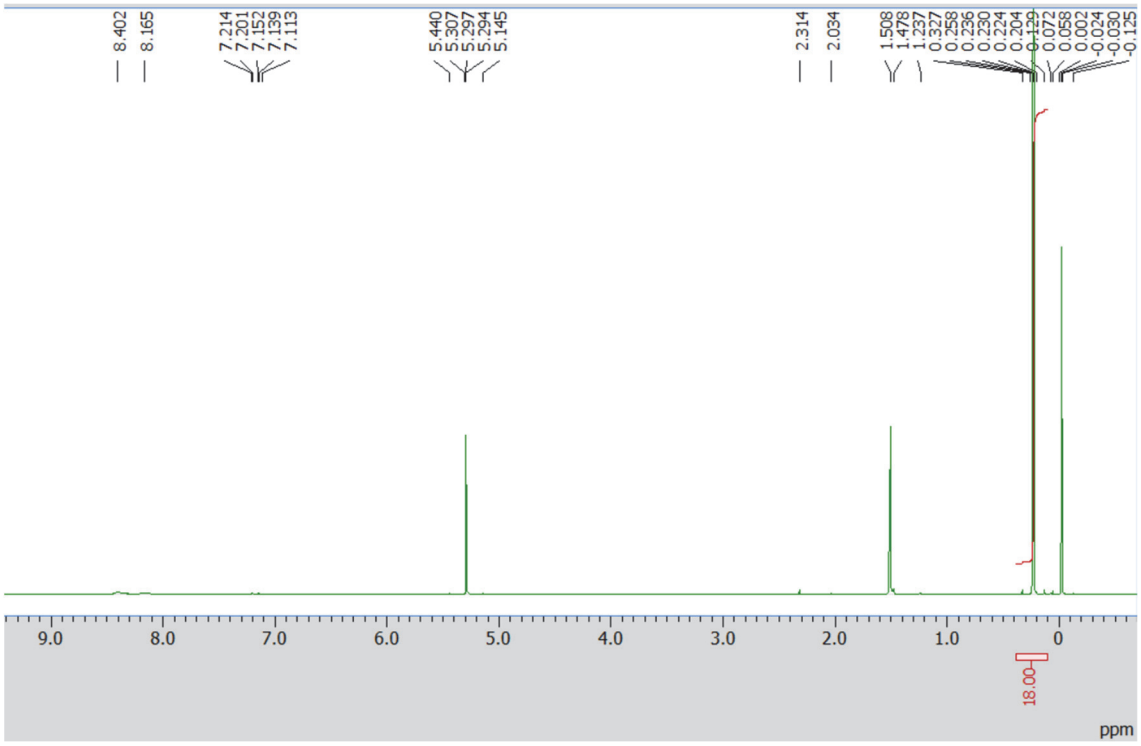


Fig. S14. ^{1}H NMR spectrum of DbCz-TTM with 1,4-BTMSB-d4 as internal standard.

UV-Visible and PL spectra

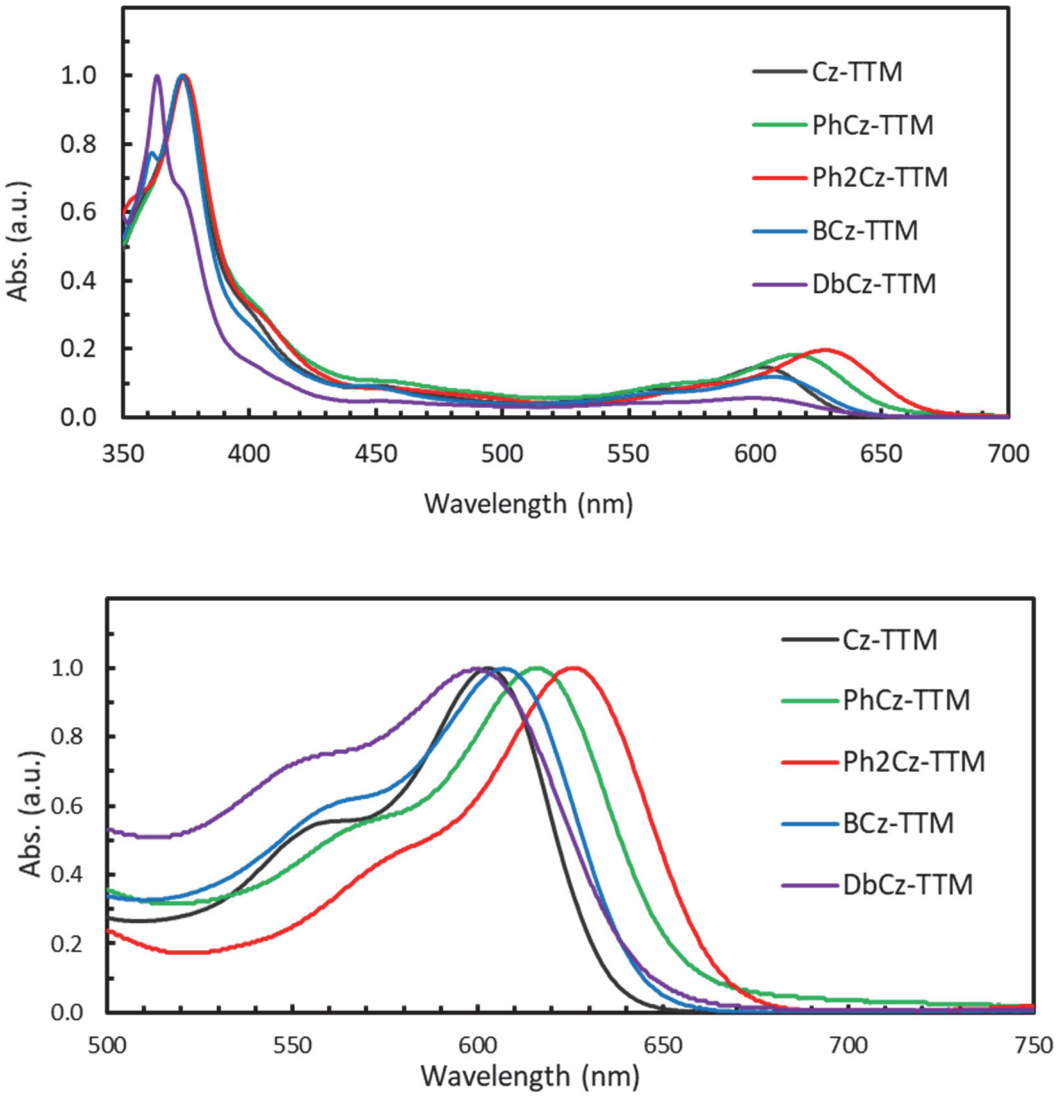


Fig. S15. UV-vis spectra of TTM derivatives in cyclohexane.

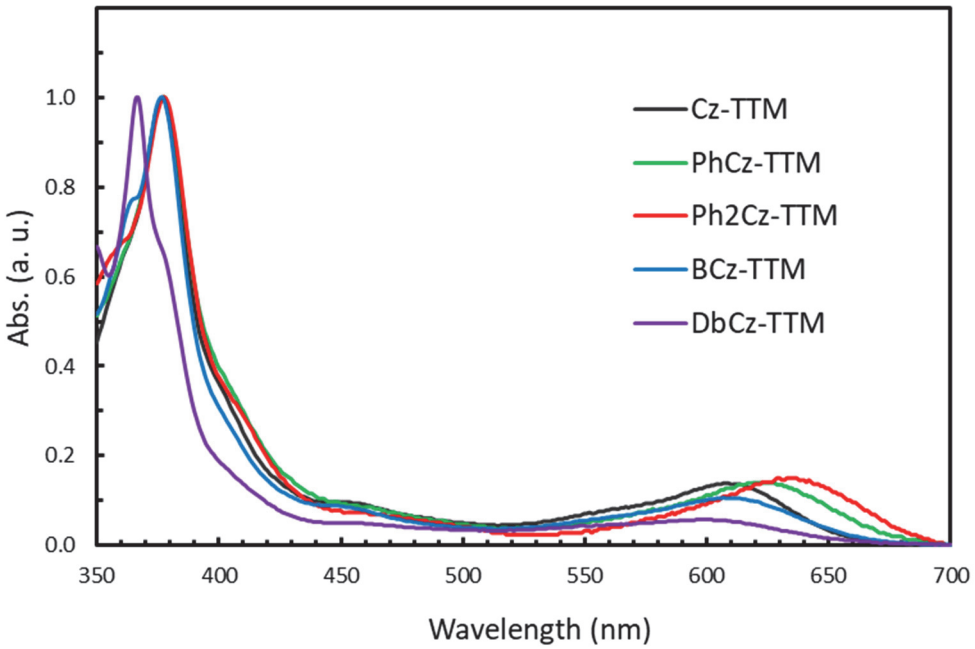


Fig. S16. UV-vis spectra of TTM derivatives in toluene.

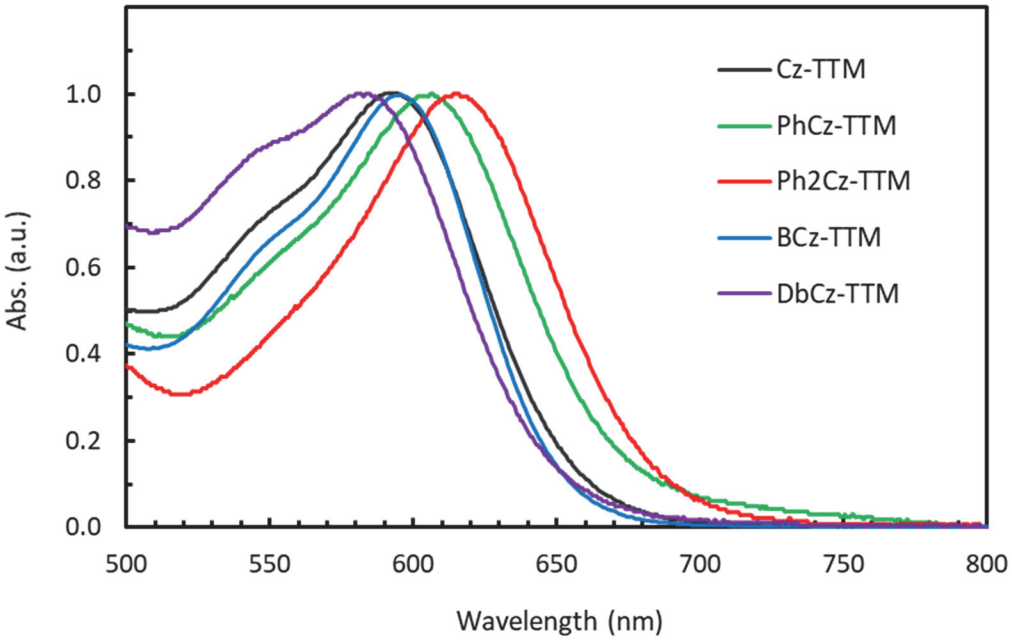


Fig. S17. UV-vis spectra of TTM derivatives in chloroform.

Table S2. Photophysical properties of TTM derivatives in various solvents after calibration with the purity of each radical.

Radicals	Solvent	λ_a (nm)	λ_{PL} (nm)	λ_a-λ_{PL} (cm^{-1})	τ (ns)	PLQY (%)	k_f(10^6 s^{-1})	k_{nr}(10^6 s^{-1})	ε (M^{-1} cm^{-1})	$t_{1/2}$ (10^3 s)
Cz-TTM	Cyclohexane	603	628	660	41.7	78	19	5	-	2.40
	Toluene	609	675	1606	25.6	54	21	18	-	-
	Chloroform	597	-	-	-	-	-	-	3.7×10^3	-
PhCz-TTM	Cyclohexane	616	648	802	34.5	62	18	11	-	25.52
	Toluene	622	701	1812	5.0	6	12	190	-	-
	Chloroform	608	-	-	-	-	-	-	2.9×10^3	-
Ph2Cz-TTM	Cyclohexane	628	661	795	32.3	69	22	10	-	47.21
	Toluene	635	720	1859	8.4	10	12	110	-	-
	Chloroform	618	-	-	-	-	-	-	3.1×10^3	-
BCz-TTM	Cyclohexane	607	637	776	37.0	61	17	10	-	11.86
	Toluene	611	701	2101	1.8	1	7.4	560	-	-
	Chloroform	596	-	-	-	-	-	-	3.2×10^3	-
DbCz-TTM	Cyclohexane	599	629	796	25.0	3	1.2	39	-	60.83
	Toluene	599	-	-	25.6	< 1	-	-	-	-
	Chloroform	584	-	-	-	-	-	-	2.8×10^3	-

Table S3. Photophysical properties of TTM derivatives in various solvents before calibration with the purity of each radical.

