Supporting Information

Water-soluble luminescent *tris*(2,4,6-trichlorophenyl)methyl radical-carbazole dyad

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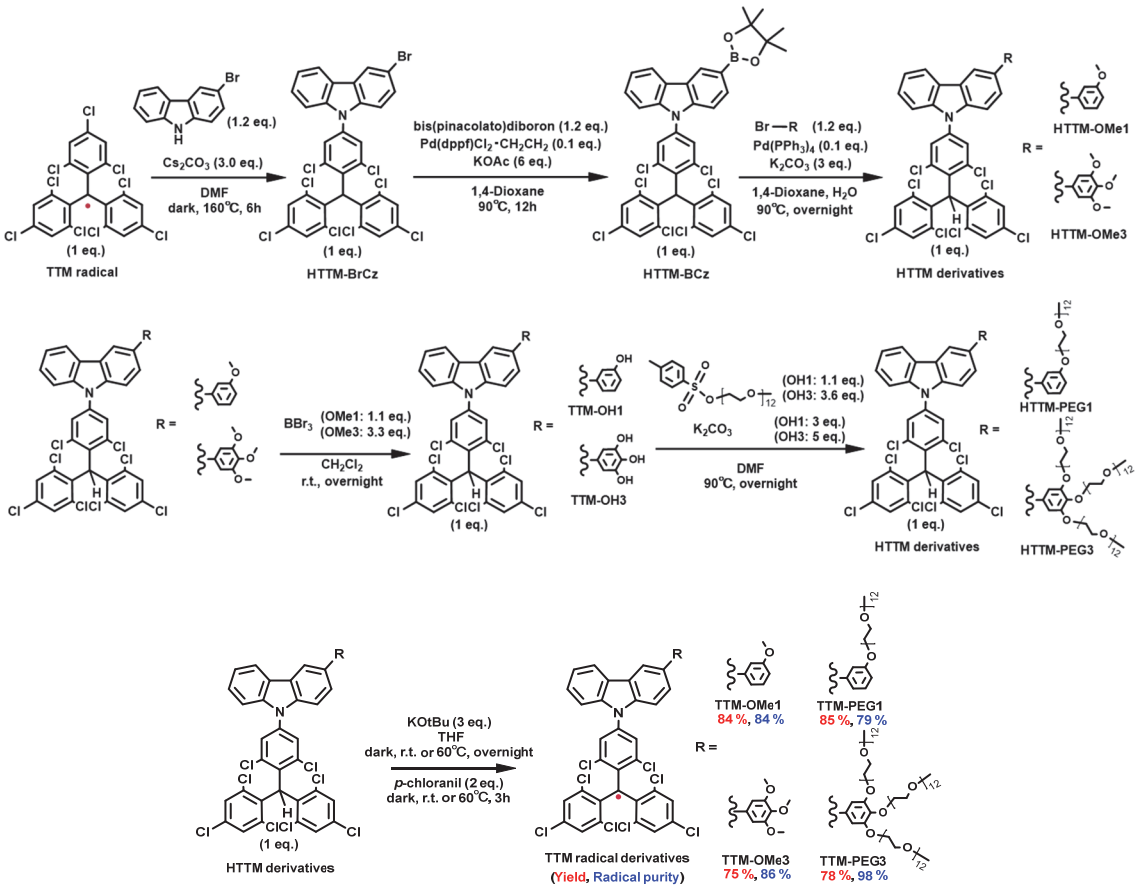
Experimental section

Chemicals. All chemicals were purchased from FUJIFILM Wako Pure Chemical Co., Kanto Kagaku Co., Ltd., TCI chemicals, Aldrich, or BLD pharm and used without further purification unless otherwise noted. Dehydrated solvents were used in all syntheses, and spectroanalytical grade solvents were used in all spectroscopy measurements.

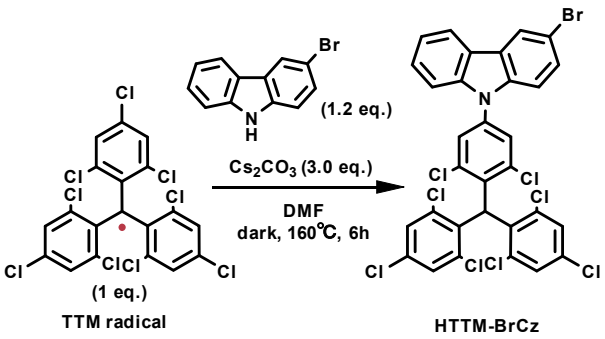
General. The NMR spectra were obtained using JNM-ECZ400 (400MHz) and JNM-ECA600 (600MHz). ^{1}H NMR and ^{13}C NMR were measured with TMS as the internal standard. The elemental analysis was performed at the Service Center of the Elementary Analysis of Organic Compounds, Faculty of Science, Kyushu University. The NMR relaxaion time was measured using a Spinsolve ULTRA 43 MHz ^{1}H NMR (Magritek Ltd.). The UV-vis absorption 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 (with 360 nm center bandpath filter). 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 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 excitation light of third harmonics of the Nd:YAG laser (wavelength: 355 nm, pulse width: 29±4 ps, repetition rate: 10 Hz, laser power: 2.0 mW) was continuously irradiated to the samples, and the time dependence of the PL intensity at a peak wavelength was detected by the analyzer. The Dunamic light scattering (DLS) measurements were performed using Otsuka Electronics Co. Ltd. ELSZeno and analized using Marquardt method. All calculations were performed using the Gaussian16 program package Revision C.01.[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 was used as the counter electrode, Ag/Ag^{+} was used as the reference electrode, and the redox couple ferrocenium/ferrocene was used as the external standard. The scan rate was 50 $mV \cdot s^{-1}$. Tetrabutylammonium hexafluorophosphate ($TBAPF_6$) in dichloromethane (0.1 M) was used as the supporting electrolyte.

Synthesis



Scheme S1. Synthesis of alkoxy group substituted TTM radicals.

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



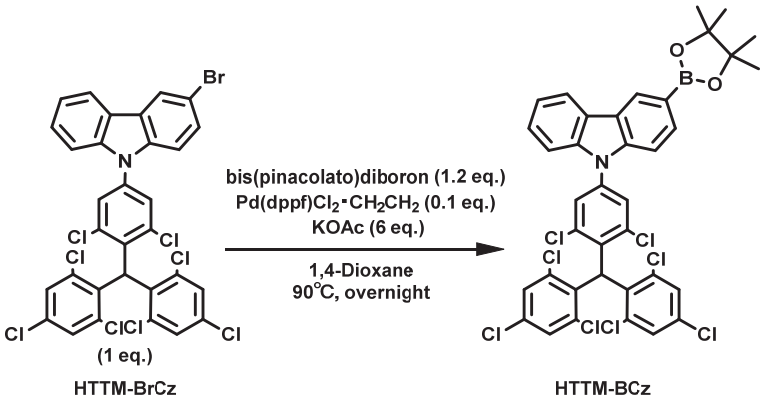
Under nitrogen atmosphere and in the dark, a mixture of TTM (5.0g, 9.0 mmol), 3-bromo-carbazole (2.7 g, 11.0 mmol), Cs_2CO_3 (9.0 g, 27.6 mmol), and anhydrous DMF (75 mL) were added into a 3-

neck flask and stirred at 160°C for 6 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. The solution was concentrated to give crude product as a dark green solid. The crude product was purified by silica gel column chromatography (hexane) to obtain HTTM-BrCz as a green powder (2.36 g, 34 %).

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

^{1}H-NMR (400 MHz, $CDCl_3$) δ 8.23 (d, J = 1.8 Hz, 1H), 8.07 (d, J = 7.8 Hz, 1H), 7.57 (d, J = 2.3 Hz, 1H), 7.54-7.41 (m, 6H), 7.35-7.28 (m, 4H), 6.85 (s, 1H)

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

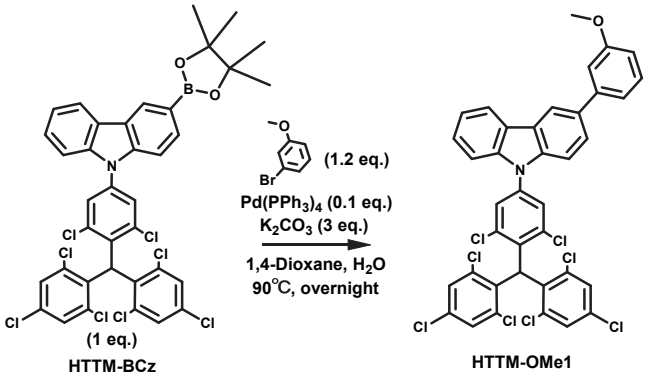


Under nitrogen atmosphere, a mixture of HTTM-BrCz (2.5 g, 3.3 mmol), bis(pinacolato)diboron (1.0 g, 3.9 mmol), [1,1'-bis(diphenylphosphino)ferrocene]palladium(II) dichloride dichloromethane adduct (0.28 g, 0.34 mmol), KOAc (2.0 g, 20.4 mmol), and anhydrous 1,4-Dioxane (50 mL) were added into a 3-neck flask and stirred at 90°C for overnight. After the solution cooled to room temperature, the mixture was poured into pure water. The mixture was extracted with chloroform (3 × 50 mL) and the combined organic phases were dried over Na_2SO_4. The solution was concentrated to give crude product as a dark green solid. The crude product was purified by silica gel column chromatography (hexane: chloroform = 2: 1) to obtain HTTM-BCz as a green powder (1.55 g, 58 %).

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

^{1}H-NMR (400 MHz, $CDCl_3$)δ 8.62 (s, 1H), 8.16 (d, J = 7.8 Hz, 1H), 7.89 (dd, J = 8.2, 0.9 Hz, 1H), 7.60 (d, J = 2.3 Hz, 1H), 7.47 (d, J = 2.3 Hz, 1H), 7.45-7.40 (m, 5H), 7.35-7.28 (m, 3H), 6.86 (s, 1H), 1.41 (s, 12H)

HTTM-OMe1



Under nitrogen atmosphere, a mixture of HTTM-BCz (501 mg, 0.62 mmol), 3-bromoanisole (0.1 mL, 0.80 mmol), K_2CO_3 (267 mg, 1.93 mmol), $Pd(PPh_3)_4$ (74 mg, 0.06 mmol), and anhydrous 1,4-Dioxane (10 mL) and pure water (2.5 mL) were added into a 3-neck flask and stirred at 90°C for overnight. After the solution cooled to room temperature, the mixture was poured into pure water. The mixture was extracted with chloroform (3 × 50 mL) and the combined organic phases were dried over Na_2SO_4. The solution was concentrated to give crude product as a dark green solid. The crude product was purified by preparative GPC (eluent: chloroform) to obtain HTTM-OMe1 as a pale green powder (285 mg, 58 %).

