Electronic Supplementary Material (ESI) for ChemComm.

Electronic Supplementary Information

Cation-responsive turn-on fluorescence and absence of heavy atom effect of pyridyl-substituted triarylmethyl radicals

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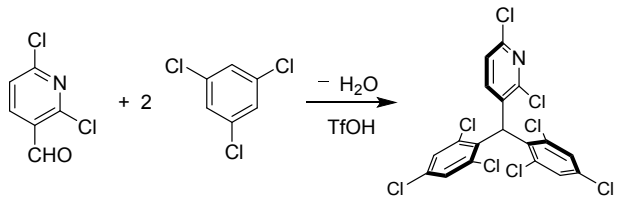
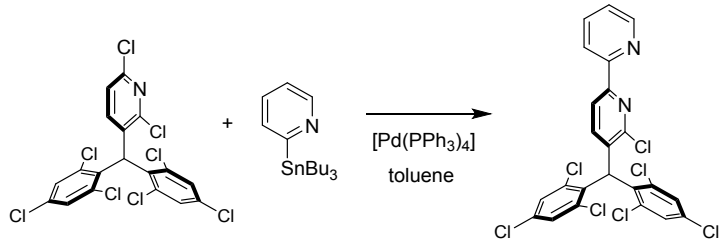
Contents

Synthesis of (2,6-dichloro-3-pyridyl)bis(2,4,6-trichlorophenyl)methane (αH-iPyBTM)



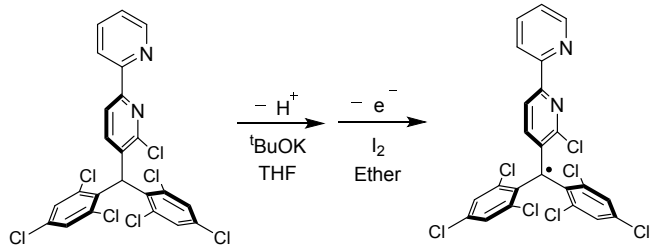
2,6-Dichloro-3-pyridine carboxaldehyde (0.352 g, 2.0 mmol, 1 eq.), 1,3,5-trichlorobenzene (3.63 g, 20 mmol, 10 eq.), and trifluoromethanesulfonic acid (3.0 g, 20 mmol, 10 eq.) were heated to 185 °C for 2 h by microwave irradiation. The reaction mixture was cooled to r.t. and all components were dissolved in CH_2Cl_2 or water. The water layer was neutralized to pH 7 using $NaHCO_3$ aq, separated from organic layer, and extracted with CH_2Cl_2 (3 × 25 mL). The combined organic phases were washed with $NaHCO_3$ aq, and dried by Na_2SO_4. The organic layer was purified by SiO_2 column chromatography (CH_2Cl_2 : hexane = 1:2), and dried in vacuo to afford iPyBTMH (0.722 g, 1.39 mmol, 69%) as a white solid. **^{1}H NMR** (500 MHz, $CDCl_3$): δ 7.35 (s, 4H), 7.18 (d, J = 8.1 Hz, 1H), 7.15 (d, J = 8.1 Hz, 1H), 6.55 (s, 1H). **Elem. Anal.** Calcd for $C_{18}H_7NCl_8$: C 41.51, H 1.35, N 2.69. Found, C 41.34, H 1.63, N 2.78.

Synthesis of [2-chloro-6-(2-pyridyl)-3-pyridyl]bis(2,4,6-trichlorophenyl)methane (αH-*o*PyPyBTM′)



Under a nitrogen atmosphere, αH-iPyBTM (416 mg, 0.80 mmol), tributyl(2-pyridyl)tin (0.3 mL, 0.94 mmol), and tetrakis(triphenylphosphine)palladium(0) (49 mg, 0.042 mmol) in toluene (~5 mL) were stirred at 110 °C for 15 h. Reaction mixture was purified by SiO_2 column chromatography (CH_2Cl_2 : hexane = 1:1) and dried in vacuo to afford αH-*o*PyPyBTM′ (366 mg, 0.65 mmol, 81% yield). **^{1}H NMR** (500 MHz, $CDCl_3$): δ 8.66 (d, J = 5.5 Hz, 1H), 8.43 (d, J = 8.0 Hz, 1H), 8.26 (d, J = 8.0 Hz, 1H), 7.82 (t, J = 7.7 Hz, 1.8 Hz, 1H), 7.36 (s, 4H), 7.33-7.29 (m, 2H), 6.65 (s, 1H). **HRMS** (FAB-MS) m/z: $[M+H]^+$ Calcd for $C_{23}H_{12}Cl_7N_2$ 560.8820; Found 560.8840.