Radicals	Solvent	λ_a (nm)	λ_{PL} (nm)	λ_a-λ_{PL} (cm^{-1})	τ (ns)	PLQY (%)	k_f(10^6 s^{-1})	k_{nr}(10^6 s^{-1})	ε (M^{-1} cm^{-1})	$t_{1/2}$ (10^3 s)
Cz-TTM	Cyclohexane	603	628	660	41.7	78	19	5	-	2.81
	Toluene	609	675	1606	25.6	54	21	18	-	-
	Chloroform	597	-	-	-	-	-	-	3.1×10^3	-
PhCz-TTM	Cyclohexane	616	648	802	34.5	62	18	11	-	25.73
	Toluene	622	701	1812	5.0	6	12	190	-	-
	Chloroform	608	-	-	-	-	-	-	2.9×10^3	-
Ph2Cz-TTM	Cyclohexane	628	661	795	32.3	69	22	10	-	47.48
	Toluene	635	720	1859	8.4	10	12	110	-	-
	Chloroform	618	-	-	-	-	-	-	3.1×10^3	-
BCz-TTM	Cyclohexane	607	637	776	37.0	61	17	10	-	11.95
	Toluene	611	701	2101	1.8	1	7.4	560	-	-
	Chloroform	596	-	-	-	-	-	-	3.2×10^3	-
DbCz-TTM	Cyclohexane	599	629	796	25.0	3	1.2	39	-	61.18
	Toluene	599	-	-	25.6	< 1	-	-	-	-
	Chloroform	584	-	-	-	-	-	-	2.8×10^3	-

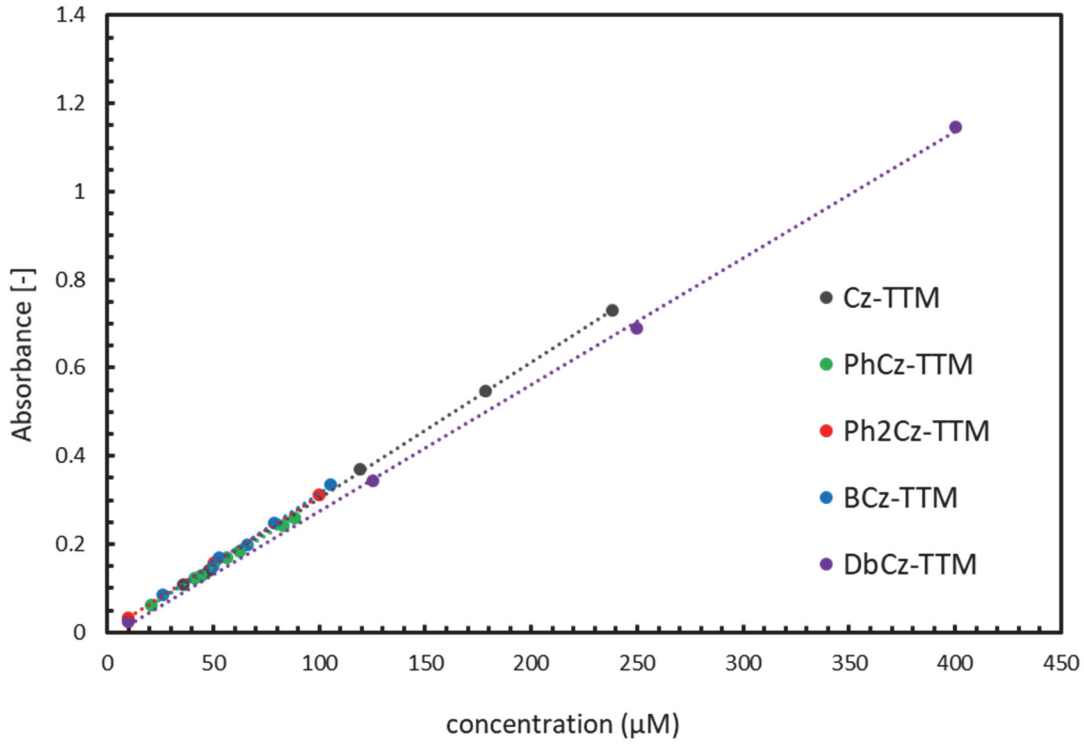


Fig. S18. Concentration dependence of absorbance of TTM derivatives in chloroform. This data was used to determine the molar absorption coefficient (ε).

Computation

Quantum chemical calculations were performed on UB3LYP/6-31G** . Structures were optimized in vacuum.

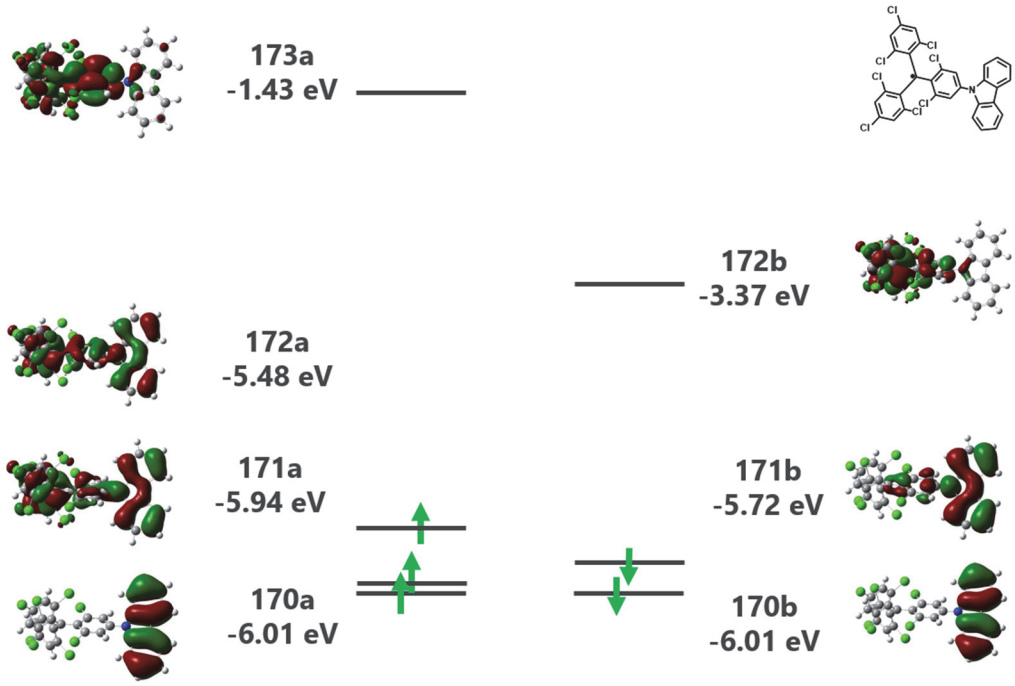


Fig. S19. Energy levels of Cz-TTM by UB3LYP/6-31G**.

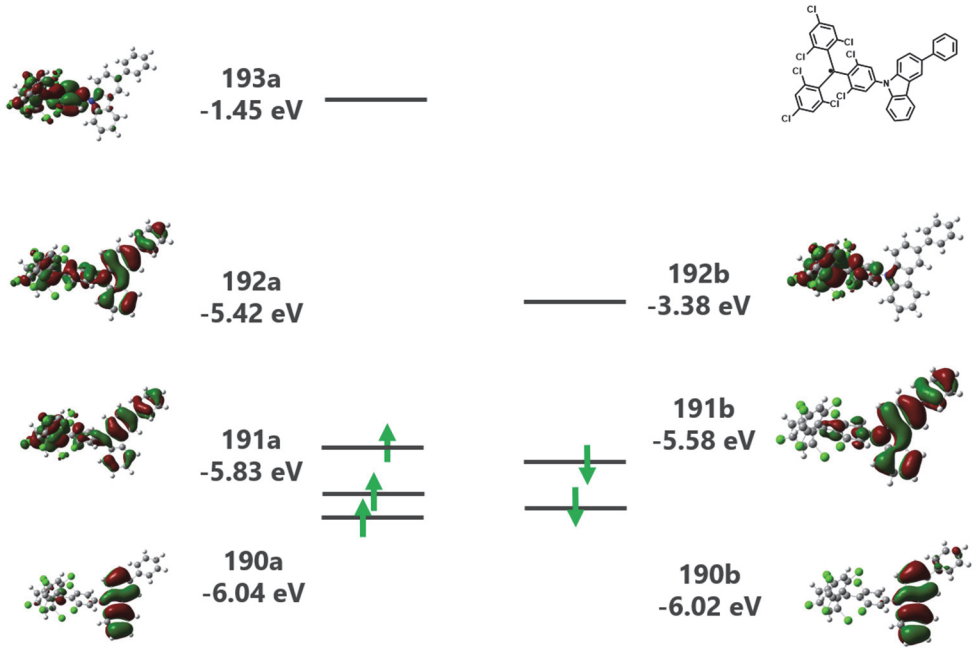


Fig. S20. Energy levels of PhCz-TTM by UB3LYP/6-31G**.

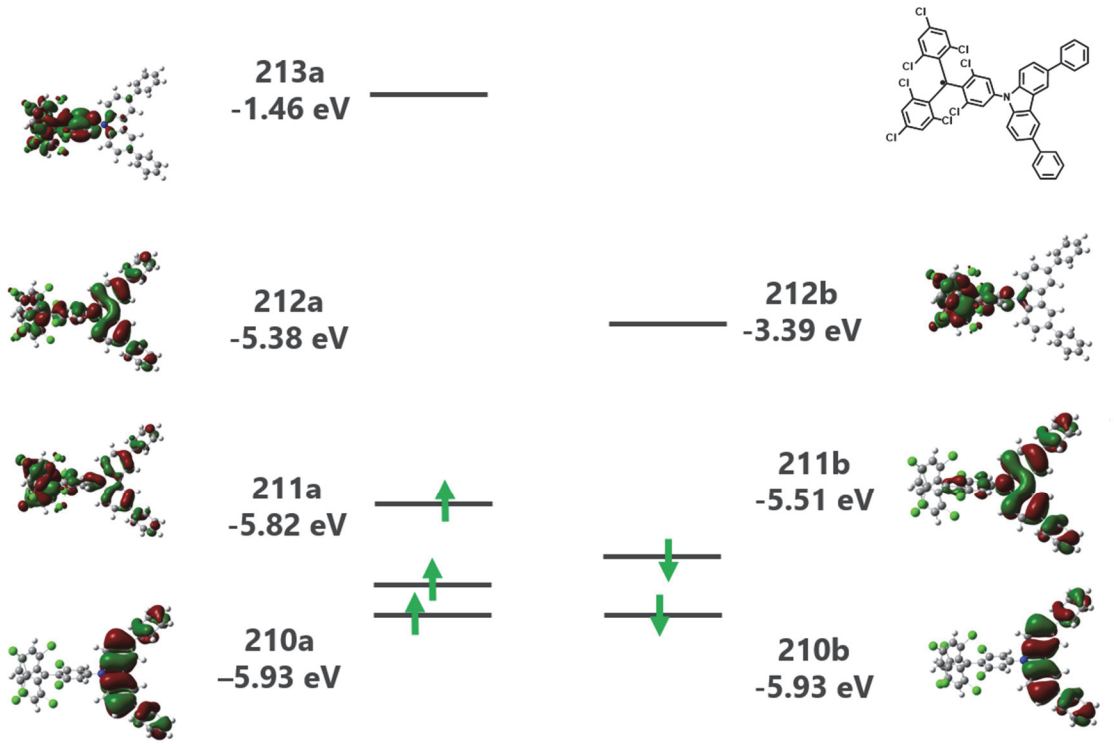


Fig. S21. Energy levels of Ph2Cz-TTM by UB3LYP/6-31G**.

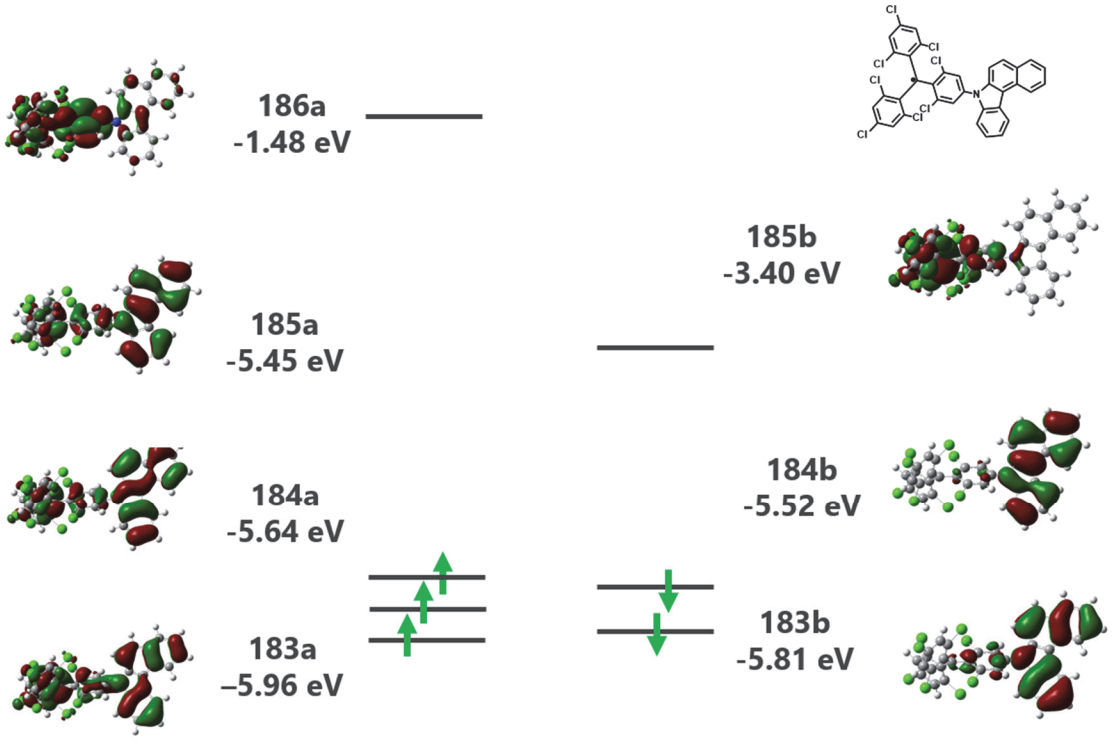


Fig. S22. Energy levels of BCz-TTM by UB3LYP/6-31G**.

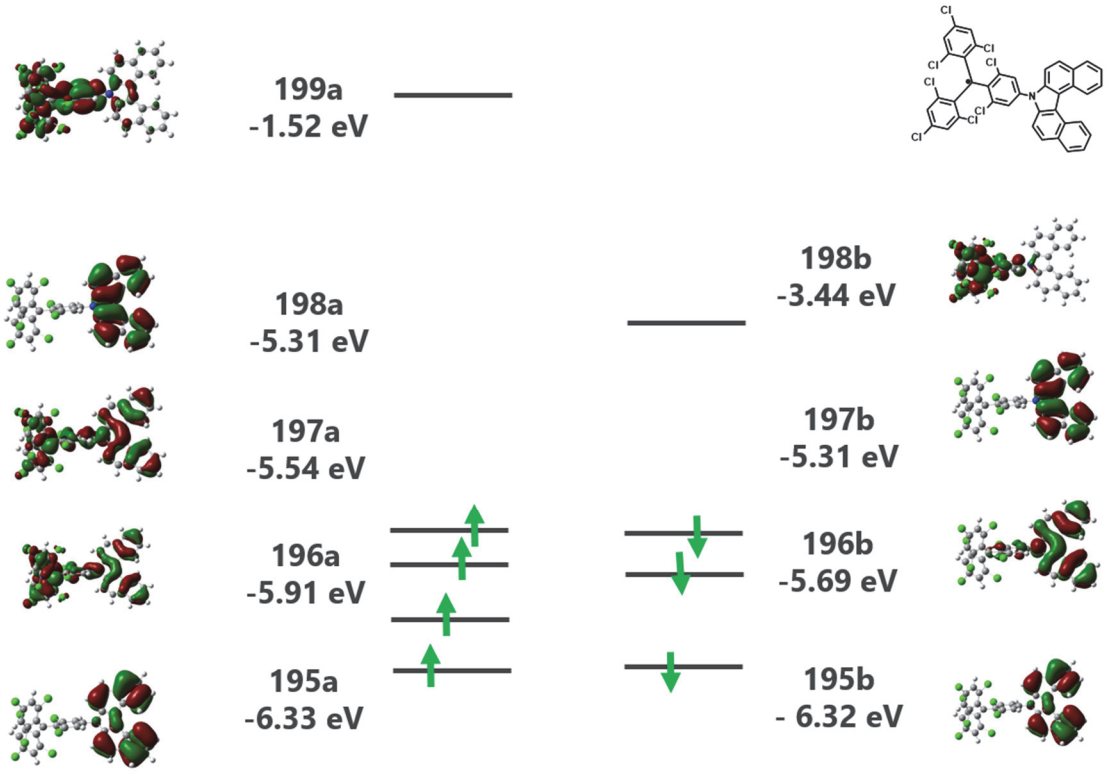


Fig. S23. Energy levels of DbCz-TTM by UB3LYP/6-31G**.