^{1}H-NMR (400 MHz, CD_2Cl_2) δ 8.37 (d, J = 1.4 Hz, 1H), 8.20 (d, J = 7.8 Hz, 1H), 7.73-7.68 (m, 2H), 7.55-7.31 (m, 11H), 7.26 (t, J = 2.1 Hz, 1H), 6.91 (dd, J = 7.8, 2.3 Hz, 1H), 6.88 (s, 1H), 3.90 (s, 3H)

^{13}C-NMR (151 MHz, $CDCl_3$) δ 160.0, 143.2, 140.5, 139.6, 138.5, 138.0, 137.9, 137.7, 137.2, 134.2, 134.0, 134.0, 133.8, 130.2, 130.1, 129.8, 128.5, 128.1, 126.6, 126.5, 125.9, 124.3, 123.9, 121.0, 120.6, 119.9, 119.1, 113.2, 112.1, 109.8, 109.7, 55.4, 50.1

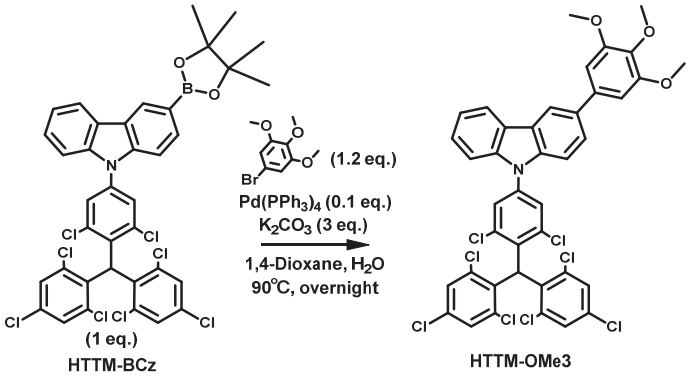
MALDI-TOF-MS (Matrix: 1,8,9-Trihydroxyanthracene)

$[M]^+$ Calcd for 790.9072; Found 790.9497

Elemental analysis

Calcd for $C_{38}H_{21}Cl_8NO$, C: 57.69, H: 2.68, N: 1.77; Found, C: 57.95, H: 2.74, N: 1.73

HTTM-OMe3



Under nitrogen atmosphere and in the dark, a mixture of HTTM-BCz (502 mg, 0.62 mmol), 5-bromo-1,2,3-trimethoxybenzene (175 mg, 0.81 mmol), K_2CO_3 (268 mg, 1.94 mmol), $Pd(PPh_3)_4$ (73 mg, 0.06 mmol), and anhydrous 1,4-Dioxane (10 mL) and pure water (2.5 mL) were added into a 3-neck flask and stirred at 90°C for overnight. After the solution cooled to room temperature, the mixture was poured into pure water. The mixture was extracted with chloroform (3 × 50 mL) and the combined organic phases were dried over Na_2SO_4. The solution was concentrated to give crude product as a dark green solid. The crude product was purified by preparative GPC (eluent: chloroform) to obtain HTTM-OMe3 as a pale green powder (338 mg, 64 %).

^{1}H-NMR (400 MHz, CD_2Cl_2) δ 8.32 (d, J = 1.8 Hz, 1H), 8.21 (d, J = 7.8 Hz, 1H), 7.70-7.67 (m, 2H), 7.54-7.45 (m, 6H), 7.37-7.32 (m, 3H), 6.91 (s, 2H), 6.88 (s, 1H), 3.95 (s, 6H), 3.83 (s, 3H)

^{13}C-NMR (151 MHz, $CDCl_3$) δ 153.5, 140.5, 139.5, 138.5, 138.0, 138.0, 137.9, 137.8, 137.7, 137.3, 137.2, 134.6, 134.0, 134.0, 133.8, 130.1, 130.1, 128.5, 128.1, 126.6, 126.4, 125.8, 124.2, 123.8, 121.0, 120.6, 118.9, 109.8, 109.8, 104.7, 61.0, 56.3, 50.1

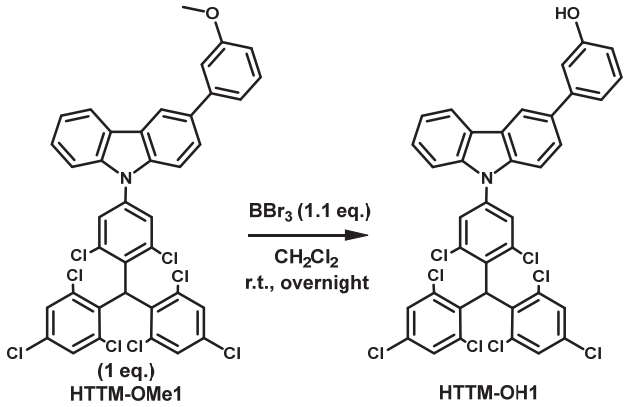
MALDI-TOF-MS (Matrix: 1,8,9-Trihydroxyanthracene)

$[M]^+$ Calcd for 850.9284; Found 851.0293

Elemental analysis

Calcd for $C_{40}H_{25}Cl_8NO_3$, C: 56.44, H: 2.96, N: 1.65; Found, C: 56.43, H: 2.97, N: 1.50

HTTM-OH1



Under nitrogen atmosphere and in the dark, a mixture of HTTM-OMe1 (169 mg, 0.21 mmol) and anhydrous CH_2Cl_2 (1 mL) were added into a 2-neck flask, and then, BBr3 (1M CH_2Cl_2 solution) (0.23 mL) was added slowly at -78°C and stirred at room temperature for overnight. The mixture was poured into ice-water and extracted with chloroform (3 × 50 mL), and the combined organic phases were dried over Na_2SO_4. The solution was concentrated to give crude product as a dark green solid. The crude product was purified by silica gel column chromatography (hexane: ethyl acetate = 4: 1) to obtain HTTM-OH1 as a pale green powder (146 mg, 88 %).

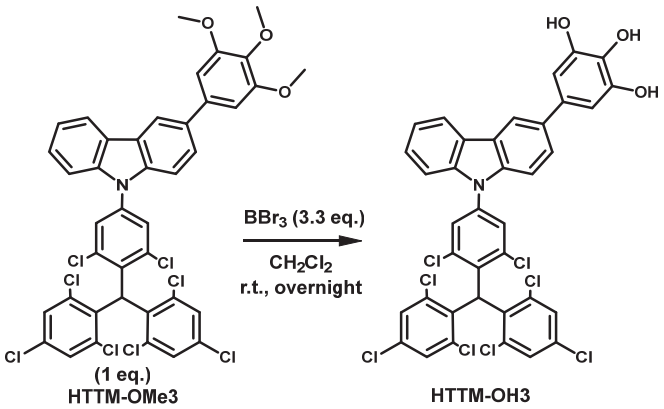
^{1}H-NMR (400 MHz, CD_2Cl_2) δ 8.35 (d, J = 1.8 Hz, 1H), 8.19 (d, J = 7.8 Hz, 1H), 7.71-7.67 (m, 2H), 7.54-7.45 (m, 6H), 7.37-7.29 (m, 5H), 7.21 (d, J = 1.8 Hz, 1H), 6.88 (s, 1H), 6.83 (dd, J = 7.8, 1.4 Hz, 1H), 5.09 (s, 1H)

^{13}C-NMR (151 MHz, $CDCl_3$) δ 155.9, 143.5, 140.5, 139.6, 138.5, 138.0, 137.9, 137.7, 137.2, 134.0, 133.8, 130.1, 130.1, 128.5, 128.1, 126.6, 126.4, 125.7, 124.3, 123.8, 121.0, 120.6, 119.9, 119.0, 114.2, 113.7, 109.8, 109.8, 50.0

Elemental analysis

Calcd for $C_{37}H_{19}Cl_8NO$, C: 57.18, H: 2.46, N: 1.80; Found, C: 57.58, H: 2.66, N: 1.81

HTTM-OH3



Under nitrogen atmosphere and in the dark, a mixture of HTTM-OMe3 (503 mg, 0.59 mmol) and anhydrous CH_2Cl_2 (3 mL) were added into a 2-neck flask, and then, BBr3 (1M CH_2Cl_2 solution) (2 mL) was added slowly at -78°C and stirred at room temperature for overnight. After the solution cooled to room temperature, the mixture was poured into ice-water. The mixture was extracted with chloroform (3 × 50 mL) and the combined organic phases were dried over Na_2SO_4. The solution was concentrated to give crude product as a dark green solid. The crude product was purified by silica gel column chromatography (chloroform : methanol = 9 : 1) to obtain HTTM-OH3 as a pale green powder (392 mg, 82 %).

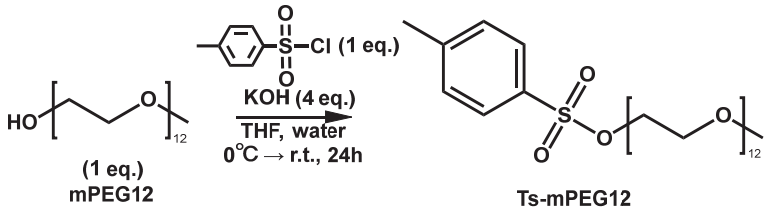
^{1}H-NMR (400 MHz, CD_2Cl_2) δ 8.26 (s, 1H), 8.16 (d, J = 7.8 Hz, 1H), 7.66-7.60 (m, 2H), 7.53-7.45 (m, 6H), 7.33 (dd, J = 10.3, 2.1 Hz, 3H), 6.87 (d, J = 2.7 Hz, 3H), 5.42 (s, 3H)

^{13}C-NMR (151 MHz, $CDCl_3$) δ 144.3, 140.4, 139.2, 138.4, 138.0, 137.8, 137.6, 137.2, 134.4, 134.0, 133.8, 133.8, 133.6, 130.9, 130.1, 130.1, 128.5, 127.9, 126.5, 126.3, 125.4, 124.2, 123.8, 120.9, 120.5, 118.5, 109.7, 107.2, 50.0

Elemental analysis

Calcd for $C_{37}H_{19}Cl_8NO_3$, C: 54.92, H: 2.37, N: 1.73; Found, C: 54.82, H: 2.27, N: 1.69

Ts-mPEG12

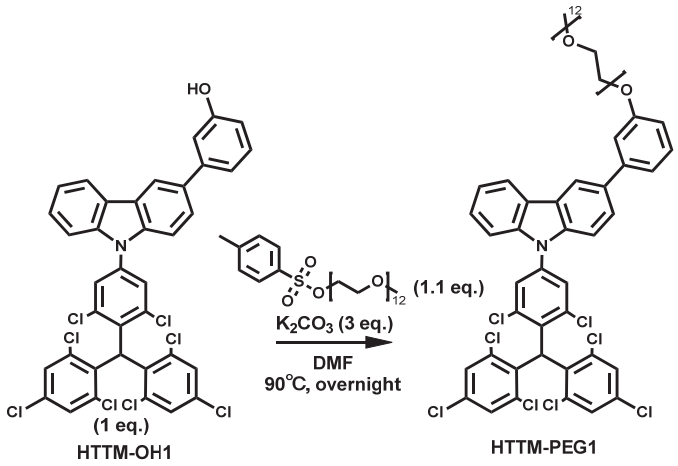


A mixture of Dodecaethylene glycol monomethyl ether (mPEG12) (2.0 g, 3.57 mmol) and anhydrous THF (4.5 mL) were added into a bottom round flask and stirred at 0°C for 10 min, and then, KOH (8 mM aqueous solution) (1.78 mL) was added slowly and stirred at 0°C for 10 min. Subsequently, *p*-Toluenesulfonyl chloride (686 mg, 3.60 mmol) was added and stirred at room temperature for 2 days. The mixture was poured into pure water. The mixture was extracted with chloroform (3 × 50 mL) and the combined organic phases were dried over Na_2SO_4. The solution was concentrated to give crude product as a transparent viscous liquid. The crude product was purified by silica gel column chromatography (chloroform : methanol = 19 : 1) to obtain Ts-mPEG12 as a transparent viscous liquid (2.3 g, 89 %).