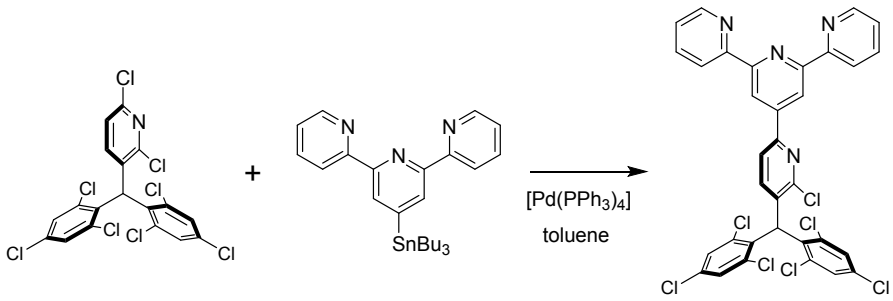
Synthesis of [2-chloro-6-(2-pyridyl)-3-pyridyl]bis(2,4,6-trichlorophenyl)methyl radical (*o*PyPyBTM′)



Under a nitrogen atmosphere, αH-*o*PyPyBTM′ (169 mg, 0.30 mmol) was dissolved in dry THF (12 mL). ^{t}BuOK in THF (1 M solution, 0.4 mL) was added dropwise, and the reaction mixture was stirred overnight in the dark. I_2 (178 mg, 0.70 mmol) in dry Et_2O (17 mL) was added dropwise and stirred for 1 h. Under ambient conditions, remaining I_2 was reduced by washing with $Na_2S_2O_3$ aq 3 times, water layer was extracted with Et_2O, and combined organic layer was dried with Na_2SO_4. The red solution was filtered, evaporated, purified by Al_2O_3 column chromatography (Et_2O : hexane = 1:1) and dried in vacuo to afford *o*PyPyBTM′ (105 mg, 0.19 mmol, 62%) as a brown solid. **HRMS** (FAB-MS) m/z: $[M+H]^+$ Calcd for $C_{23}H_{11}Cl_7N_2$ 559.8742; Found 559.8737. **ESR** Spin concentration of *o*PyPyBTM′ in toluene (9.7×10^{-5} M) was estimated by comparing the value of twice-integration of the signal intensity with that of the reference sample (4-hydroxy-

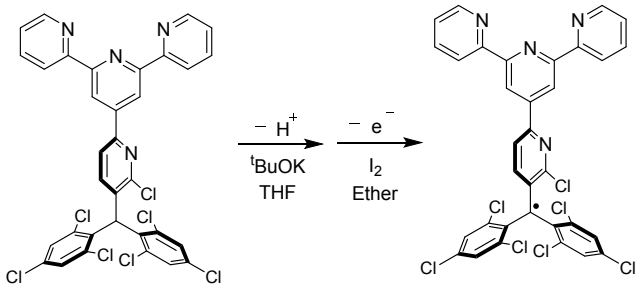
TEMPO in toluene; 1.00×10^{-4} M). The existence of $S = 1/2$ spin on one *o*PyPyBTM′ molecule was confirmed.

Synthesis of [2-chloro-6-(4′-2,2′:6′,2″-terpyridyl)-3-pyridyl]bis(2,4,6-trichlorophenyl)methane (αH-tpyPyBTM′)



Under a nitrogen atmosphere, iPyBTMH (159 mg, 0.305 mmol), 4′-(tributylstannyl)-2,2′:6′,2″-terpyridine (159 mg, 0.304 mmol), and tetrakis(triphenylphosphine)palladium(0) (34.8 mg, 0.030 mmol) in toluene (~3 mL) were stirred at 110°C for 17 h. Reaction mixture was purified by Al_2O_3 column chromatography (CH_2Cl_2 : hexane = 1:2) and dried in vacuo to afford αH-tpyPyBTM′ (110 mg, 0.153 mmol, 50% yield). **^{1}H NMR** (500 MHz, $CDCl_3$): δ 9.05 (s, 2H), 8.74 (d, J = 3.9 Hz 2H), 8.65 (d, J = 7.9 Hz, 2H), 7.89-7.86 (m, 3H), 7.37-7.31 (m, 7H), 6.67 (s, 1H). **HRMS** (FAB-MS) m/z: $[M+H]^+$ Calcd for $C_{33}H_{18}Cl_7N_4$ 714.9351; Found 714.9372.