PL spestra

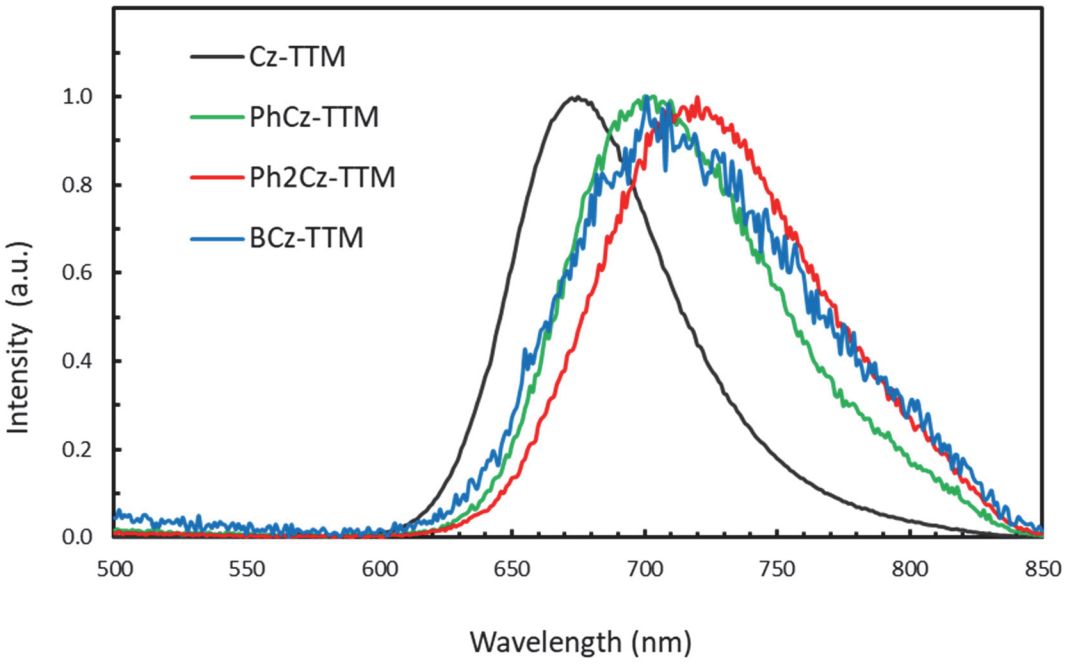


Fig. S24. PL spectra of TTM derivatives in toluene.

PL lifetime

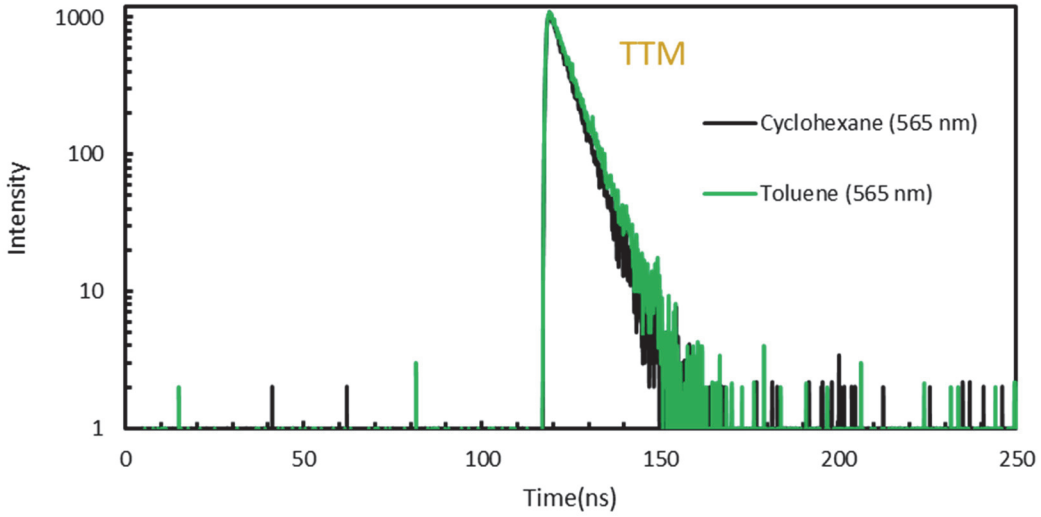


Fig. S25. PL lifetime of TTM radicals (room temperature).

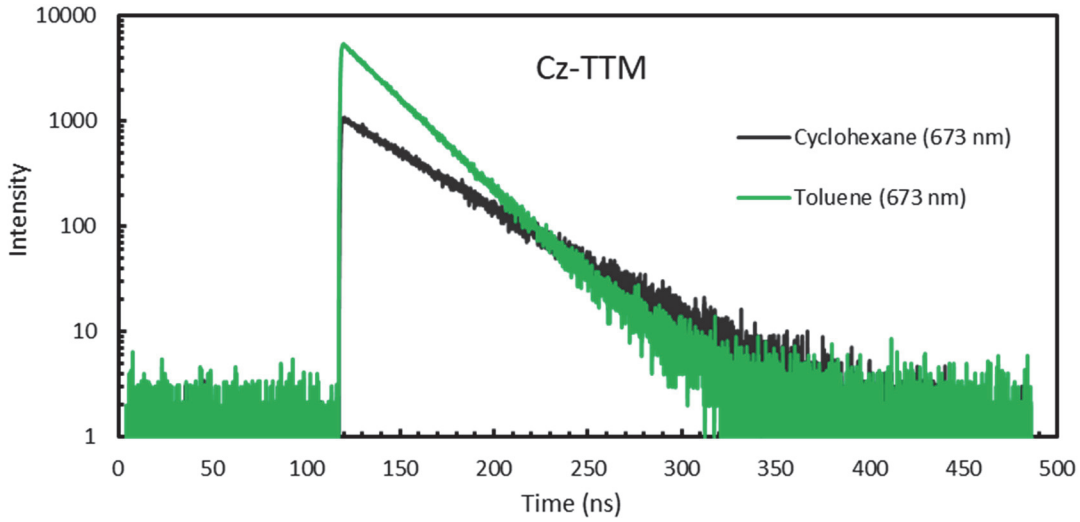


Fig. S26. PL lifetime of Cz-TTM (room temperature).

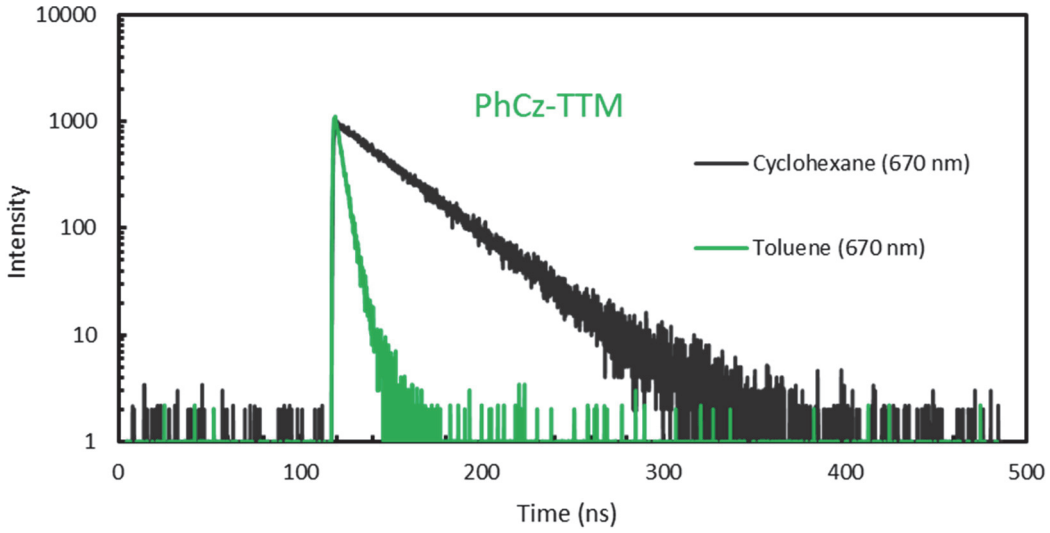


Fig. S27. PL lifetime of PhCz-TTM (room temperature).

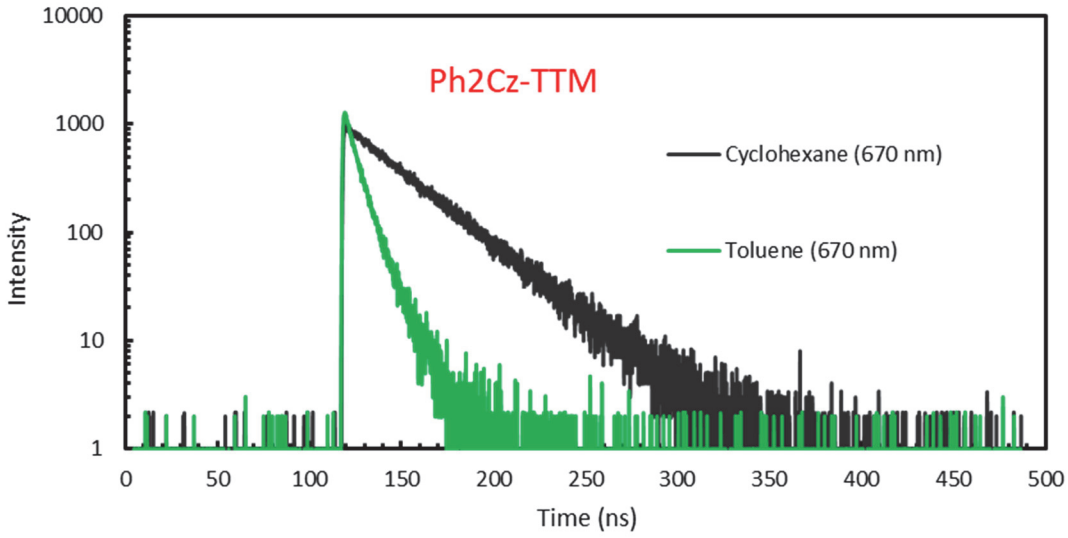


Fig. S28. PL lifetime of Ph2Cz-TTM (room temperature).

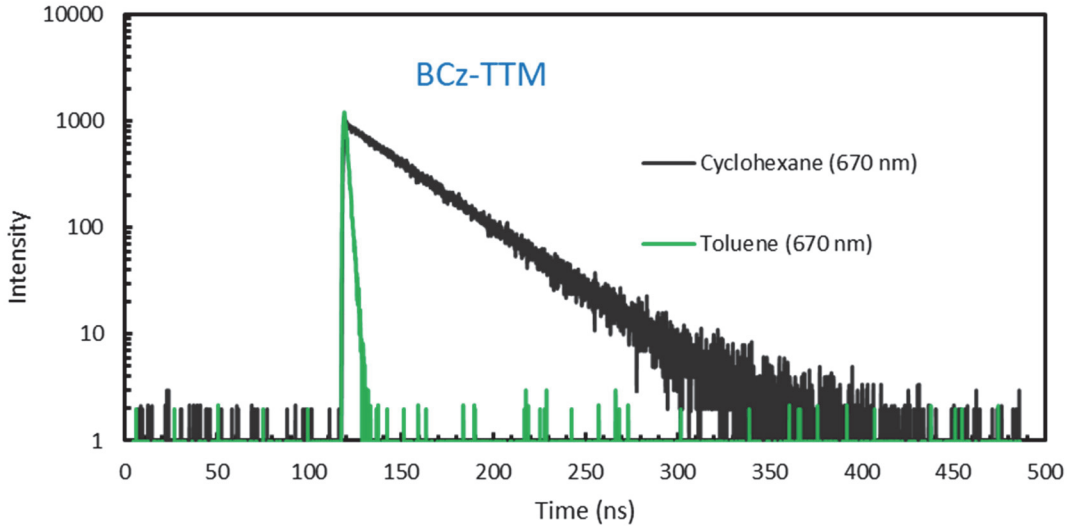


Fig. S29. PL lifetime of BCz-TTM (room temperature).

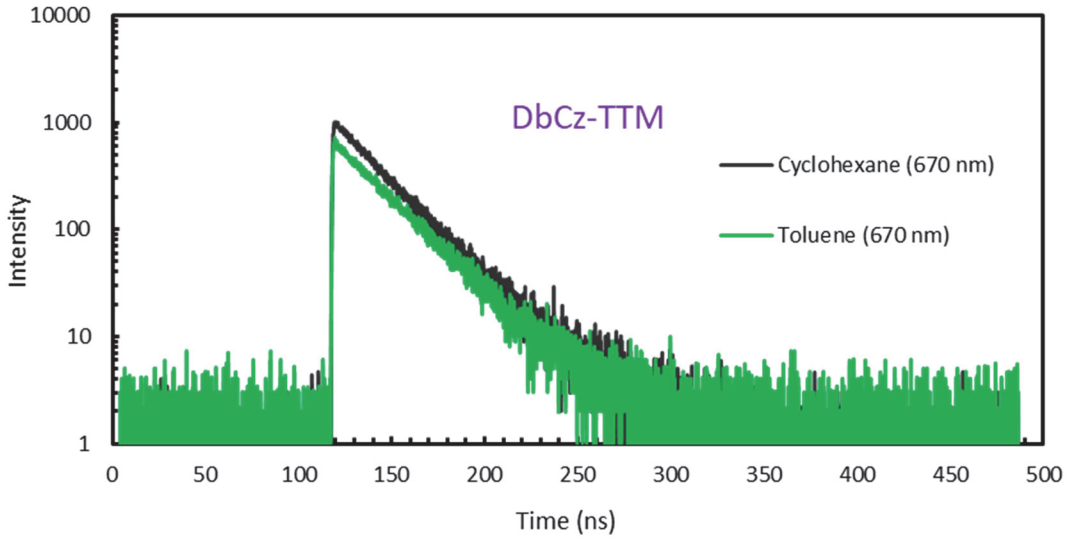


Fig. S30. PL lifetime of DbCz-TTM (room temperature).