The ^{1}H NMR spectrum was identical to the previous report.[3]

^{1}H-NMR (400 MHz, $CDCl_3$) δ 7.80 (dd, J = 6.9, 1.8 Hz, 2H), 7.34 (d, J = 8.2 Hz, 2H), 4.16 (t, J = 5.0 Hz, 2H), 3.82-3.45 (m, 46H), 3.38 (s, 3H), 2.45 (s, 3H)

HTTM-PEG1



Under nitrogen atmosphere, a mixture of HTTM-OH1 (133 mg, 0.17 mmol), Ts-mPEG12 (156 mg, 0.22 mmol), K_2CO_3 (72 mg, 0.52 mmol) and anhydrous DMF (1.4 mL) were added into a 2-neck flask and stirred at 90°C for overnight. After the solution cooled to room temperature, the mixture was poured into pure water. The mixture was extracted with chloroform (3 × 50 mL) and the combined organic phases were dried over Na_2SO_4. The solution was concentrated to give crude product as a dark green viscous liquid. The crude product was purified by preparative GPC (eluent: chloroform) to obtain HTTM-PEG1 as a dark green viscous liquid (170 mg, 76 %).

^{1}H-NMR (400 MHz, CD_2Cl_2)δ 8.37 (d, J = 1.8 Hz, 1H), 8.19 (d, J = 7.8 Hz, 1H), 7.73-7.68 (m, 2H), 7.55-7.45 (m, 5H), 7.42-7.29 (m, 5H), 6.92 (dd, J = 8.2, 1.8 Hz, 1H), 6.88 (s, 1H), 4.24-3.48 (m, 48H), 3.33 (s, 3H)

^{13}C-NMR (151 MHz, $CDCl_3$) δ 159.2, 143.1, 140.5, 139.6, 138.5, 138.0, 137.9, 137.7, 137.2, 134.2, 134.0, 134.0, 134.0, 133.8, 130.2, 130.1, 129.8, 128.5, 128.1, 126.5, 126.4, 125.8, 124.3, 123.9, 121.0, 120.6, 120.0, 119.0, 113.9, 112.7, 109.8, 109.7, 71.9, 70.9, 70.6, 70.6, 69.8, 67.5, 59.0, 50.1

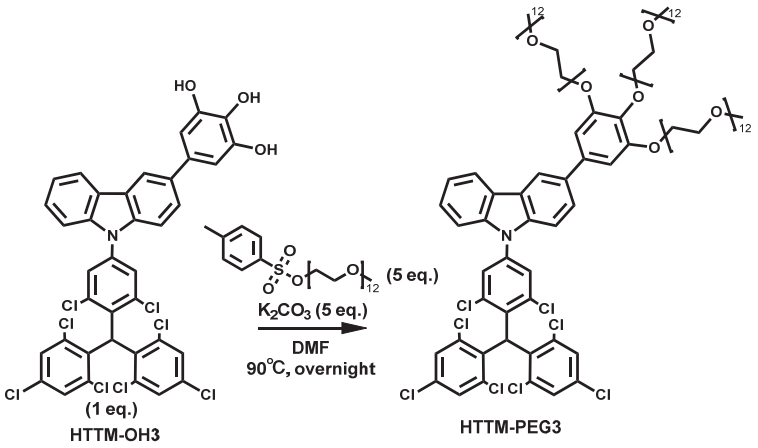
MALDI-TOF-MS (Matrix: 1,8,9-Trihydroxyanthracene)

$[M+K]^+$ Calcd for 1358.1850; Found 1358.4505

Elemental analysis

Calcd for $C_{62}H_{69}Cl_8NO_{13}$ ($+H_2O$), C: 55.66, H: 5.35, N: 1.05; Found, C: 55.88, H: 5.47, N: 0.98

HTTM-PEG3



Under nitrogen atmosphere, a mixture of HTTM-OH3 (307 mg, 0.38 mmol), Ts-mPEG12 (1.34 g, 1.87 mmol), K_2CO_3 (286 mg, 2.07 mmol) and anhydrous DMF (1.0 mL) were added into a 2-neck flask and stirred at 90°C for overnight. After the solution cooled to room temperature, the mixture was poured into pure water. The mixture was extracted with chloroform (3 × 50 mL) and the combined organic phases were dried over Na_2SO_4. The solution was concentrated to give crude product as a dark green viscous liquid. The crude product was purified by preparative GPC (eluent: chloroform) to obtain HTTM-PEG3 as a dark green viscous liquid (768 mg, 83 %).

^{1}H-NMR (400 MHz, CD_2Cl_2) δ 8.31 (d, J = 1.4 Hz, 1H), 8.21 (d, J = 7.8 Hz, 1H), 7.68-7.64 (m, 2H), 7.54-7.43 (m, 6H), 7.37-7.32 (m, 3H), 6.96 (d, J = 5.5 Hz, 2H), 6.88 (d, J = 3.2 Hz, 1H), 4.29-3.48 (m, 144H), 3.41-3.33 (m, 9H)

^{13}C-NMR (151 MHz, $CDCl_3$) δ 152.9, 138.5, 138.0, 137.7, 137.2, 134.0, 133.8, 130.1, 130.1, 128.5, 128.0, 126.4, 125.7, 123.8, 121.0, 120.7, 118.8, 109.8, 107.4, 72.4, 71.9, 70.8, 70.6, 70.6, 70.5, 69.8, 69.0, 59.0, 50.1

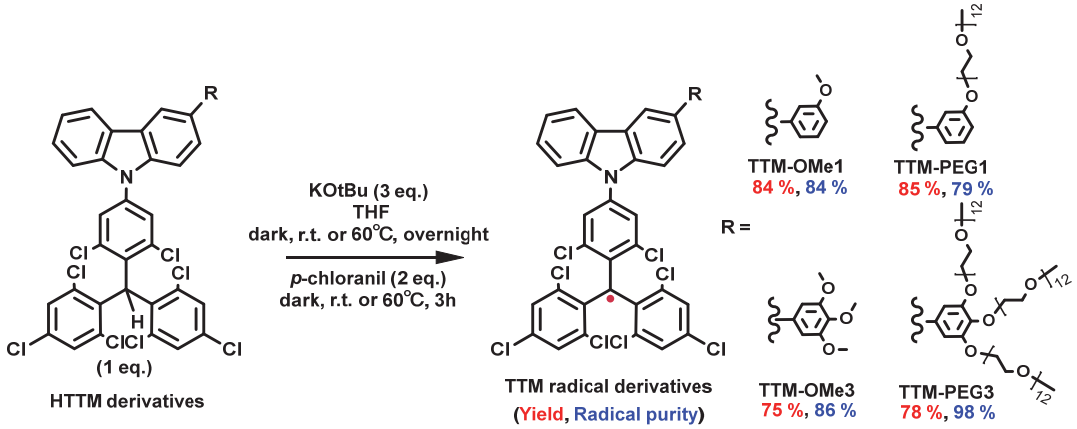
MALDI-TOF-MS (Matrix: 1,8,9-Trihydroxyanthracene)

$[M+K]^+$ Calcd for 2475.8387; Found 2475.1421

Elemental analysis

Calcd for $C_{112}H_{169}Cl_8NO_{39}$ ($+H_2O$), C: 54.79, H: 7.02, N: 0.57; Found, C: 54.82, H: 6.89, N: 0.54

General synthesis of radicals



TTM-OMe1

Under nitrogen atmosphere and in the dark, a mixture of HTTM-OMe1 (101 mg, 0.13 mmol), KOtBu (47 mg, 0.42 mmol), and anhydrous THF (5 mL) were added into a 3-neck flask and stirred at room temperature for overnight, and then, *p*-chloranil (66 mg, 0.27 mmol) was added and stirred at room temperature for 3 h. The solution was concentrated to give crude product as a dark green solid. The crude product was purified by preparative GPC (eluent: chloroform) to obtain TTM-OMe1 as a dark green powder (84 mg, 84 %).

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

$[M]^+$ Calcd for 789.8994; Found 790.0898

Elemental analysis

Calcd for $C_{38}H_{20}Cl_8NO$, C: 57.76, H: 2.55, N: 1.77; Found, C: 57.78, H: 2.69, N: 1.99

TTM-OMe3

Under nitrogen atmosphere and in the dark, a mixture of HTTM-OMe3 (55 mg, 0.06 mmol), KOtBu (29 mg, 0.26 mmol), and anhydrous THF (2.5 mL) were added into a 3-neck flask and stirred at room temperature for overnight, and then, *p*-chloranil (35 mg, 0.14 mmol) was added and stirred at room temperature for 3h. The solution was concentrated to give crude product as a dark green solid. The crude product was purified by preparative GPC (eluent: chloroform) to obtain TTM-OMe3 as a dark green powder (41 mg, 75 %).

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

$[M]^+$ Calcd for 849.9205; Found 850.0114

Elemental analysis

Calcd for $C_{38}H_{20}Cl_8NO$, C: 56.51, H: 2.85, N: 1.65; Found, C: 56.89, H: 2.80, N: 1.66

TTM-PEG1

Under nitrogen atmosphere and in the dark, a mixture of HTTM-PEG1 (154 mg, 0.12 mmol), KOtBu (41 mg, 0.37 mmol), and anhydrous THF (3 mL) were added into a 3-neck flask and stirred at room temperature for overnight, and then, *p*-chloranil (64 mg, 0.26 mmol) was added and stirred at room temperature for 3h. The solution was concentrated to give crude product as a dark green viscous liquid. The crude product was purified by silica gel column chromatography (chloroform : methanol = 19 : 1) to obtain TTM-PEG1 as a dark green viscous liquid (130 mg, 85 %).

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

$[M+K]^+$ Calcd for 1357.1772; Found 1357.4584

Elemental analysis

Calcd for $C_{38}H_{20}Cl_8NO$, C: 56.47, H: 5.20, N: 1.06; Found, C: 56.34, H: 5.22, N: 1.05

TTM-PEG3

Under nitrogen atmosphere and in the dark, a mixture of HTTM-PEG3 (204 mg, 0.08 mmol), KOtBu (30 mg, 0.27 mmol), and anhydrous THF (10 mL) were added into a 3-neck flask and stirred at 60℃ for overnight, and then, *p*-chloranil (19 mg, 0.08 mmol) was added and stirred at 60℃ for overnight. The solution was concentrated to give crude product as a dark green viscous liquid. The crude product was purified by preparative GPC (eluent: chloroform) to obtain TTM-PEG3 as a dark green viscous liquid (160 mg, 78 %).