Synthesis of [2-chloro-6-(4′-2,2′:6′,2″-terpyridyl)-3-pyridyl]bis(2,4,6-trichlorophenyl)methyl radical (tpyPyBTM′)



Under a nitrogen atmosphere, αH-tpyPyBTM′ (106 mg, 0.148 mmol) was dissolved in dry THF (6 mL). ^{t}BuOK in THF (1 M solution, 0.2 mL) was added dropwise, and the reaction mixture was stirred overnight in the dark. I_2 (95 mg, 0.374 mmol) in dry Et_2O (10 mL) was added dropwise and stirred for 1 h. Under ambient conditions, remaining I_2 was reduced by washing with $Na_2S_2O_3$ aq 3 times, water layer was extracted with Et_2O, and combined organic layer was dried with Na_2SO_4. The red solution was filtered, evaporated, purified by Al_2O_3 column chromatography (CH_2Cl_2 : hexane = 1:2) and dried in vacuo to afford tpyPyBTM′ (75 mg, 0.104 mmol, 69%) as a brown solid. **HRMS** (FAB-MS) m/z: $[M+H]^+$ Calcd for $C_{33}H_{17}Cl_7N_4$ 713.9273; Found 713.9258. **ESR** Spin concentration of tpyPyBTM′ in toluene (9.0×10^{-5} M) was estimated by comparing the value of twice-integration of the signal intensity with that of the reference sample (4-hydroxy-TEMPO in toluene; 1.09×10^{-4} M). The existence of $S = 1/2$ spin on one tpyPyBTM′ molecule was confirmed.

X-ray structural analysis of $[Nd(tpyPyBTM')(NO_3)_3(H_2O)](CH_3CN)_2$

Neodymium nitrate hexahydrate (4.4 mg, 0.010 mmol) in CH_3CN was added dropwise to a stirred solution of tpyPyBTM′ (7.2 mg, 0.010 mmol) in CH_2Cl_2. Green flat crystals suitable for structure analysis formed after standing overnight (5.8 mg, 0.0051 mmol, 51%).[1] Diffraction data for X-ray analysis were collected with an AFC10 diffractometer coupled with a Rigaku Saturn CCD system equipped with a rotating-anode X-ray generator producing graphite-monochromated MoKα radiation (λ = 0.7107 Å). Lorentz polarization and numerical absorption corrections were performed with the program *Crystal Clear 1.3.6.* Structures were solved by the direct method using SIR 92 software[2] and refined against F^2 using SHELXL-97.[3] *Crystal Structure 4.0* software was used to prepare the material for publication.

The crystallographic data are listed in Table S1. CCDC 1535850 contains the supplementary crystallographic data of this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Instruments

Microwave synthesis was conducted using Biotage Initiator+. NMR spectra in $CDCl_3$ were measured with a Bruker US-500 spectrometer. The reported chemical shift of the solvent residual peak (δ 7.26) was used for calibration of the ^{1}H NMR spectra. ESR spectra were recorded with a JEOL JES-FA200 spectrometer with X-band microwave. Sample solutions were charged in a 5mmϕ sample tube. Magnetic field was calibrated with the Mn^{2+}/MgO standard. FAB-MS was performed with a JEOL MStation JMS-700 spectrometer. ESI–TOF mass spectra were recorded using an LCT Micromass spectrometer. UV-vis absorption spectra were recorded with a JASCO V-570 spectrometer. Steady-state emission spectra were measured with a JASCO FP-8600 spectrometer. Absolute photoluminescence quantum yields were measured with a Hamamatsu Photonics C9920-02G. Fluorescence lifetime measurements were performed using a Hamamatsu Photonics Quantaurus-Tau C11367-02.

Titration experiments

Fig. 3 (a) Absorption: To *o*PyPyBTM′ in dichloromethane (2×10^{-5} M, 2 mL), TfOH in methanol (1×10^{-3} M, 8, 16, 24, 32, 40 μL) was added. Emission (λ_{ex} = 441 nm): To *o*PyPyBTM′ in dichloromethane (5×10^{-6} M, 2 mL), TfOH in methanol (1×10^{-3} M, 2, 4, 6, 8, 10, 12 μL) was added.

Fig. 3 (b) Absorption: To tpyPyBTM′ in dichloromethane (2×10^{-5} M, 2 mL), TfOH in methanol (1×10^{-3} M, 8, 16, 24, 32, 40, 48 μL) was added. Emission (λ_{ex} = 438 nm): To tpyPyBTM′ in dichloromethane (5×10^{-6} M, 2 mL), TfOH in methanol (1×10^{-3} M, 2, 4, 6, 8, 10 μL) was added.

Fig. 3 (c) Absorption: To tpyPyBTM′ in dichloromethane (2×10^{-5} M, 2 mL), zinc acetate in methanol (1×10^{-3} M, 8, 16, 24, 32, 40, 48 μL) was added. Emission (λ_{ex} = 429 nm): To tpyPyBTM′ in dichloromethane (5×10^{-6} M, 2 mL), zinc acetate in methanol (1×10^{-3} M, 2, 4, 6, 8, 10, 12 μL) was added.