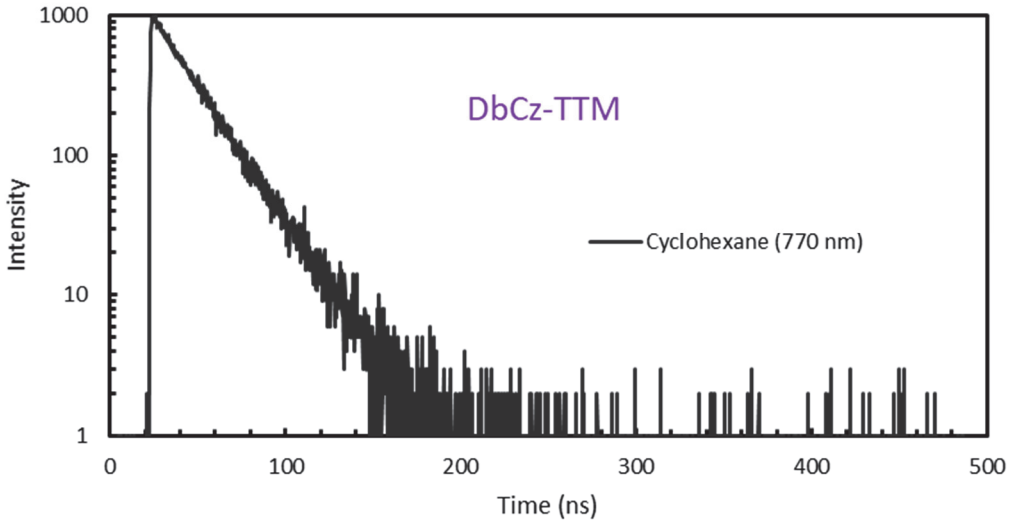


Fig. S31. PL lifetime of DbCz-TTM (room temperature).

Cyclic voltanmetry

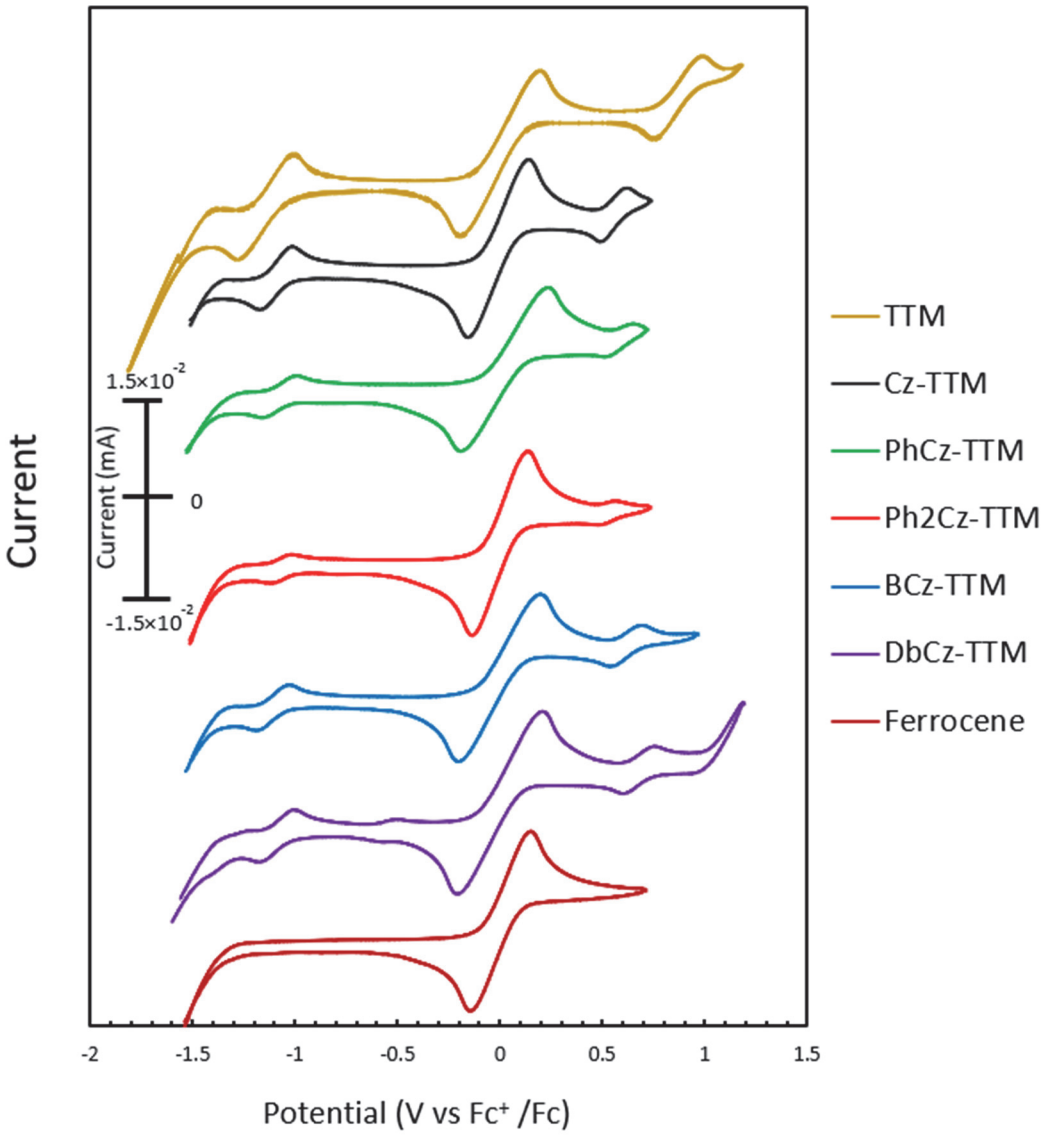


Fig. S32. Cyclic voltammogram of TTM derivatives.

Photostability

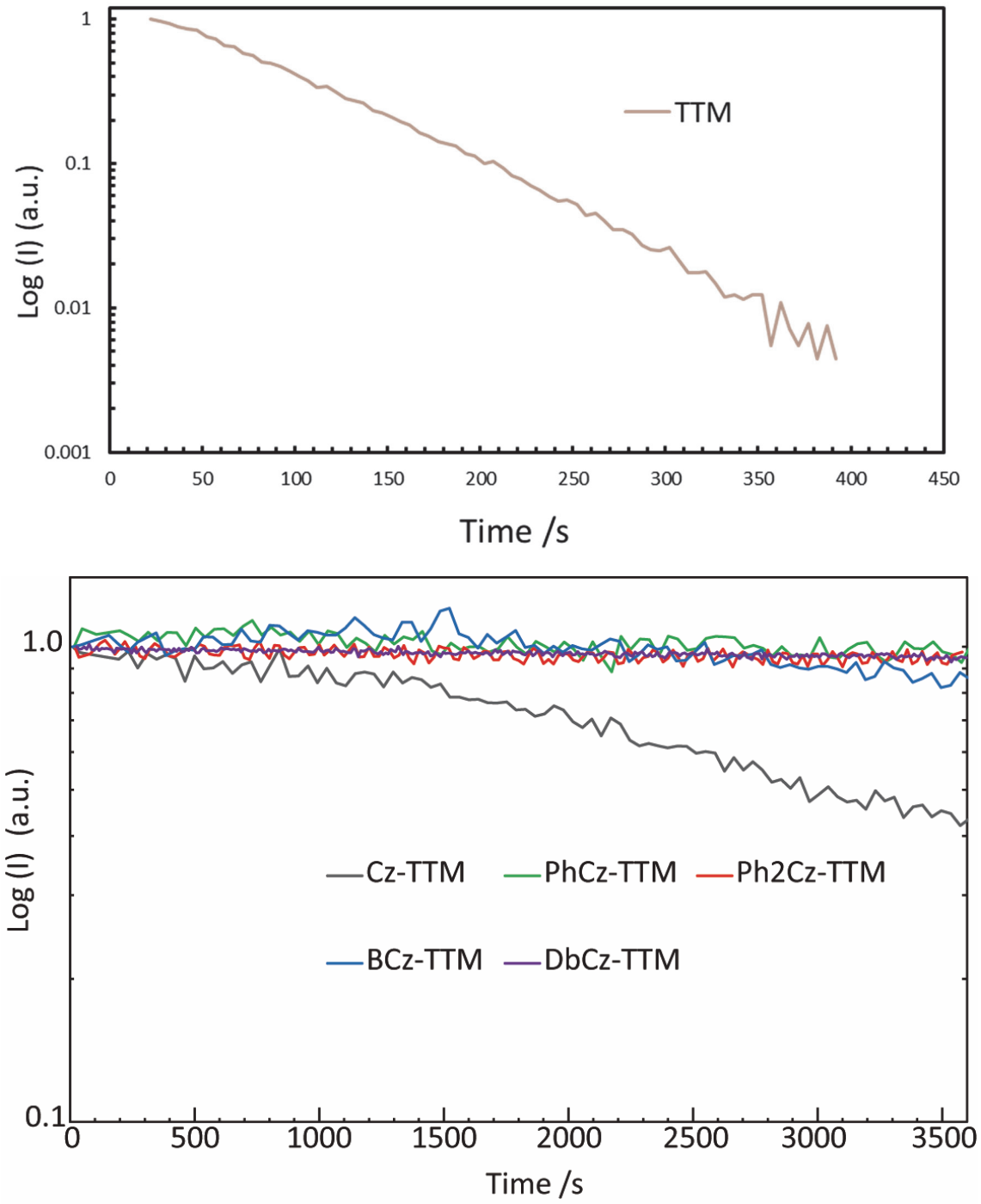


Fig. S33. Time dependence of the emission intensity (I) for radicals in cyclohexane under 355 nm pulsed laser radiation (power: 0.7 mW, beam diameter (1/e² level) : ~3 mm, pulse width: 28 ps, repetition rate:10 Hz).

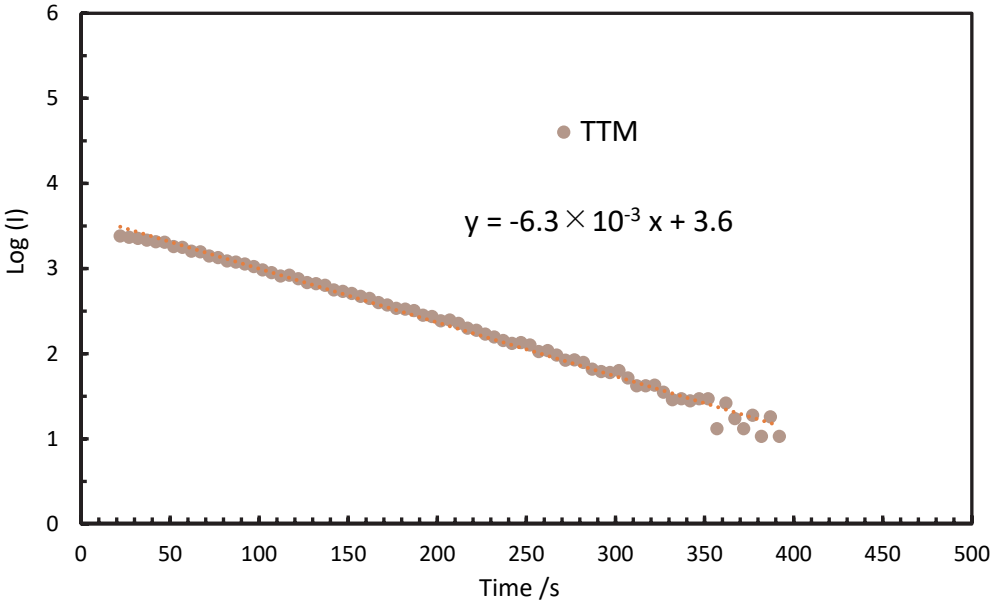


Fig. S34. Time dependence of the emission intensity (I) for TTM in cyclohexane under 355 nm pulased laser radiation (power: 0.7 mW, beam diameter (1/e² level) : ~3 mm, pulse width: 28 ps, repetition rate:10 Hz).

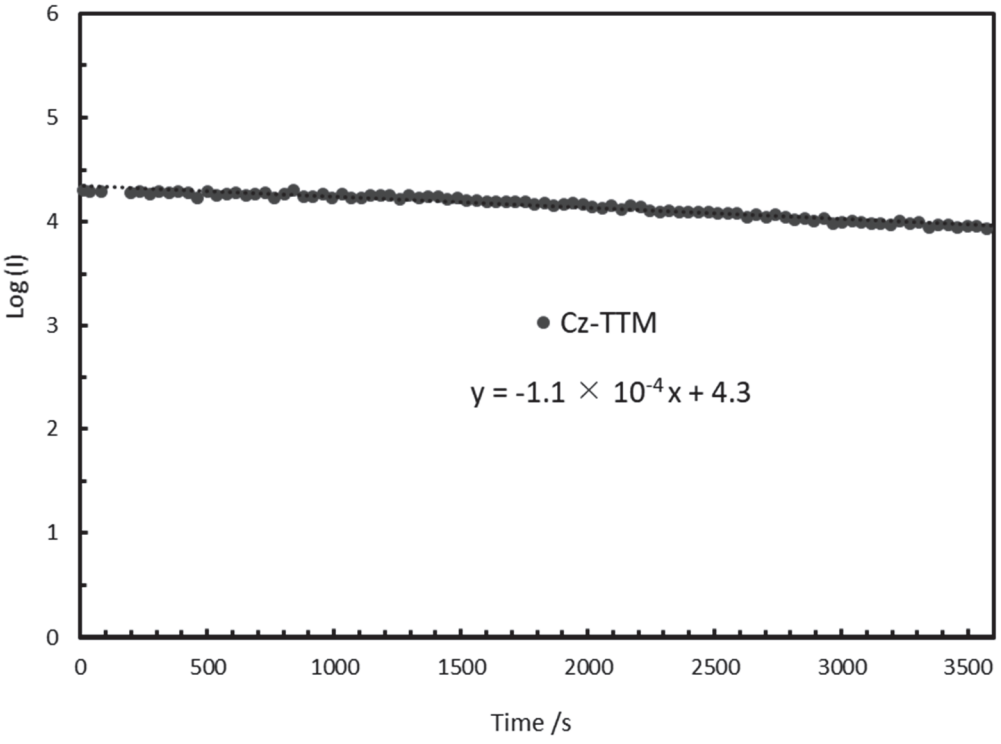


Fig. S35. Time dependence of the emission intensity (I) for Cz-TTM in cyclohexane under 355 nm pulased laser radiation (power: 0.7 mW, beam diameter (1/e² level) : ~3 mm, pulse width: 28 ps, repetition rate:10 Hz).