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

$[M+K]^+$ Calcd for 2474.8308; Found 2475.1988

Elemental analysis

Calcd for $C_{38}H_{20}Cl_8NO+2H_2O$, C: 54.41, H: 7.01, N: 0.57; Found, C: 54.39, H: 6.90, N: 0.67

NMR spectra

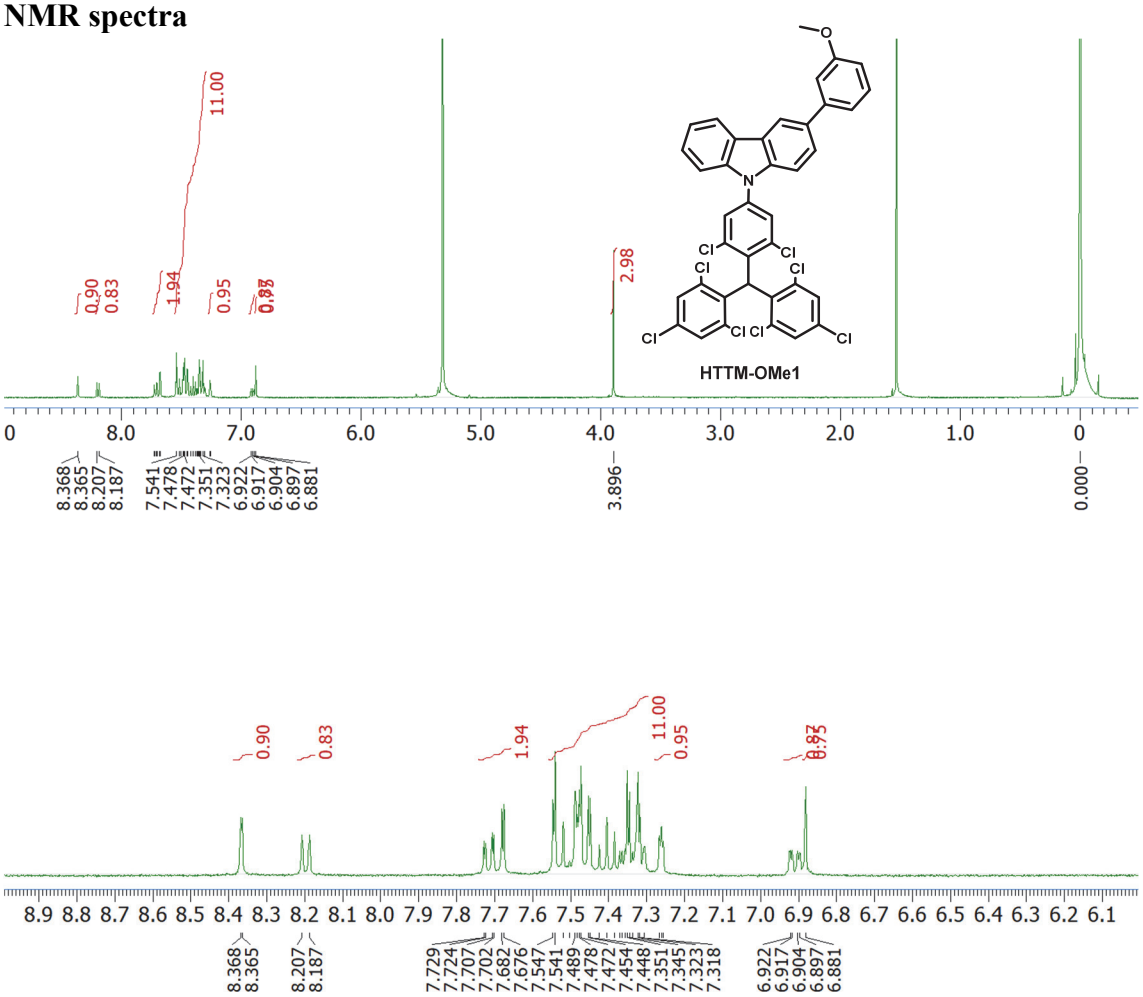


Figure S1. ^{1}H NMR spectra of HTTM-OMe1 in CD_2Cl_2.

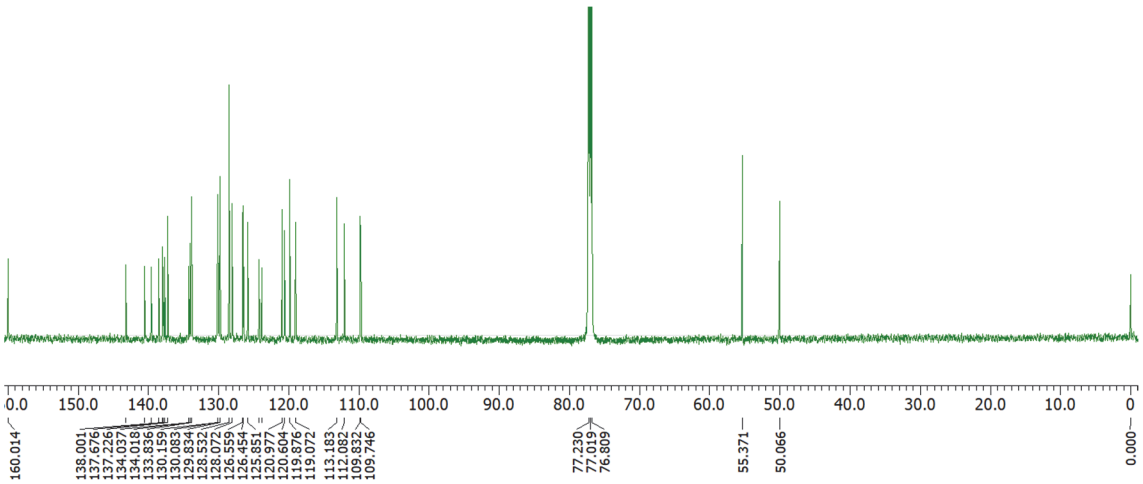


Figure S2. ^{13}C NMR spectra of HTTM-OMe1 in $CDCl_3$.

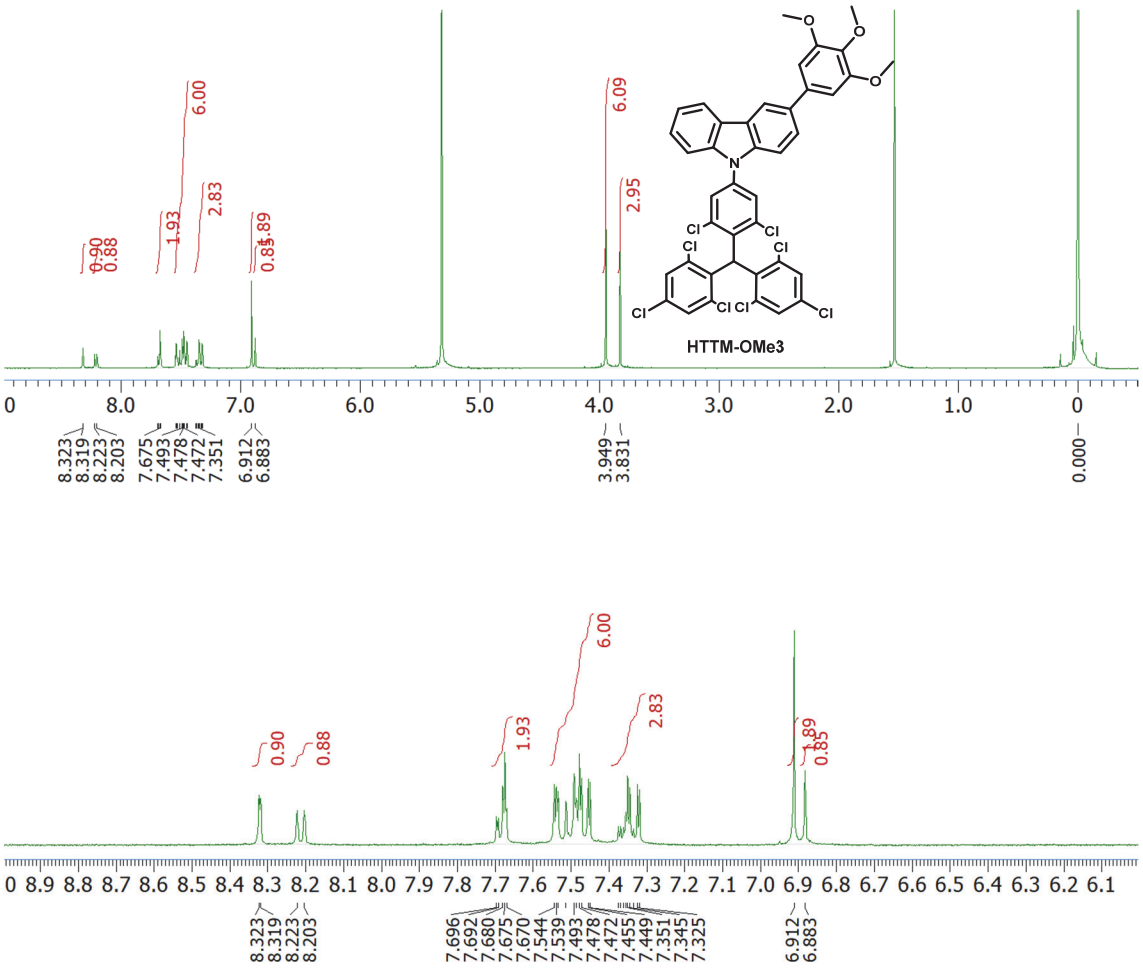


Figure S3. ^{1}H NMR spectra of HTTM-OMe3 in CD_2Cl_2.

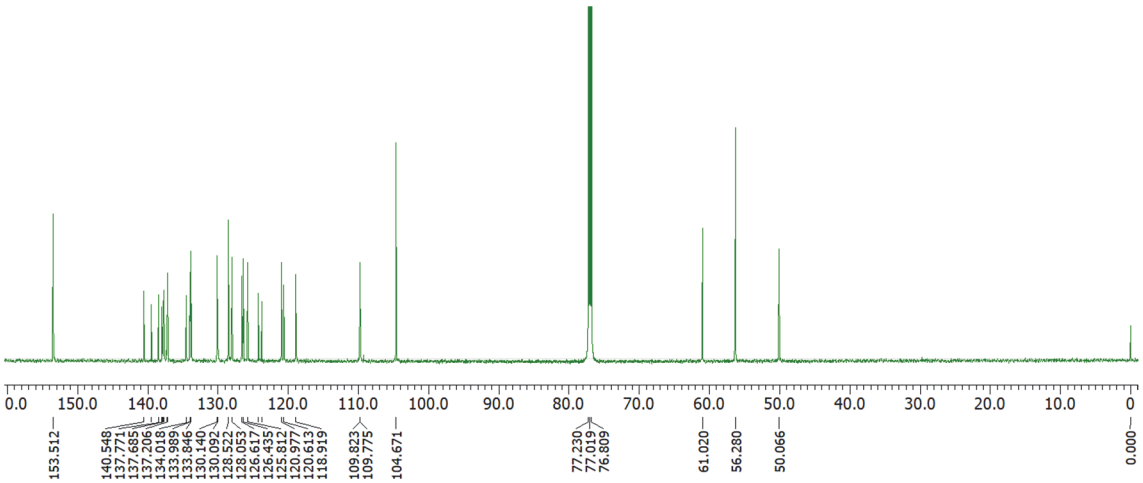


Figure S4. ^{13}C NMR spectra of HTTM-OMe3 in $CDCl_3$.

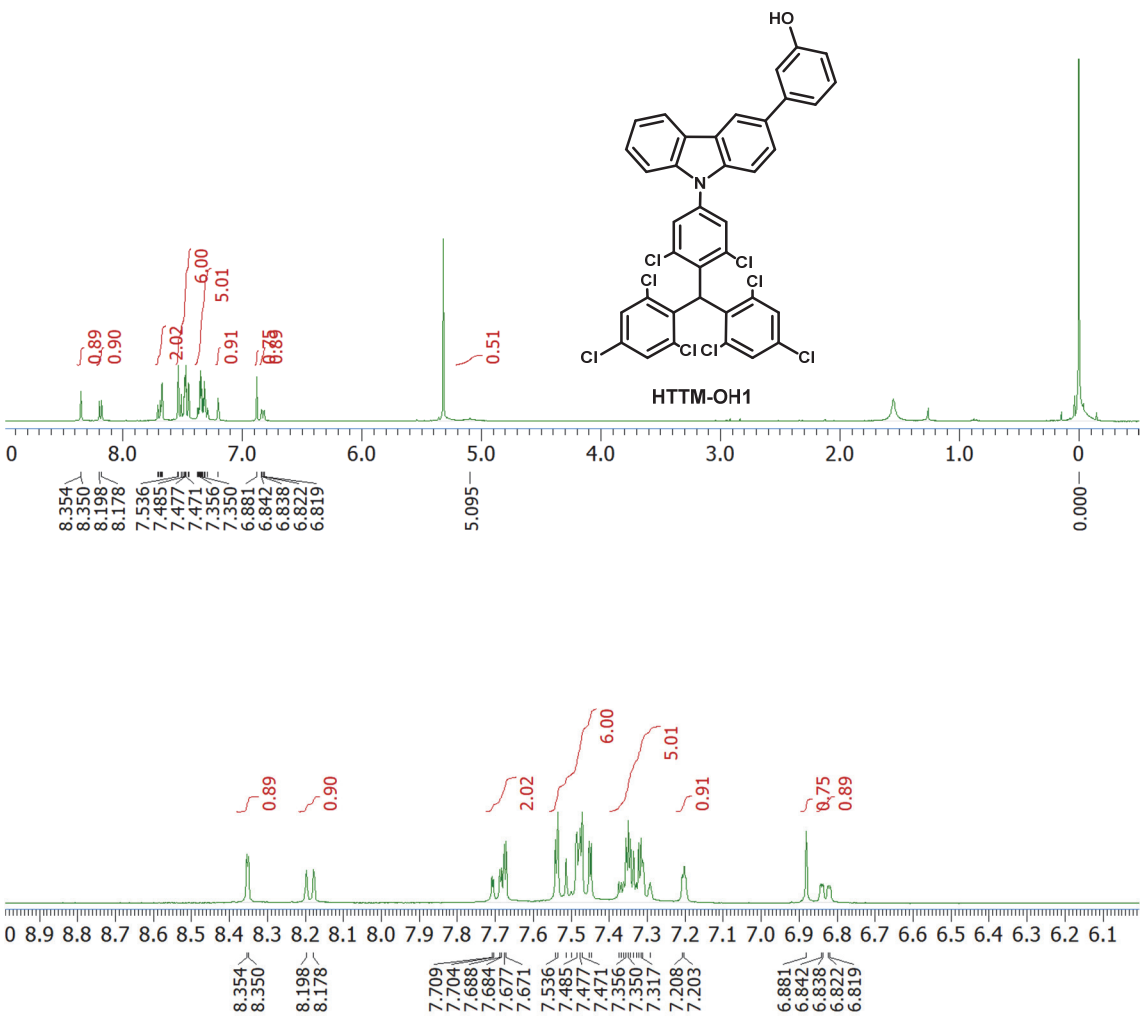


Figure S5. ^{1}H NMR spectra of HTTM-OH1 in CD_2Cl_2.

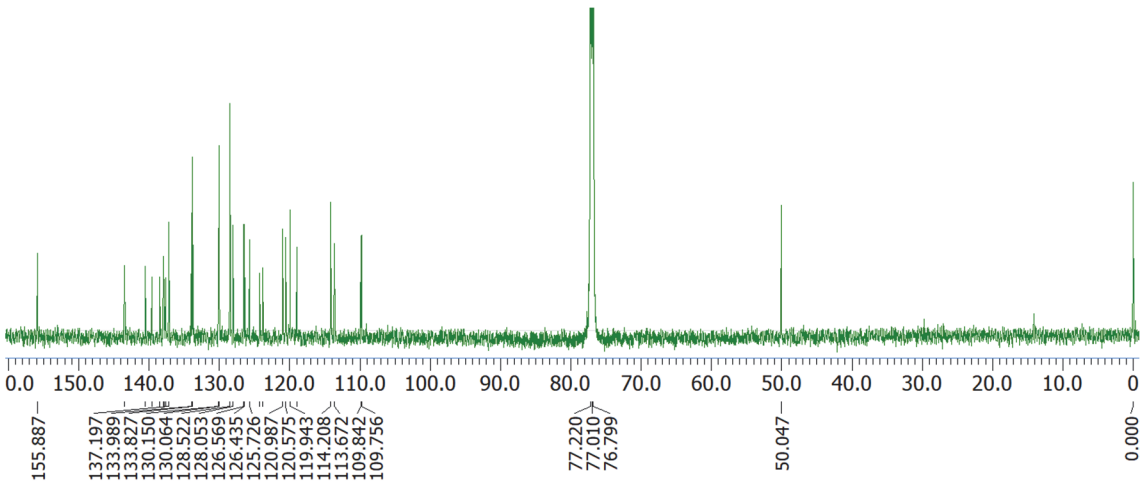


Figure S6. ^{13}C NMR spectra of HTTM-OH1 in $CDCl_3$.

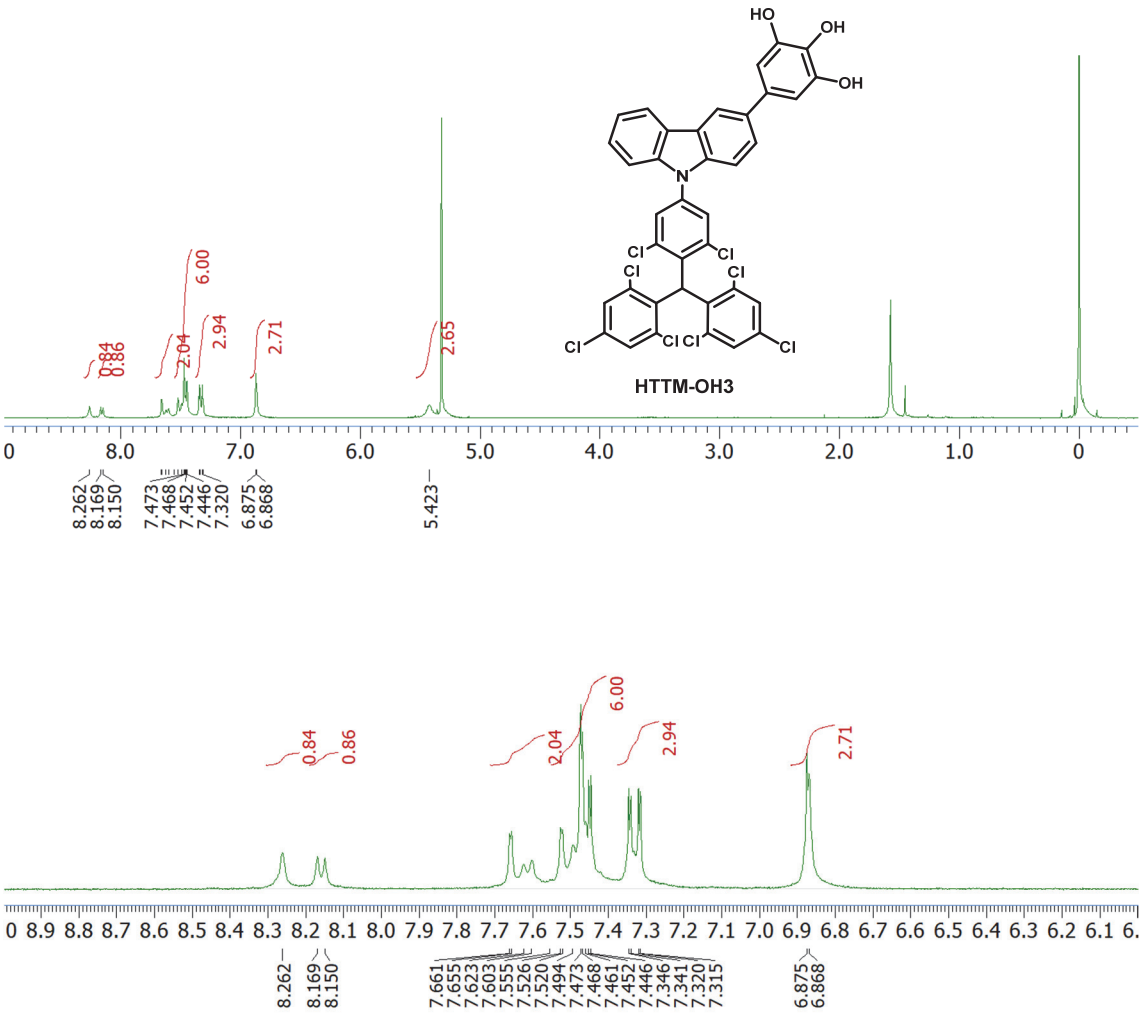


Figure S7. ^{1}H NMR spectra of HTTM-OH3 in CD_2Cl_2.

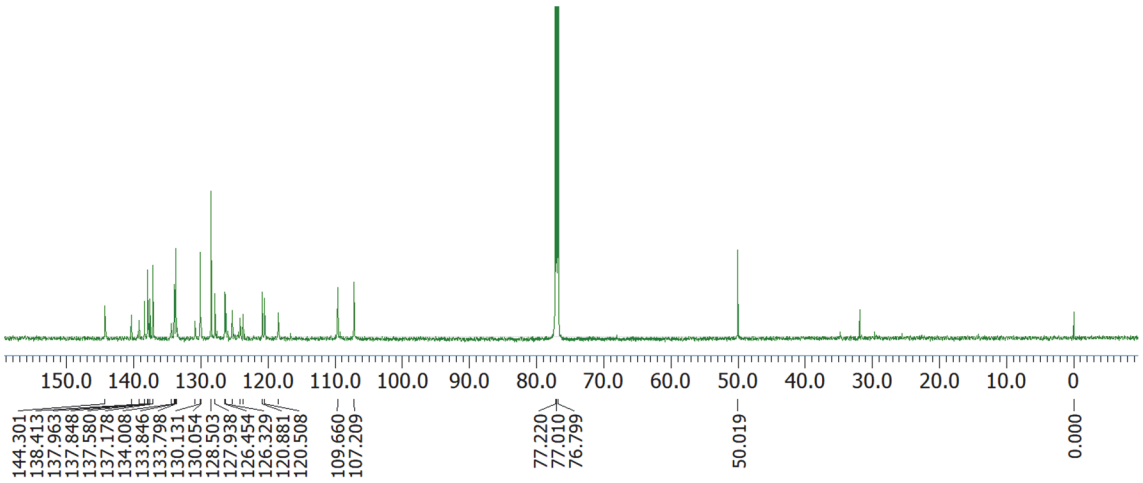


Figure S8. ^{13}C NMR spectra of HTTM-OH3 in $CDCl_3$.