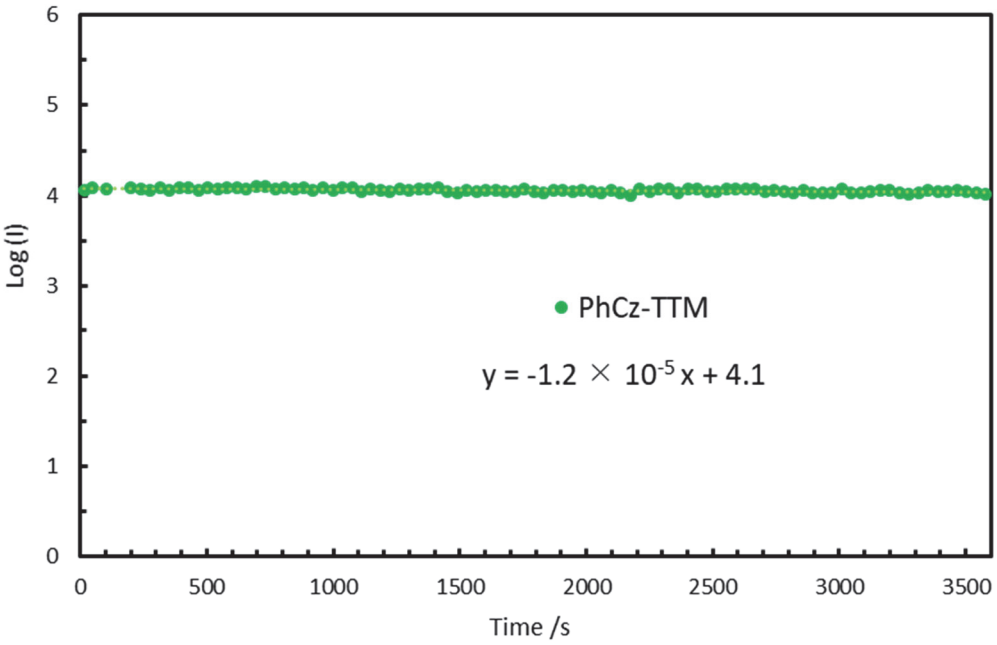


Fig. S36. Time dependence of the emission intensity (I) for PhCz-TTM in cyclohexane under 355 nm pulased laser radiation (power: 0.7 mW, beam diameter (1/e² level) : ~3 mm, pulse width: 28 ps, repetition rate:10 Hz).

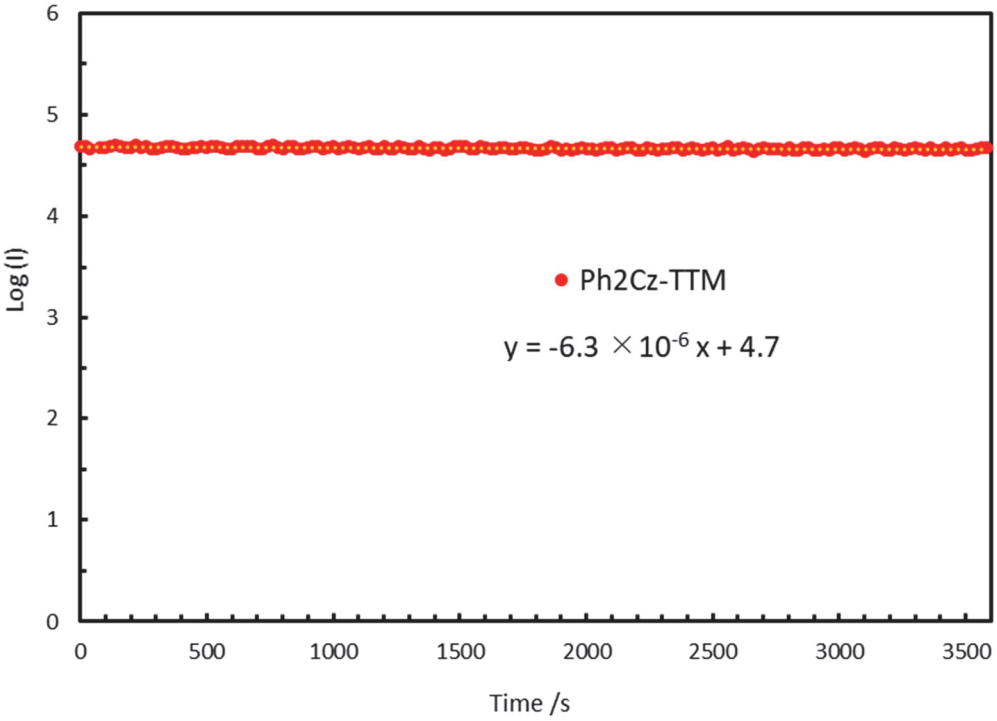


Fig. S37. Time dependence of the emission intensity (I) for Ph2Cz-TTM in cyclohexane under 355 nm pulased laser radiation (power: 0.7 mW, beam diameter (1/e² level) : ~3 mm, pulse width: 28 ps, repetition rate:10 Hz).

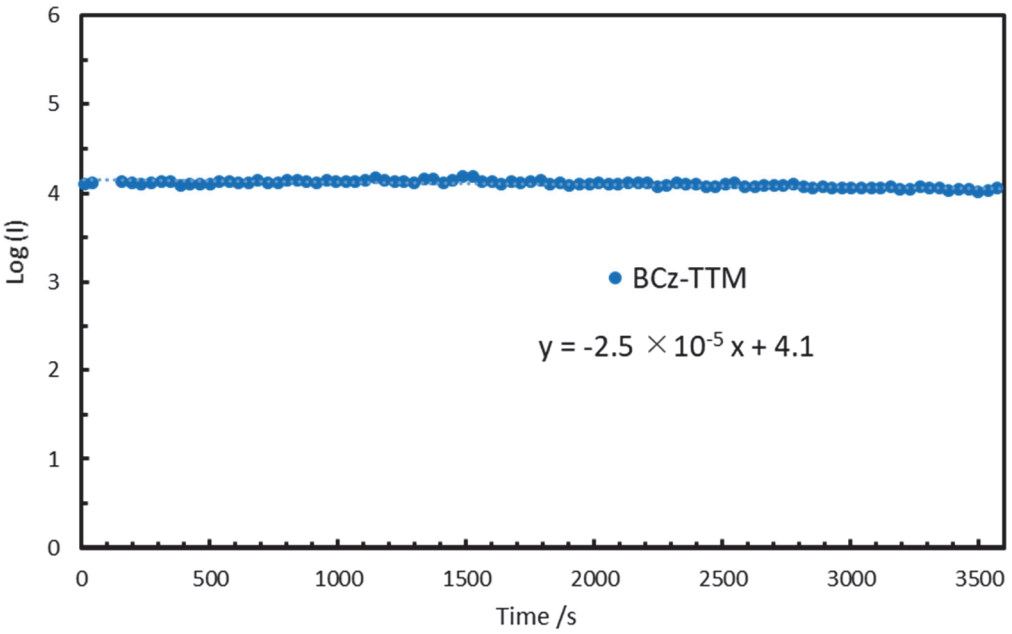


Fig. S38. Time dependence of the emission intensity (I) for BCz-TTM in cyclohexane under 355 nm pulased laser radiation (power: 0.7 mW, beam diameter (1/e² level) : ~3 mm, pulse width: 28 ps, repetition rate:10 Hz).

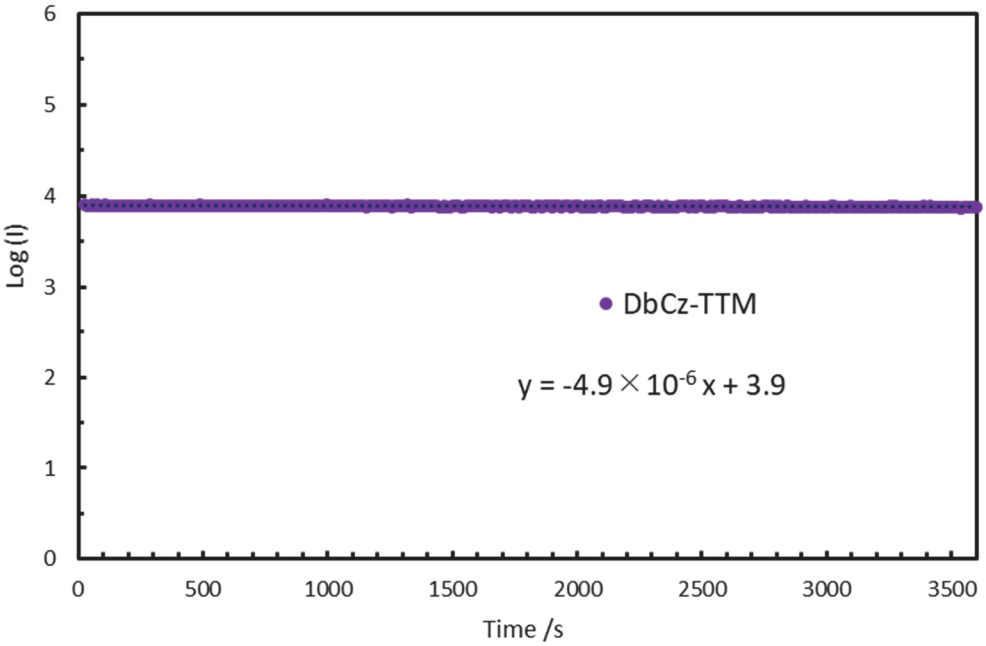


Fig. S39. Time dependence of the emission intensity (I) for DbCz-TTM in cyclohexane under 355 nm pulased laser radiation (power: 0.7 mW, beam diameter (1/e² level) : ~3 mm, pulse width: 28 ps, repetition rate:10 Hz).

Table S4. Calibration data for photostability. Photostability was calibrated using the absorption coefficients of radicals and their precursors. The half life ($t_{1/2}$) was determined by fitting the result with the equation $I(t) = I_0 \times (\frac{1}{2})^{\frac{t}{t_{1/2}}}$ where *I(t)* is the intensity at a specific time, I_0 is the initial intensity, and *t* is time.

Radicals	$t_{1/2}$ (10^3 s)	Purity	Absorption coefficient of radical precursors (10^3[-], 355 nm)	Absorption coefficient of radicals (10^3[-], 355 nm)	Calibrated half-life $t_{1/2}$ (10^3 s)
Cz-TTM	2.81	83	2.8	19.7	2.40
PhCz-TTM	25.73	99	3.1	16.2	25.52
Ph2Cz-TTM	47.48	99	6.8	22.8	47.15
BCz-TTM	11.95	99	9.1	33.2	11.86
DbCz-TTM	61.18	99	12.5	29.5	60.83

MS spectra

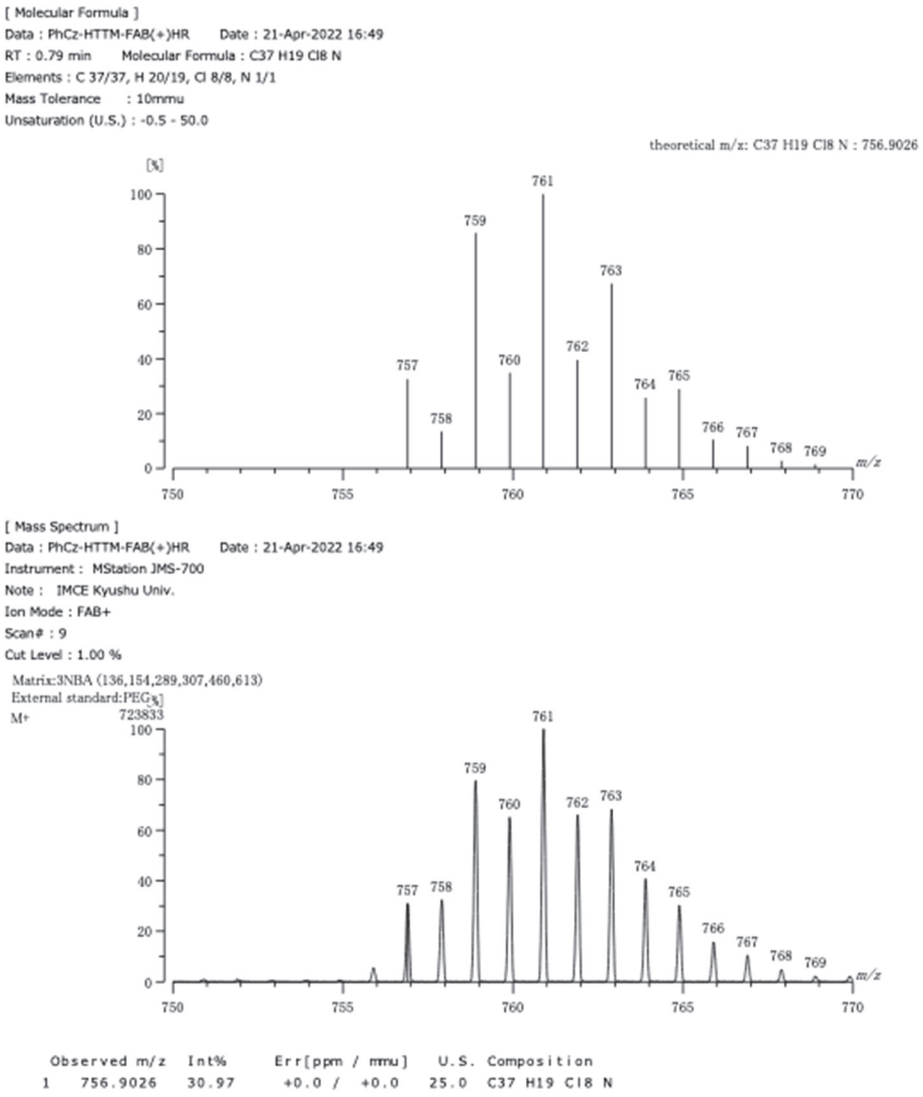


Fig. S40. FAB-MS spectrum of PhCz-HTTM.