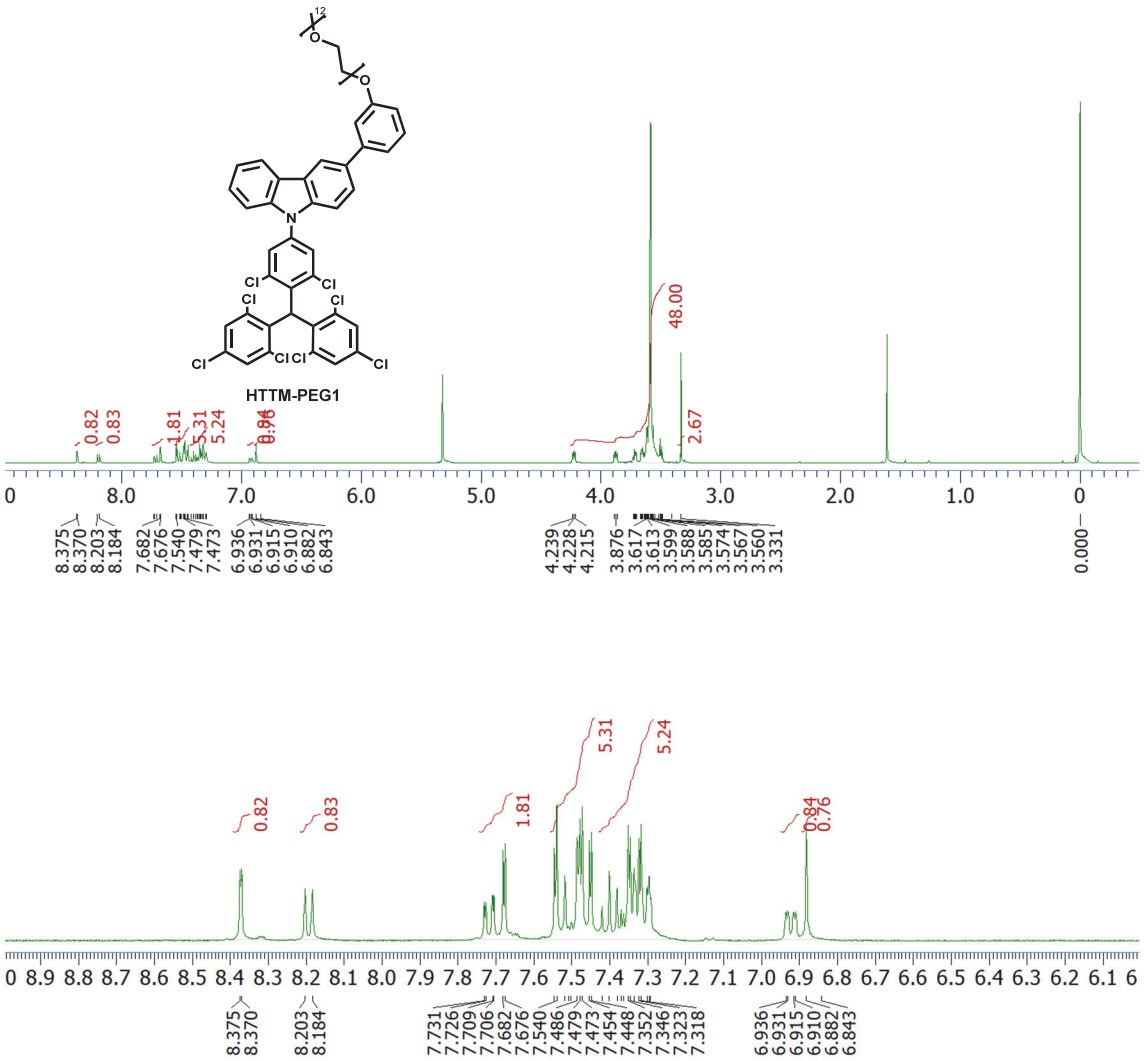


Figure S9. ^{1}H NMR spectra of HTTM-PEG1 in CD_2Cl_2.

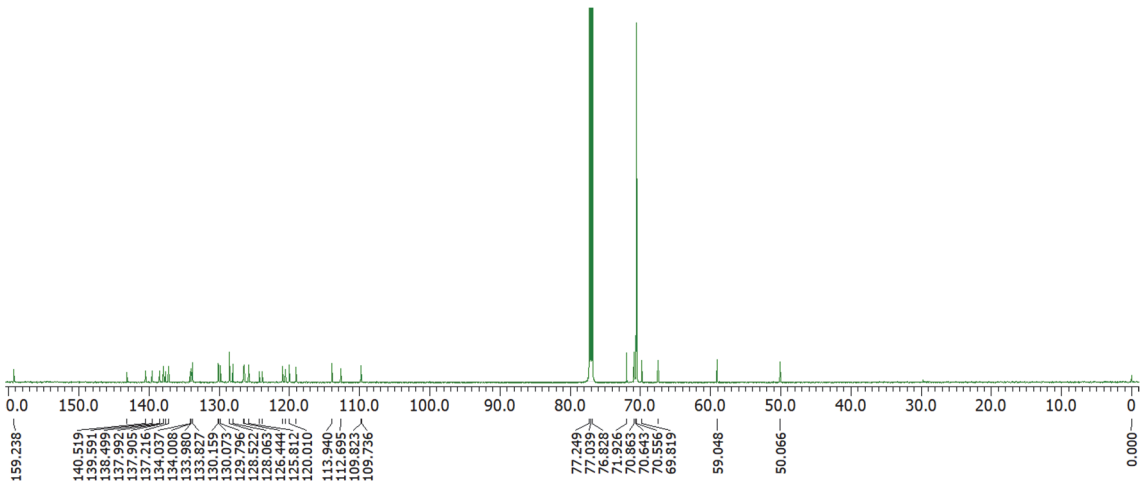


Figure S10. ^{13}C NMR spectra of HTTM-PEG1 in $CDCl_3$.

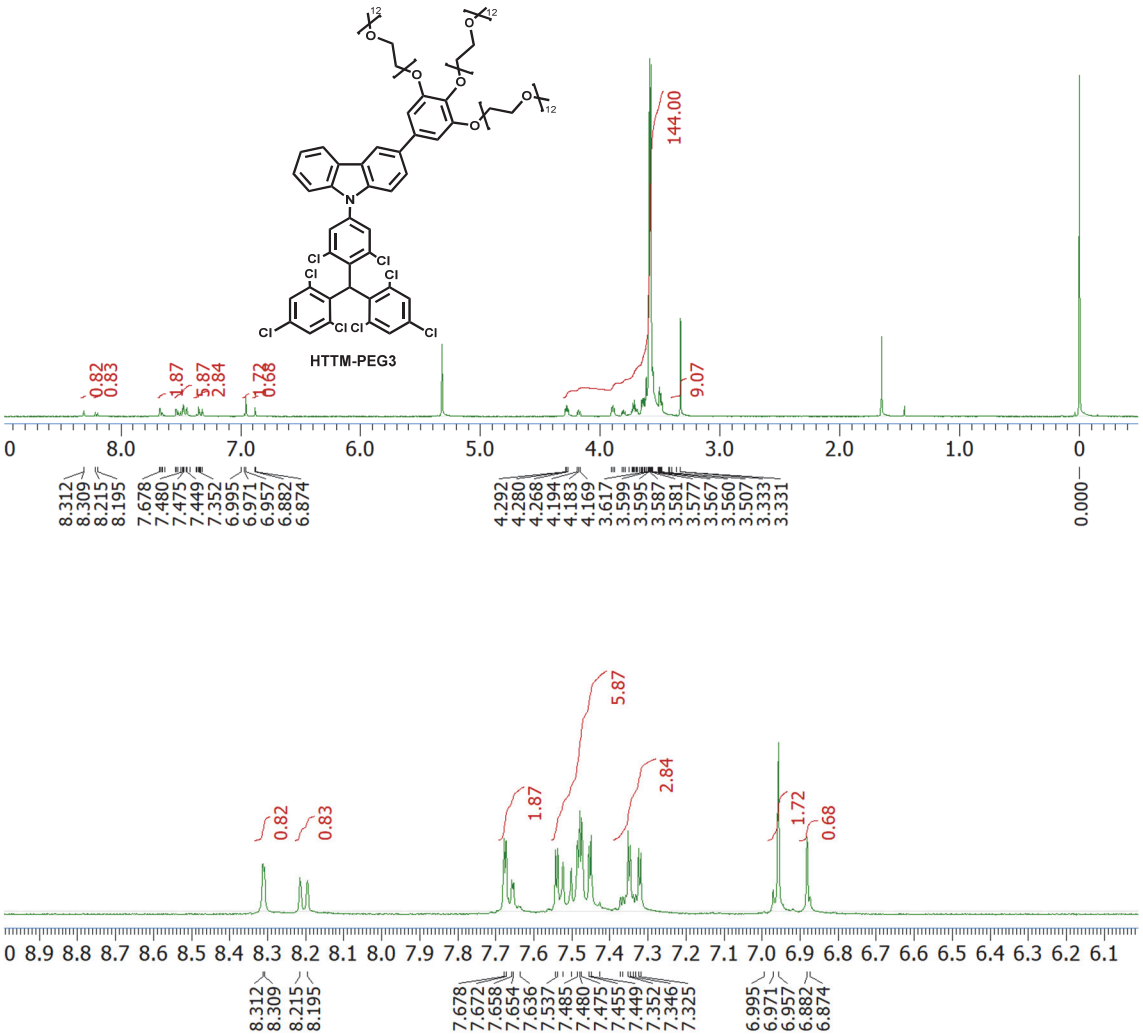


Figure S11. ^{1}H NMR spectra of HTTM-PEG3 in CD_2Cl_2.

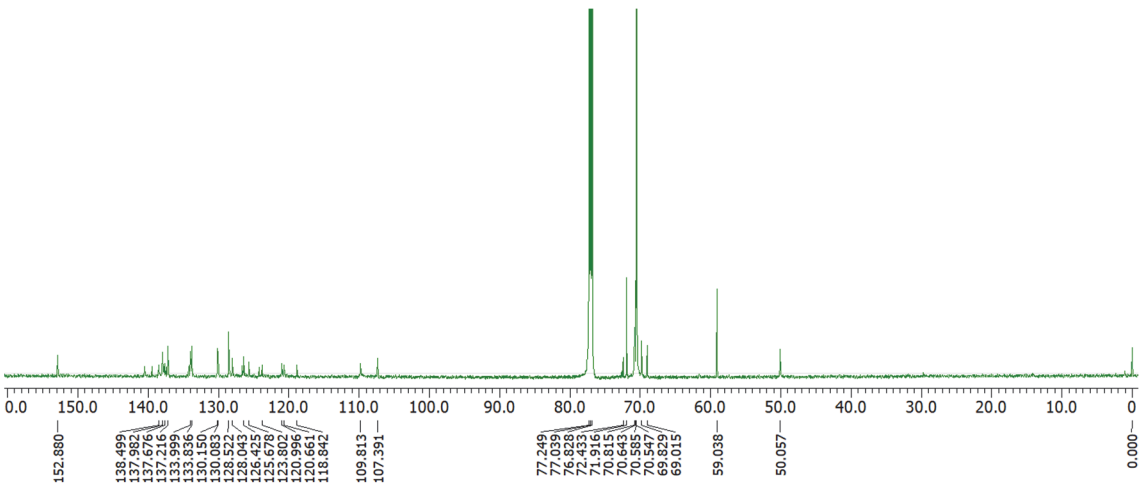


Figure S12. ^{13}C NMR spectra of HTTM-PEG3 in $CDCl_3$.

ESR spectra

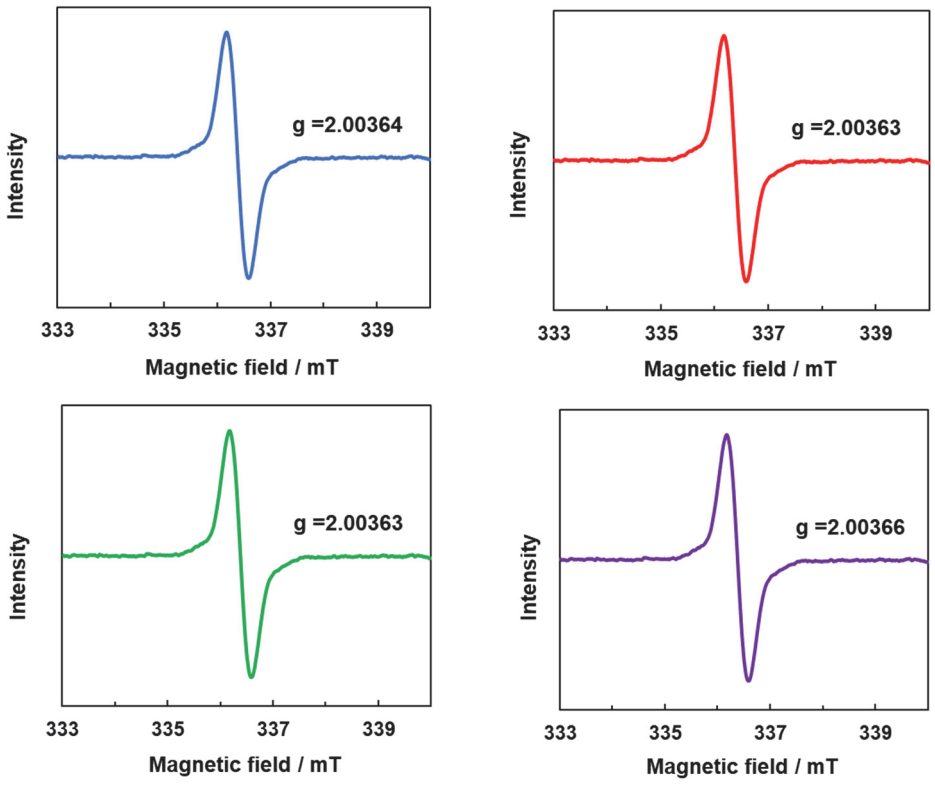


Figure S13. ESR spectra of TTM-OMe1 (blue), TTM-OMe3 (red), TTM-PEG1 (green), and TTM-PEG3 (purple) in 10^{-5} M CH_2Cl_2 at room temperature.

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.

$$S_x = \frac{I_x J_0}{I_0 J_x} S_0$$

S_x : Amount of spin in TTM-(OMe1, OMe3, PEG1, PEG3)

S_0 : Amount of spin in TEMPOL

I_x : Integral value of TTM-(OMe1, OMe3, PEG1, PEG3)

I_0 : Integral value of TEMPOL

J_x : Integral value of Mn^{2+} marker during TTM-(OMe1, OMe3, PEG1, PEG3) measurement

J_0 : Integral value of Mn^{2+} marker during TEMPOL measurement

DLS histogram

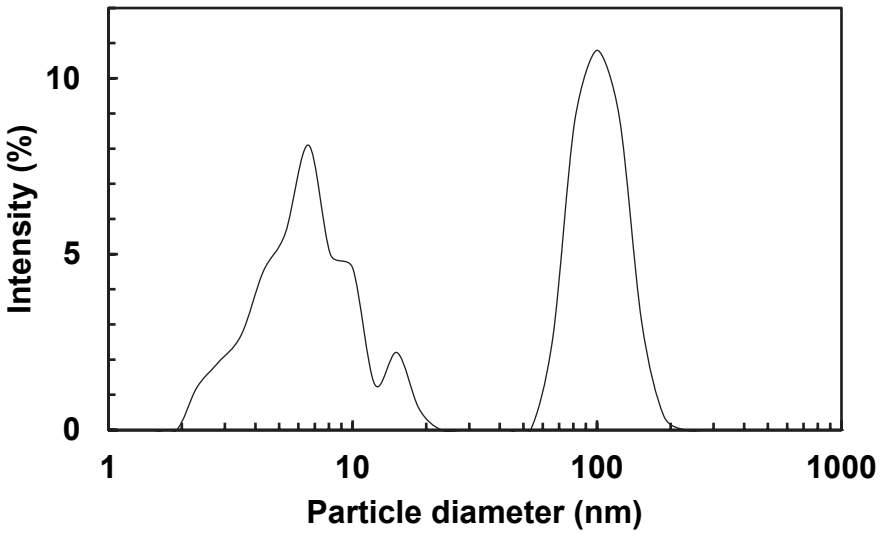


Figure S14. DLS histogram of TTM-PEG3 1 mM aqueous solution.

PL spectra

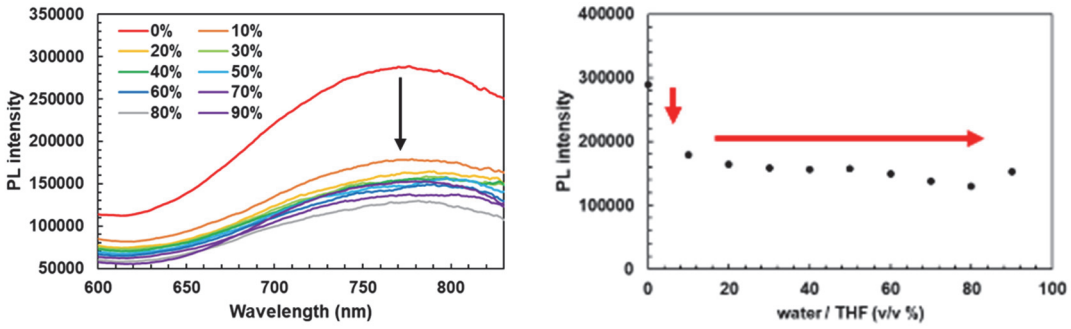


Figure S15. (Left) PL spectra of TTM-PEG3 in different ratios of water/THF (v/v %) mixture. (right) PL peak intensity plot of TTM-PEG3 in different ratios of water/THF (v/v %) mixture.

Solvent effect

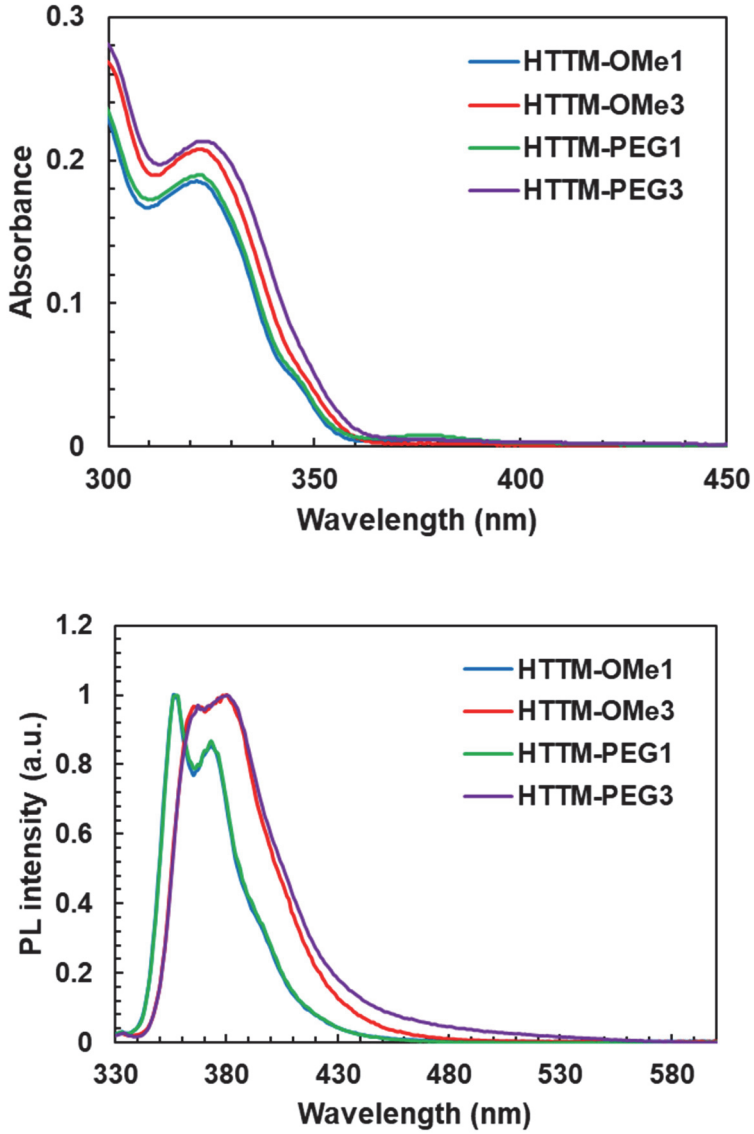


Figure S16. (Left) UV-vis absorption and (right) PL spectra of HTTM-(OMe1, OMe3, PEG1, PEG3) in toluene (10^{-5} M) (excitation wavelength: 290 nm).

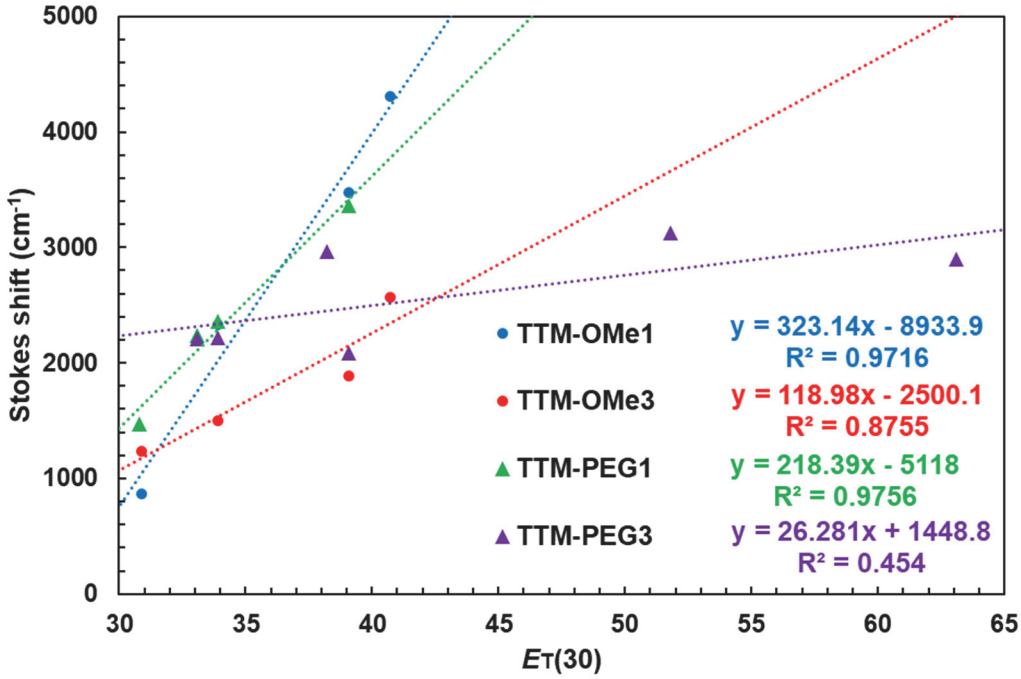


Figure S17. Lippert-Mataga plots of radicals.