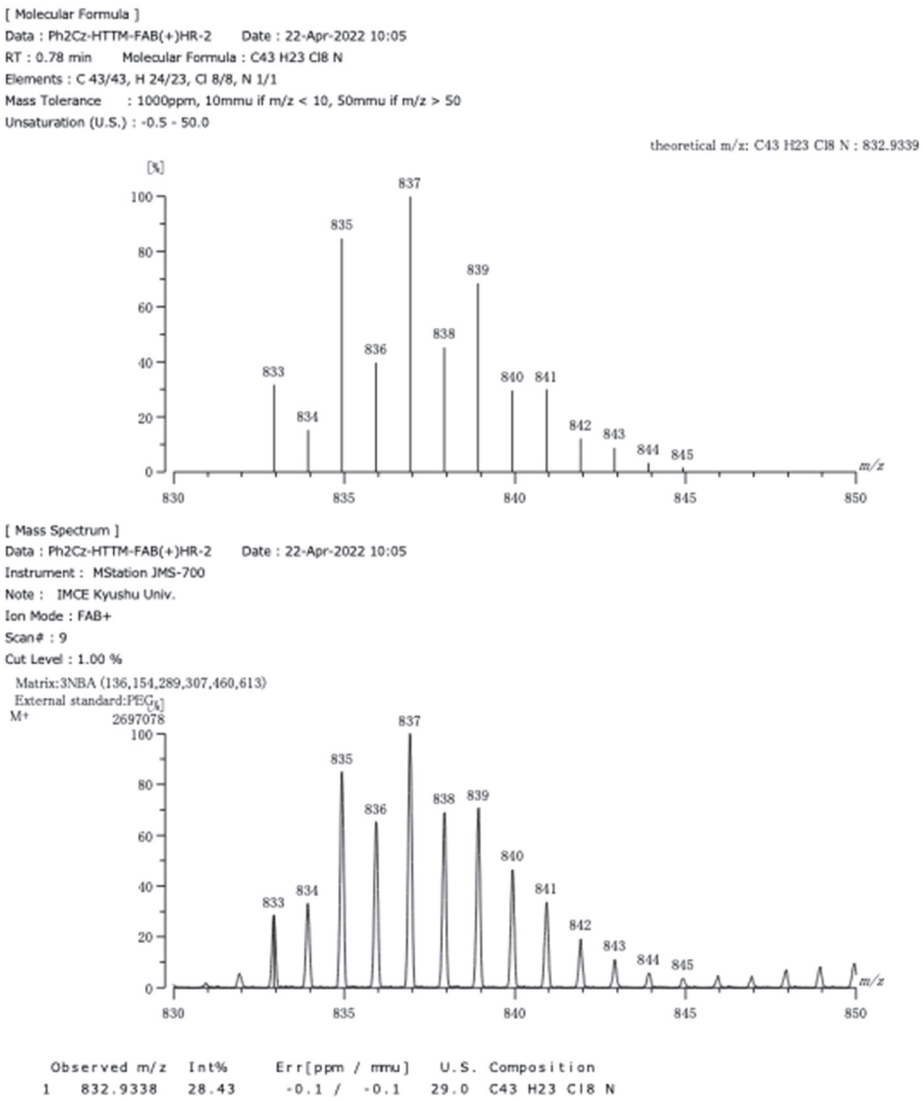


Fig. S41. FAB-MS spectrum of Ph2Cz-HTTM.

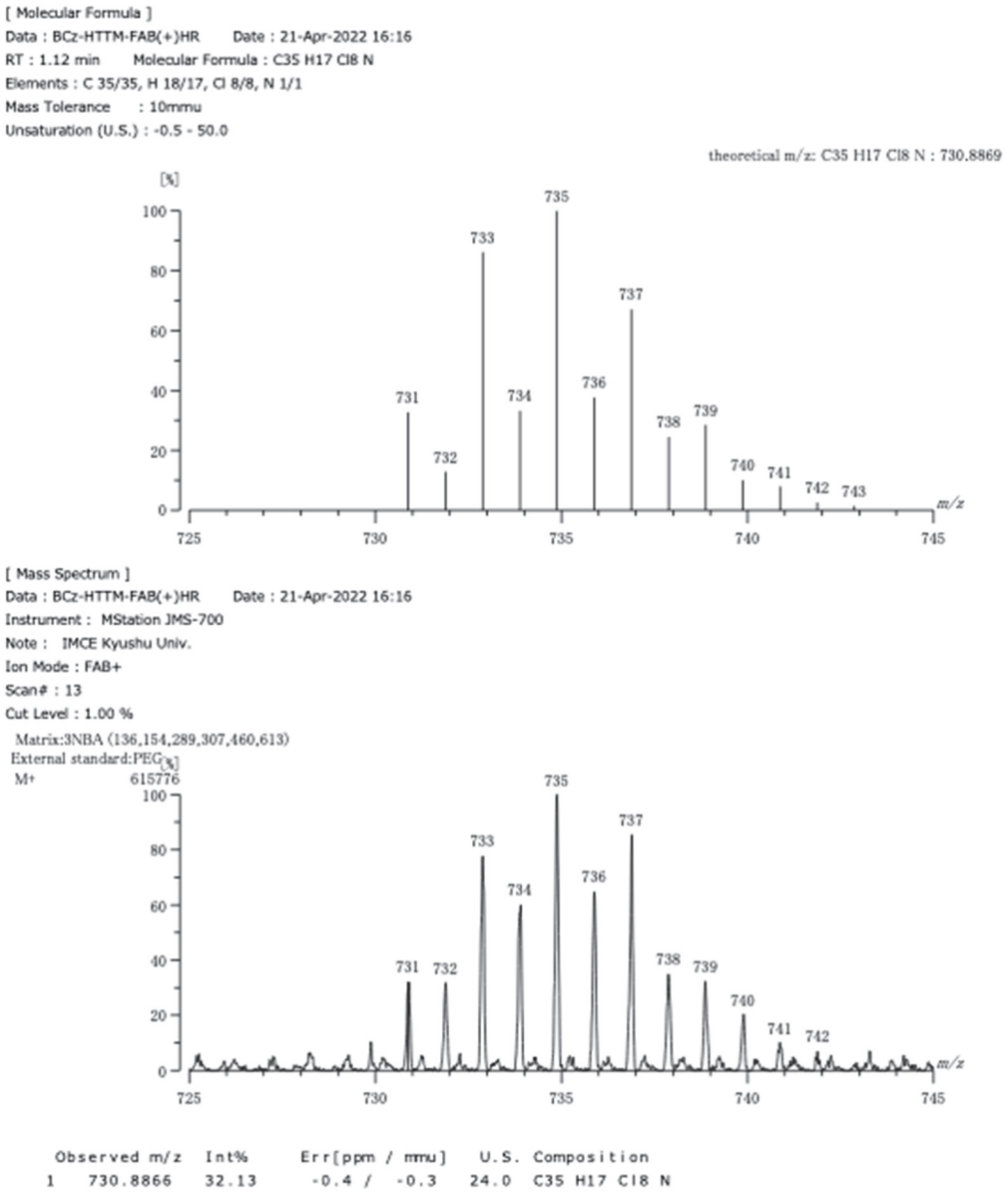


Fig. S42. FAB-MS spectrum of BCz-HTTM.

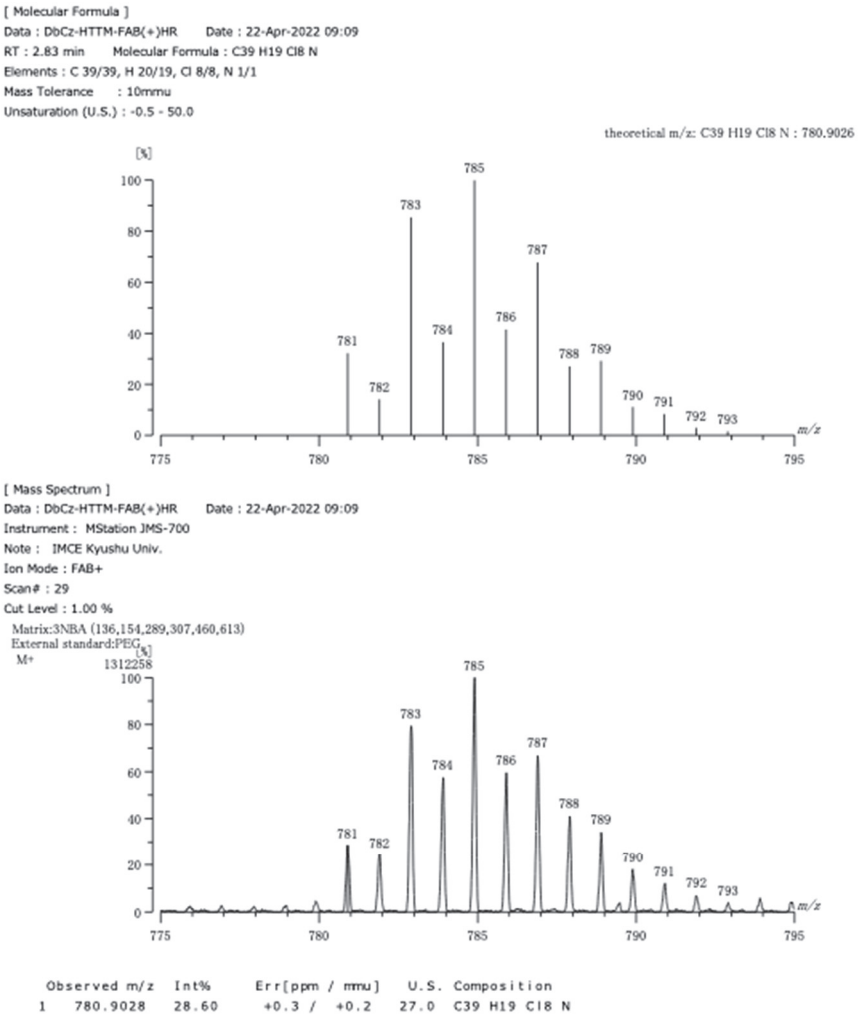


Fig. S43. FAB-MS spectrum of DbCz-HTTM.

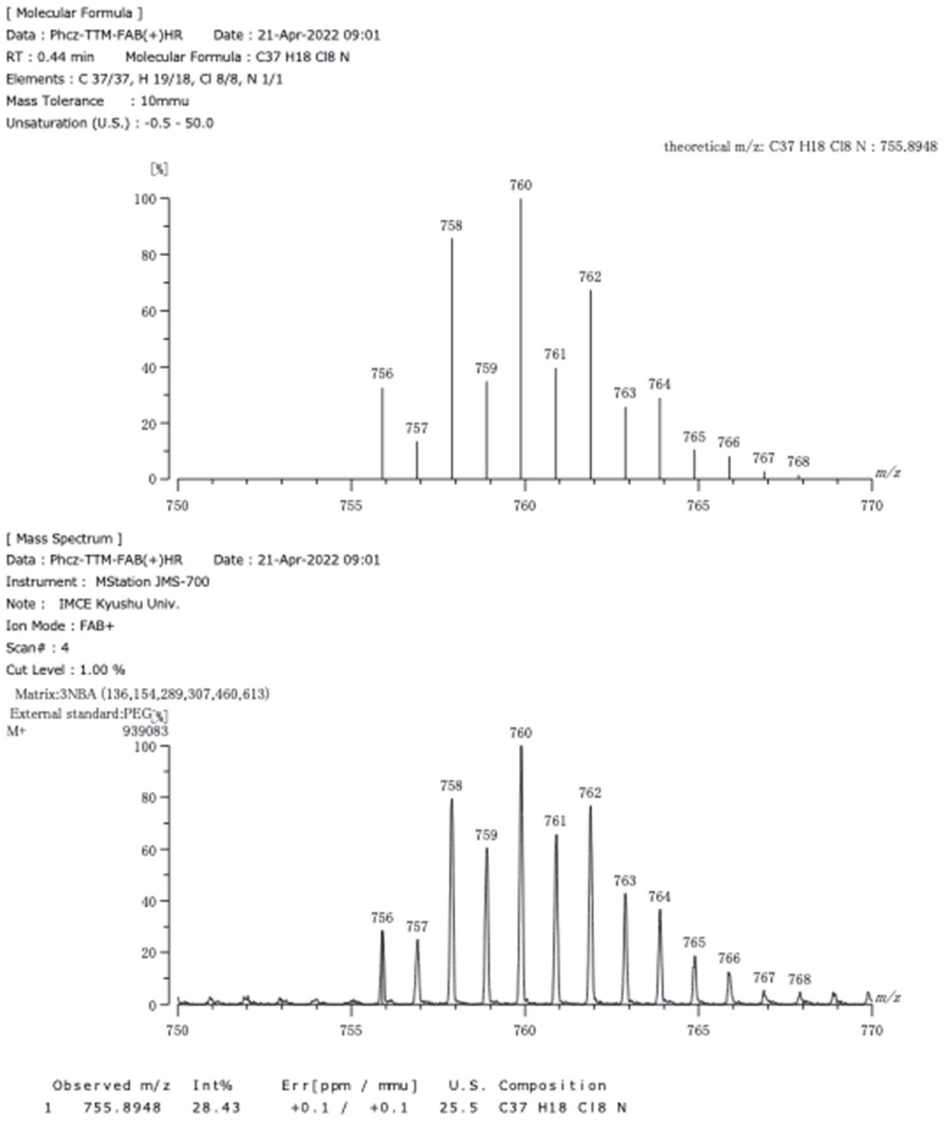


Fig. S44. FAB-MS spectrum of PhCz-TTM.