Table S1. Solvent polarity parameters, absorption wavelength, emission wavelength and Stokes shift for radicals.

Radicals	Solvent	E_T (30)	λ_{Abs} (nm)	λ_{PL} (nm)	λ_{Abs}-λ_{PL} (cm^{-1})
TTM-OMe1	Dichloromethane	40.7	607	822	4309
	Chloroform	39.1	608	771	3477
	Toluene	33.9	623	729	2334
	Cyclohexane	30.9	617	652	870
TTM-OMe3	Dichloromethane	40.7	609	722	2570
	Chloroform	39.1	608	687	1891
	Toluene	33.9	626	691	1503
	Cyclohexane	30.9	622	674	1240
TTM-PEG1	Chloroform	39.1	608	764	3358
	Toluene	33.9	624	732	2364
	p-Xylene	33.1	624	725	2233
	Cyclohexane	30.9	619	681	1471
	Water	63.1	634	777	2903
	Ethanol	51.8	614	760	3129
TTM-PEG3	Chloroform	39.1	611	699	2087
	1,2-Dimethoxyethane	38.2	621	761	2962
	Toluene	33.9	629	731	2218
	p-Xylene	33.1	628	729	2206

PL lifetime

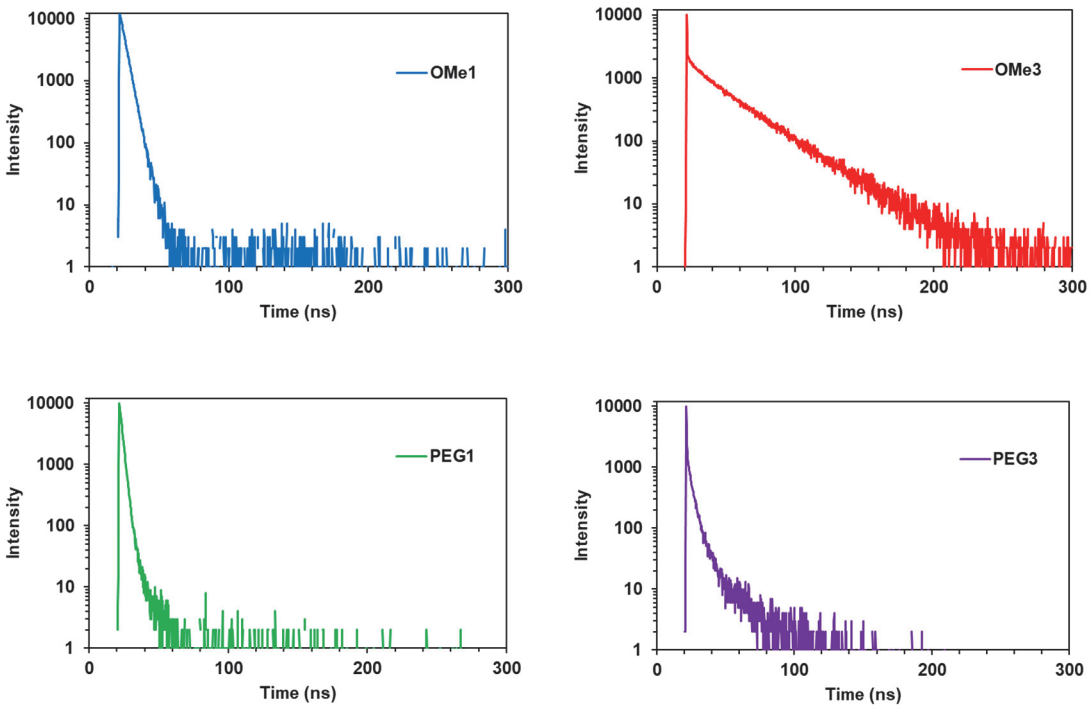


Figure S18. PL lifetime of alkoxy group substituted TTM radicals in diluted toluene solution.

Photostability

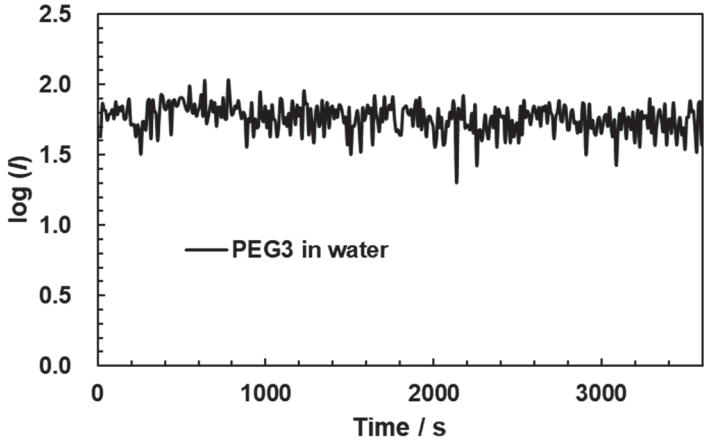


Figure S19. Photostability of TTM-PEG3 investigated by monitoring the PL intensity during continuous irradiation with a 355 nm pulsed laser in water. Note that the absorbance of TTM-PEG3 was controlled to be 0.5 at 355 nm, and the solutions were stirred during the measurement.

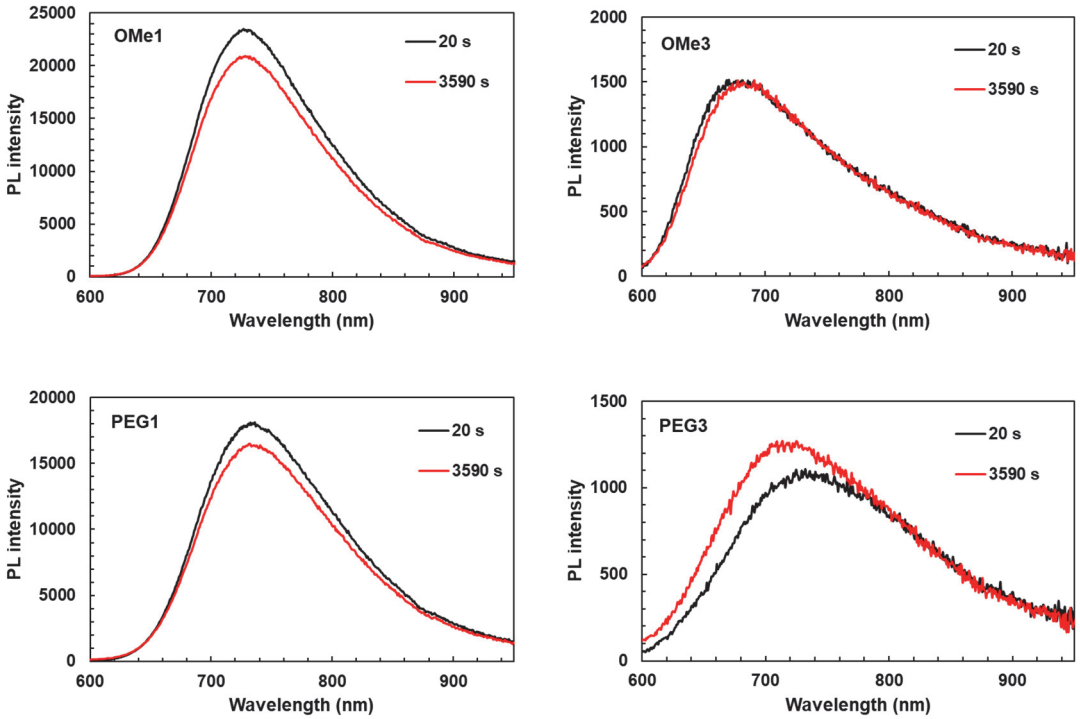


Figure S20. PL spectra of methoxylated and PEGylated TTM-Cz radicals in toluene under continuous 20 and 3590 seconds laser irradiation.

Chemical structures of MRI contrast agents

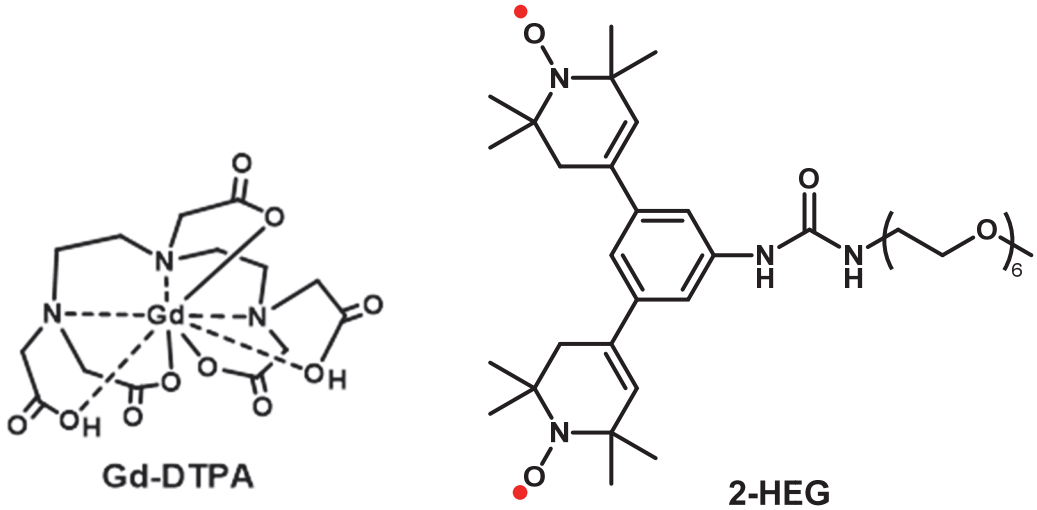


Figure S21. Chemical structures of MRI contrast agents; Gd complex and TEMPO derivatives.

Electrochemical properties

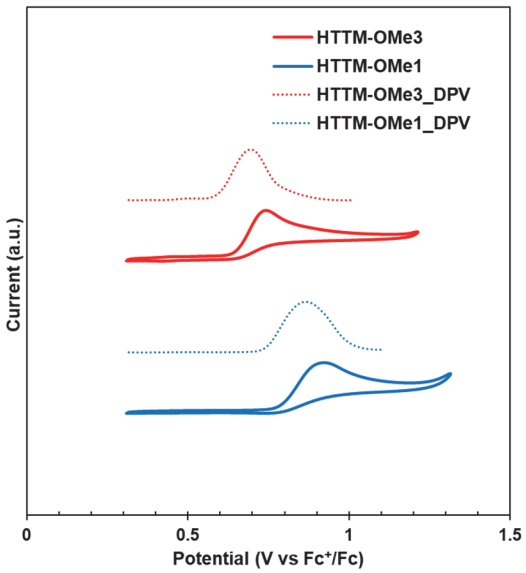


Figure S22. Cyclic voltammogram (CV) and differential pulse voltammogram (DPV) of HTTM-OMe1 and HTTM-OMe3 in CH_2Cl_2.

Reference

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, Gaussian, Inc., Wallingford CT, 2016.

2. A. Abdurahman, Q. Peng, O. Ablikim, X. Ai, and F. Li, *Mater. Horiz*., 2019, **6**, 1265.

3. R. A. Kumar, D. V. Jawale, E. Oheix, V. Geertsen, E. Gravel, and E. Doris, *Adv. Synth. Catal.*, 2020, **362**, 4425.