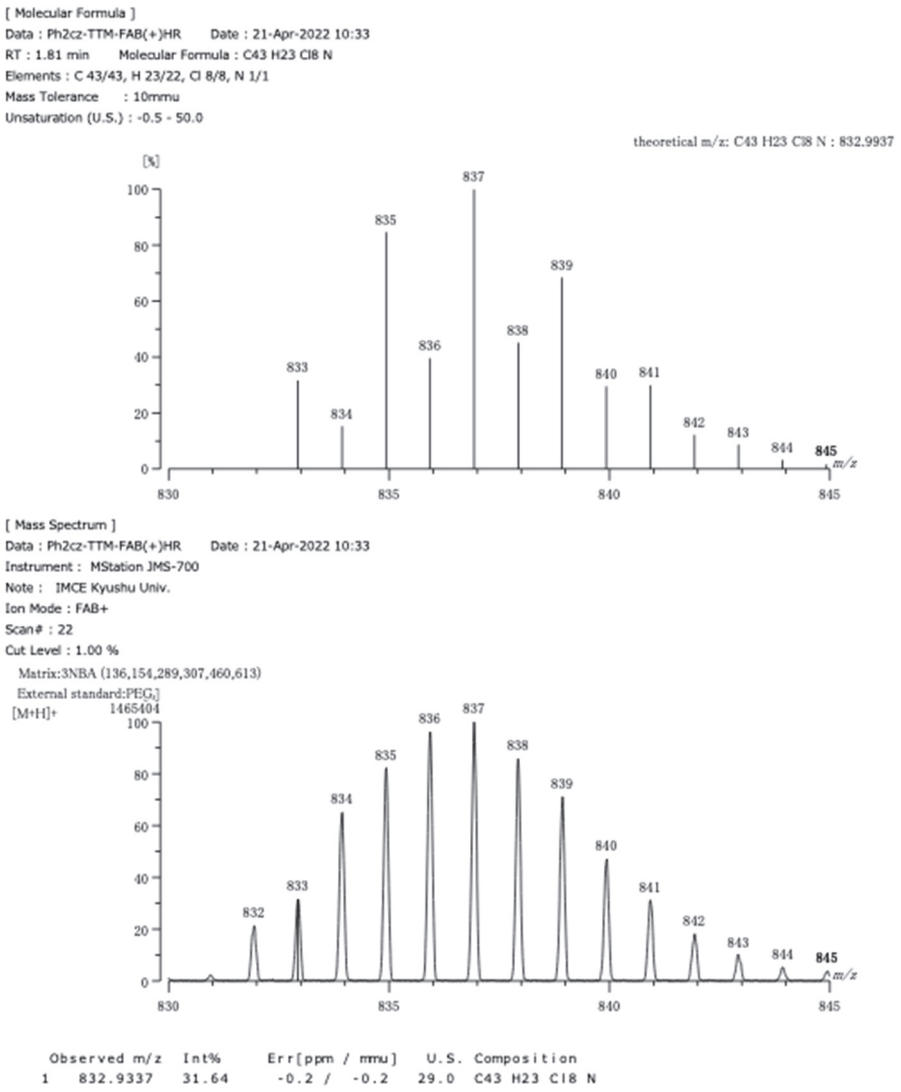


Fig. S45. FAB-MS spectrum of Ph2Cz-TTM.

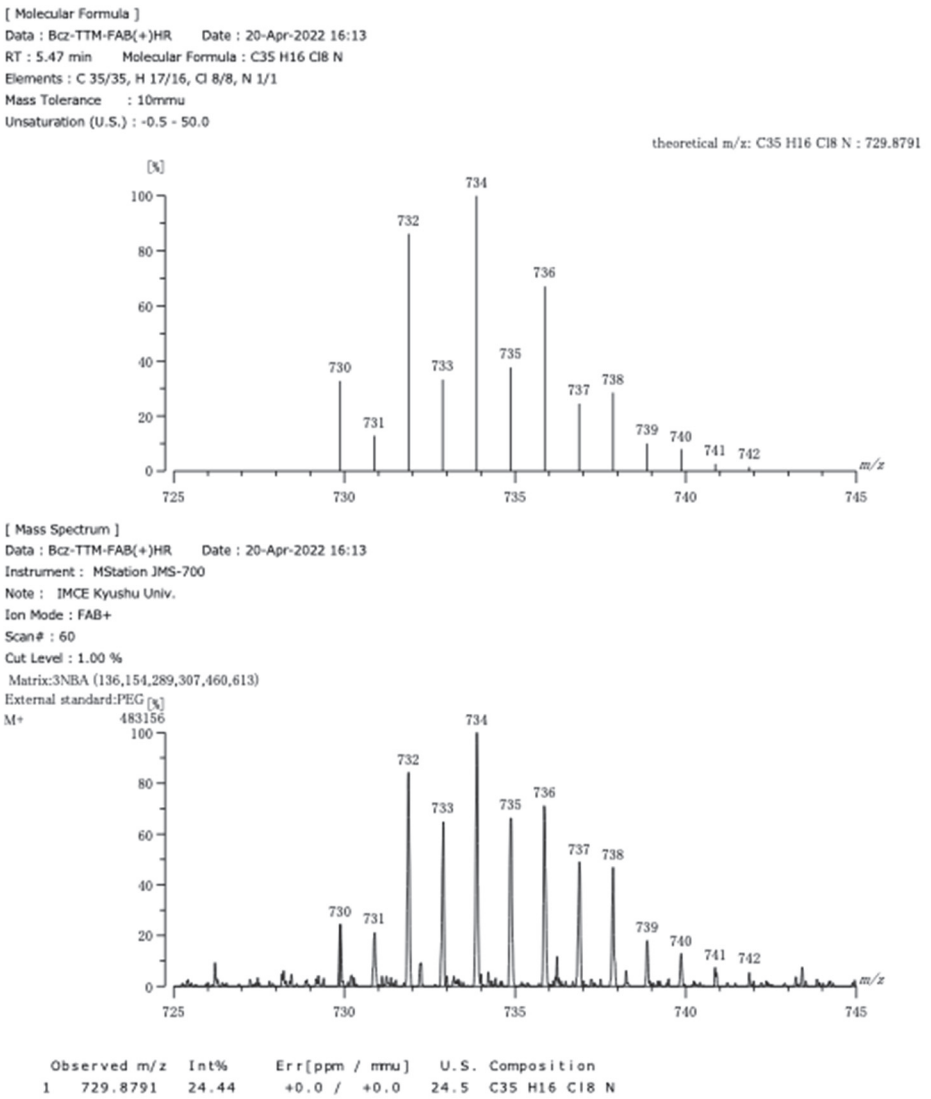


Fig. S46. FAB-MS spectrum of BCz-TTM.

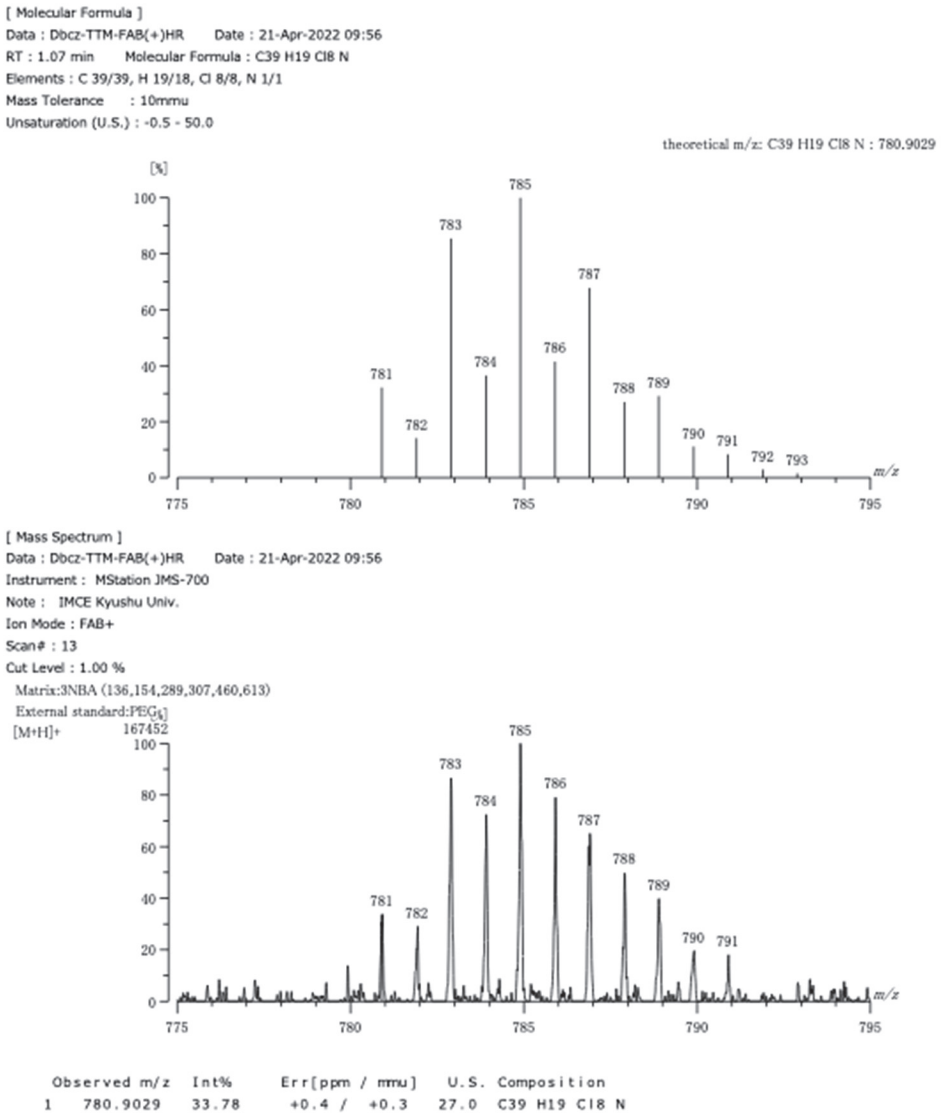


Fig. S47. FAB-MS spectrum of DbCz-TTM.

Initial conditions of calculation

Table S5 Cartesian coordinates of the Cz-TTM at the UB3LYP/6-31G level.**

Cz-TTM	x	y	z
C	-7.00932065	-0.7309838	-2.94490814
C	-5.66148588	-0.83718999	-3.32462502
C	-4.62987174	-0.60728302	-2.41628081
C	-4.98080211	-0.25751596	-1.11005046
C	-6.33522499	-0.16504743	-0.70538481
C	-7.35200716	-0.40110126	-1.63704175
H	-7.78873968	-0.91469081	-3.67771019
H	-5.4131448	-1.10775337	-4.34642565
H	-3.59365873	-0.7081167	-2.71820725
H	-8.39453439	-0.33312302	-1.34023394
C	-4.98083436	0.25746611	1.11000648
C	-4.62993853	0.60720987	2.41625169
C	-5.66157748	0.83715198	3.32455876
C	-7.0094023	0.73100147	2.94479083
C	-7.35205304	0.40113912	1.63690981
C	-6.3352452	0.16505086	0.70528968
H	-3.59373245	0.70800189	2.7182165
H	-5.4132637	1.10770042	4.34636996
H	-7.7888415	0.91473419	3.67756502
H	-8.39457186	0.33320049	1.34006321
N	-4.15813765	-0.00003513	-0.00000744
C	-2.74815893	-0.00003537	0.00001739
C	-2.03875732	-0.72707501	0.96092698
C	-2.03871648	0.72701422	-0.96085452
C	-0.65032496	-0.70984057	0.95884085
H	-2.56684719	-1.30385109	1.7092559
C	-0.65028456	0.70978377	-0.95870129
H	-2.56677219	1.30380411	-1.70919659
C	0.12001224	-0.00002679	0.00008491
C	1.59244834	-0.00000075	0.00010437
C	2.33103338	1.27131648	-0.11307197
C	2.03607316	2.40240651	0.69197883
C	3.39412298	1.46161757	-1.03387216

C	2.72222553	3.60831853	0.59524104
C	4.10132364	2.65386696	-1.14786309
C	3.75552549	3.7228655	-0.3284117
H	2.46488368	4.43389574	1.24594899
H	4.89327919	2.74824928	-1.8793956
Cl	0.12031397	-1.57681897	2.27706887
Cl	0.12043342	1.57682622	-2.27684132
Cl	0.82171715	2.32452623	1.95562899
Cl	3.83571194	0.20929638	-2.17989187
Cl	4.6317412	5.23115981	-0.46097877
C	2.33107977	-1.27130185	0.11315957
C	3.39428276	-1.46161487	1.03382502
C	2.03603927	-2.4023674	-0.69189182
C	4.10151211	-2.65385924	1.14769345
C	2.72221501	-3.60827586	-0.59527339
C	3.75562883	-3.72283724	0.32825044
H	4.89355379	-2.7482559	1.8791308
H	2.46479736	-4.43383942	-1.24596872
Cl	3.83598093	-0.20932852	2.17984043
Cl	0.8214908	-2.32446399	-1.95535584
Cl	4.63187264	-5.23112804	0.46067331

Table S6 Cartesian coordinates of the PhCz-TTM at the UB3LYP/6-31G level.**

PhCz-TTM	x	y	z
C	6.49729494	0.41257548	-0.86176132
C	5.26764306	0.76589631	-1.46309787
C	4.03983462	0.45898007	-0.88564836
C	4.04272469	-0.23006758	0.32904792
C	5.25634046	-0.57987749	0.96803204
C	6.47536467	-0.26032879	0.36633598
H	5.28067652	1.32243708	-2.39474585
H	3.11652512	0.76737509	-1.36270152
H	7.40772397	-0.55184979	0.84012368
C	3.49153178	-1.25713772	2.28571389
C	2.82361467	-1.86403973	3.35193196
C	3.59787252	-2.43163012	4.36227719

C	5.0010007	-2.40519824	4.31276377
C	5.66008123	-1.81557729	3.23807152
C	4.90606169	-1.23857493	2.21068466
H	1.74128154	-1.90567753	3.39444106
H	3.10097192	-2.90707116	5.20249485
H	5.57434907	-2.85508501	5.11716701
H	6.74517654	-1.80833473	3.19285575
N	2.96885875	-0.64080548	1.13504081
C	1.60126253	-0.46897272	0.83809071
C	0.73332884	0.08226145	1.78571989
C	1.0934528	-0.84595263	-0.4089979
C	-0.61360513	0.23687232	1.48594639
H	1.10568543	0.38957808	2.75444231
C	-0.25213958	-0.6586954	-0.6958079
H	1.74491974	-1.28282458	-1.15482765
C	-1.17985617	-0.11561961	0.23218771
C	-2.60713602	0.06715851	-0.0792001
C	-3.37861194	-1.03495028	-0.68310253
C	-3.35601203	-2.35736792	-0.16824873
C	-4.20425785	-0.85821195	-1.8238637
C	-4.07699747	-3.40694098	-0.72769179
C	-4.94067828	-1.88777225	-2.40025535
C	-4.86846673	-3.1603899	-1.84428229
H	-4.03467496	-4.39300378	-0.28370768
H	-5.54200713	-1.69934918	-3.28011481
Cl	-1.61626207	0.84192387	2.79434976
Cl	-0.74343741	-1.07482876	-2.32944332
Cl	-2.47116025	-2.74577479	1.29600762
Cl	-4.2799876	0.68306724	-2.65772971
Cl	-5.7851028	-4.4679942	-2.55856062
C	-3.26791514	1.3527897	0.21231373
C	-4.5048362	1.44038663	0.90272964
C	-2.7179769	2.60196434	-0.17711434
C	-5.14093839	2.64587215	1.17972702
C	-3.32873493	3.82220155	0.09187431
C	-4.54255456	3.83260329	0.7705165

H	-6.07628924	2.65433899	1.72405995
H	-2.87161645	4.74432371	-0.24274598
Cl	-5.28508329	0.00883774	1.54978068
Cl	-1.24506449	2.68850924	-1.12621671
Cl	-5.32663395	5.35820874	1.11392845
C	7.78416045	0.75698873	-1.51892684
C	8.89184527	1.17886814	-0.76381518
C	7.93023951	0.66912049	-2.91393046
C	10.10095332	1.49726134	-1.37968478
H	8.79419588	1.28275813	0.31275669
C	9.13796307	0.99142513	-3.53071503
H	7.0966395	0.32026094	-3.51620686
C	10.22983523	1.40604392	-2.76654153
H	10.94088234	1.8280305	-0.77536841
H	9.22869855	0.90866421	-4.61005798
H	11.17115896	1.65614859	-3.24679799

Table S7 Cartesian coordinates of the Ph2Cz-TTM at the UB3LYP/6-31G level.**

Ph2Cz-TTM	x	y	z
C	5.29357042	-3.0299659	0.29830813
C	3.93166019	-3.40795061	0.32478447
C	2.89834783	-2.480527	0.23780002
C	3.23917616	-1.13085668	0.12772452
C	4.59304298	-0.72085193	0.07714655
C	5.61111461	-1.67214707	0.16732681
H	3.6815737	-4.46226708	0.38598831
H	1.865167	-2.80862219	0.23598664
H	6.65035321	-1.35814612	0.15621195
C	3.23912708	1.13085855	-0.12770024
C	2.8982492	2.48052053	-0.23774418
C	3.93152586	3.40798384	-0.32473214
C	5.29345125	3.03005148	-0.29829063
C	5.61104666	1.67224307	-0.16733212
C	4.59301263	0.72090781	-0.07714753
H	1.86505847	2.80858069	-0.23591499
H	3.68139726	4.46229119	-0.38591613

H	6.6502968	1.35828024	-0.15623156
N	2.41567827	-0.00002156	-0.00001031
C	1.00563518	-0.00006198	-0.00000756
C	0.29643138	0.67247455	-0.99991332
C	0.29647007	-0.67264403	0.99989508
C	-1.09198901	0.67614284	-0.98279977
H	0.82421746	1.19215667	-1.78913473
C	-1.09195222	-0.67639698	0.98277779
H	0.82427902	-1.19228254	1.78912953
C	-1.86243286	-0.00016411	-0.00001758
C	-3.33471296	-0.00017323	0.00001932
C	-4.07343297	0.30416394	1.2394682
C	-3.77868337	1.43199959	2.04913491
C	-5.13672713	-0.50541001	1.71721294
C	-4.46533024	1.73099151	3.22108217
C	-5.84440198	-0.22715458	2.88182342
C	-5.49891771	0.89428371	3.6280657
H	-4.20818525	2.61394496	3.79161821
H	-6.63651724	-0.88870892	3.20764109
Cl	-1.86224184	1.64164949	-2.2307852
Cl	-1.86216541	-1.64183073	2.23084261
Cl	-2.56389796	2.60233542	1.56686211
Cl	-5.57772426	-1.99536543	0.90339503
Cl	-6.37582913	1.2573587	5.09752411
C	-4.07345636	-0.30436468	-1.23945164
C	-5.13679747	0.50522828	-1.71705001
C	-3.77860849	-1.43200784	-2.04932238
C	-5.8444714	0.22713387	-2.88169927
C	-4.46524188	-1.73084092	-3.22132282
C	-5.49890368	-0.89414237	-3.62814806
H	-6.63665361	0.888677	-3.20737908
H	-4.20800974	-2.6136629	-3.7920211
Cl	-5.57794588	1.99496422	-0.90289808
Cl	-2.56366518	-2.60227625	-1.56727968
Cl	-6.37580203	-1.25700743	-5.09766402
C	6.36294223	-4.05595428	0.39969383

C	7.54239672	-3.94834275	-0.35687724
C	6.22568276	-5.16156624	1.25632628
C	8.54836653	-4.90794016	-0.25791845
H	7.65844344	-3.11843573	-1.04762353
C	7.22970372	-6.12363897	1.35256865
H	5.33484556	-5.25261788	1.87072091
C	8.39664967	-6.00102796	0.5967537
H	9.44799125	-4.80690251	-0.85836935
H	7.10383303	-6.96564136	2.02729802
H	9.17942813	-6.74991463	0.67241014
C	6.36278512	4.05608237	-0.39967454
C	7.54222596	3.94853748	0.35692756
C	6.22550649	5.16166764	-1.25633905
C	8.54816021	4.90817256	0.25797131
H	7.65828924	3.11865429	1.04769939
C	7.22949268	6.12377687	-1.35258131
H	5.33468495	5.25266843	-1.87076334
C	8.39642361	6.00123249	-0.59673278
H	9.44777238	4.80718495	0.85844949
H	7.10360617	6.96575481	-2.02733829
H	9.17917481	6.75014742	-0.67238854

Table S8 Cartesian coordinates of the BCz-TTM at the UB3LYP/6-31G level.**

BCz-TTM	x	y	z
C	5.94861555	-1.51866278	3.62513103
C	4.56445348	-1.6092892	3.8425344
C	3.6588909	-1.19667543	2.87020186
C	4.17306565	-0.68330617	1.67728067
C	5.56870031	-0.59981349	1.42206846
C	6.45353378	-1.02459927	2.42740555
H	2.5904141	-1.27995528	3.03382565
C	4.42452701	0.14612223	-0.41839852
C	4.17483606	0.71002814	-1.68932099
C	5.25422985	1.03003397	-2.47415397
C	6.59558247	0.81472703	-2.03835972
C	6.84957294	0.26095174	-0.73734482

C	5.72055857	-0.06725862	0.07987028
H	3.16274162	0.89445528	-2.03048635
N	3.48336817	-0.22704376	0.54775078
C	2.0796123	-0.1661315	0.40612538
C	1.45083183	-0.76279128	-0.69027173
C	1.30076311	0.48966435	1.36362739
C	0.0704702	-0.68596001	-0.82413629
H	2.03512334	-1.28270024	-1.43876417
C	-0.0802663	0.53212561	1.22303604
H	1.76915879	0.96216438	2.21754709
C	-0.7696909	-0.04371594	0.12326888
C	-2.2340297	0.01988356	-0.02253354
C	-2.9374664	1.30473927	0.1465508
C	-2.5230347	2.49609953	-0.50403671
C	-4.0833578	1.44886511	0.97151717
C	-3.1752446	3.71513546	-0.35282046
C	-4.7586475	2.65358328	1.13627782
C	-4.2945902	3.78243821	0.46974349
H	-2.8245178	4.58915067	-0.88604184
H	-5.618612	2.70947019	1.79094804
Cl	-0.5888411	-1.38074225	-2.29538923
Cl	-0.9542553	1.29201935	2.54236128
Cl	-1.1870782	2.49107668	-1.64122458
Cl	-4.6822589	0.10970774	1.93296104
Cl	-5.1295115	5.30665137	0.66839207
C	-2.9982145	-1.20117311	-0.3375433
C	-3.9676989	-1.25348196	-1.37278445
C	-2.823356	-2.41815236	0.3715875
C	-4.6977984	-2.39735847	-1.67774441
C	-3.5348819	-3.57812631	0.08432537
C	-4.4720443	-3.55626617	-0.94295344
H	-5.4138474	-2.38485303	-2.48914272
H	-3.371995	-4.47447795	0.66849926
Cl	-4.2495225	0.12413439	-2.42129992
Cl	-1.7420866	-2.5177874	1.74945841
Cl	-5.3786591	-5.00508032	-1.31544063

H	5.09512378	1.46543178	-3.45663654
H	4.19171054	-2.00941574	4.7804051
C	8.19973128	0.07448628	-0.34476649
H	8.42145321	-0.34329139	0.6286976
C	9.24176754	0.41094218	-1.18415315
H	10.2658566	0.25544348	-0.85734961
C	8.99004935	0.95434216	-2.46215815
C	7.69040299	1.14973414	-2.87494923
H	7.48306748	1.56775671	-3.85673599
H	9.81807099	1.21571188	-3.11397003
H	7.52608409	-0.97765927	2.28475661
H	6.63497236	-1.84441897	4.40054259

Table S9 Cartesian coordinates of the DbCz-TTM at the UB3LYP/6-31G level.**

DbCz-TTM	x	y	z
C	-5.73877185	2.29847205	2.11928282
C	-4.36018741	2.40572157	2.47060987
C	-3.39391746	1.69972068	1.80291115
C	-3.81073544	0.77741465	0.81875943
C	-5.16171413	0.53433517	0.49518143
C	-6.15639578	1.39971677	1.07694532
H	-2.34225378	1.84199083	2.0232208
C	-3.81082466	-0.77838388	-0.81803016
C	-3.39414207	-1.70080114	-1.80214711
C	-4.36052265	-2.40637031	-2.47016483
C	-5.73915778	-2.2985591	-2.11918795
C	-6.15667857	-1.39967492	-1.07690512
C	-5.16179776	-0.53470385	-0.49486246
H	-2.3424798	-1.84347863	-2.02220097
N	-2.99361037	-0.00071424	0.00051736
C	-1.57855261	-0.00053399	0.00034524
C	-0.87286681	0.30362846	-1.1660351
C	-0.87259231	-0.30454046	1.16659256
C	0.51636453	0.28833643	-1.15843395
H	-1.40421946	0.54634809	-2.07765754

C	0.51664139	-0.28889751	1.1587583
H	-1.40373307	-0.54741374	2.07829737
C	1.28469586	-0.00018193	0.00010165
C	2.75833373	0.00000122	-0.00002582
C	3.49613865	-1.13407957	0.58607289
C	3.1988961	-2.48580588	0.27158069
C	4.56022313	-0.96129311	1.50934605
C	3.88417685	-3.56533644	0.81860031
C	5.26625622	-2.02182574	2.06722308
C	4.91858104	-3.32166382	1.71569039
H	3.62530875	-4.57593585	0.53065438
H	6.05896345	-1.8322603	2.77921834
Cl	1.28756454	0.58193246	-2.70740877
Cl	1.28816762	-0.58233709	2.70759947
Cl	1.98297591	-2.89224968	-0.92594186
Cl	5.0042378	0.63185037	2.09318736
Cl	5.79350793	-4.66730239	2.41054395
C	3.49575744	1.1342739	-0.58623911
C	4.5597307	0.96175874	-1.50969054
C	3.19822344	2.48592266	-0.27169505
C	5.26539808	2.02247166	-2.06768737
C	3.8831347	3.56562913	-0.81883162
C	4.91744878	3.32222098	-1.71609683
H	6.05803316	1.833109	-2.77981687
H	3.6240551	4.57616224	-0.53084332
Cl	5.00405279	-0.63127152	-2.09360758
Cl	1.98239754	2.89205607	0.92602858
Cl	5.79191056	4.66808317	-2.41110334
H	-4.07874426	-3.10781722	-3.25016578
H	-4.07831631	3.10728212	3.25051682
C	-7.49905785	-1.50441317	-0.62845262
H	-7.81302299	-0.94118925	0.23919878
C	-8.40158573	-2.35357317	-1.23723894
H	-9.4182953	-2.41244876	-0.85959616
C	-8.01092645	-3.15702044	-2.32790335
C	-6.69809876	-3.13591391	-2.74412704

H	-6.36664377	-3.78769185	-3.54848241
C	-7.49867245	1.50484781	0.62826593
H	-7.81262214	0.94177598	-0.23948564
C	-8.4010809	2.35417525	1.23698275
H	-9.41772162	2.41335236	0.85919997
C	-8.01036012	3.15750321	2.3277207
C	-6.69756503	3.13612819	2.74406189
H	-6.36615238	3.78745133	3.54880275
H	-8.73107292	-3.81022301	-2.81117113
H	-8.73043642	3.81080553	2.81096138

1 M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, G. A. Petersson, H. Nakatsuji, X. Li, M. Caricato, A. V. Marenich, J. Bloino, B. G. Janesko, R. Gomperts, B. Mennucci, H. P. Hratchian, J. V. Ortiz, A. F. Izmaylov, J. L. Sonnenberg, D. Williams-Young, F. Ding, F. Lipparini, F. Egidi, J. Goings, B. Peng, A. Petrone, T. Henderson, D. Ranasinghe, V. G. Zakrzewski, J. Gao, N. Rega, G. Zheng, W. Liang, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, K. Throssell, J. A. Montgomery, Jr., J. E. Peralta, F. Ogliaro, M. J. Bearpark, J. J. Heyd, E. N. Brothers, K. N. Kudin, V. N. Staroverov, T. A. Keith, R. Kobayashi, J. Normand, K. Raghavachari, A. P. Rendell, J. C. Burant, S. S. Iyengar, J. Tomasi, M. Cossi, J. M. Millam, M. Klene, C. Adamo, R. Cammi, J. W. Ochterski, R. L. Martin, K. Morokuma, O. Farkas, J. B. Foresman, and D. J. Fox, Gaussian16, Revision Rev. B.01. Gaussian Inc., Wallingford CT, 2016.

2 Q. Peng, A. Obolda, M. Zhang and F. Li, *Angew. Chem. Int. Ed.,* 2015, **54**, 7091–7095.

3 T. Miura, N. Sugimoto, R. Watanabe, T. Suematsu, Y. Takayanagi, Y. Ito, N. Saito, R. Sawa, T. Kato, Y. Fujimine, R. Koike, Y. Ohfuku, Y. Yamada, H. Utsumi, T. Suzuki Yakugaku Zasshi. 2017, **10**, 1248/yakushi.17-0