Fig. 3 (d) Absorption: To tpyPyBTM′ in dichloromethane (2×10^{-5} M, 2 mL), copper(II) acetate monohydrate in methanol (1×10^{-3} M, 8, 16, 24, 32, 40, 48 μL) was added. Emission (λ_{ex} = 438 nm): To tpyPyBTM′ in dichloromethane (5×10^{-6} M, 2 mL), copper(II) acetate monohydrate in methanol (1×10^{-3} M, 2, 4, 6, 8, 10, 12 μL) was added.

Fig. 3 (e) Absorption: To tpyPyBTM′ in dichloromethane (2×10^{-5} M, 2 mL), cobalt(II) acetate tetrahydrate in methanol (1×10^{-3} M, 8, 16, 24, 32, 40, 48 μL) was added. Emission (λ_{ex} = 431 nm): To tpyPyBTM′ in dichloromethane (5×10^{-6} M, 2 mL), cobalt(II) acetate tetrahydrate in methanol (1×10^{-3} M, 2, 4, 6, 8, 10, 12 μL) was added.

Fig. 3 (f) Absorption: To tpyPyBTM′ in dichloromethane (2×10^{-5} M, 2 mL), manganese(II) acetate tetrahydrate in methanol (1×10^{-3} M, 8, 16, 24, 32, 40, 48 μL) was added. Emission (λ_{ex} = 426 nm): To tpyPyBTM′ in dichloromethane (5×10^{-6} M, 2 mL), manganese(II) acetate tetrahydrate in methanol (1×10^{-3} M, 2, 4, 6, 8, 10, 20 μL) was added.

Fig. S5 (a) Absorption: To tpyPyBTM′ in dichloromethane (2×10^{-5} M, 2 mL), nickel(II) acetate tetrahydrate in methanol (1×10^{-3} M, 8, 16, 24, 32, 40, 48 μL) was added. Emission (λ_{ex} = 426 nm): To tpyPyBTM′ in dichloromethane (5×10^{-6} M, 2 mL), nickel(II) acetate tetrahydrate in methanol (1×10^{-3} M, 2, 4, 6, 8, 10, 30 μL) was added.

Fig. S5 (b) Absorption: To tpyPyBTM′ in dichloromethane (2×10^{-5} M, 2 mL), iron(II) sulfate heptahydrate in methanol (1×10^{-3} M, 8, 16, 24, 32, 40, 48 μL) was added. Emission (λ_{ex} = 426 nm): To tpyPyBTM′ in dichloromethane (5×10^{-6} M, 2 mL), iron(II) sulfate heptahydrate in methanol (1×10^{-3} M, 2, 4, 6, 8, 10, 14 μL) was added.

Fig. 5 (a) Absorption: To tpyPyBTM′ in dichloromethane (2×10^{-5} M, 2 mL), lanthanum(III) trifluoromethanesulfonate in methanol (1×10^{-3} M, 8, 16, 24, 32, 40 μL) was added. Emission (λ_{ex} = 433 nm): To tpyPyBTM′ in dichloromethane (5×10^{-6} M, 2 mL), lanthanum(III) trifluoromethanesulfonate in methanol (1×10^{-3} M, 2, 4, 6, 8, 10, 20 μL) was added.

Fig. 5 (b) Absorption: To tpyPyBTM′ in dichloromethane (2×10^{-5} M, 2 mL), europium(III) trifluoromethanesulfonate

in methanol (1×10^{-3} M, 8, 16, 24, 32, 40 μL) was added. Emission (λ_{ex} = 435 nm): To tpyPyBTM′ in dichloromethane (5×10^{-6} M, 2 mL), europium(III) trifluoromethanesulfonate in methanol (1×10^{-3} M, 2, 4, 6, 8, 10, 12 μL) was added.

Fig. 5 (c) Absorption: To tpyPyBTM′ in dichloromethane (2×10^{-5} M, 2 mL), neodymium(III) nitrate hexahydrate in methanol (1×10^{-3} M, 8, 16, 24, 32, 40 μL) was added. Emission (λ_{ex} = 432 nm): To tpyPyBTM′ in dichloromethane (5×10^{-6} M, 2 mL), neodymium(III) nitrate hexahydrate in methanol (1×10^{-3} M, 2, 4, 6, 8, 10, 12 μL) was added.

Fig. 5 (d) Absorption: To tpyPyBTM′ in ethyl iodide (2×10^{-5} M, 2 mL), zinc acetate in methanol (1×10^{-3} M, 80 μL) was added. Emission (λ_{ex} = 437 nm): To tpyPyBTM′ in ethyl iodide (5×10^{-6} M, 2 mL), zinc acetate in methanol (1×10^{-3} M, 80 μL) was added.

Fig. 5 (e) Absorption: To *o*PyPyBTM′ in ethyl iodide (2×10^{-5} M, 2 mL), TfOH in methanol (1×10^{-2} M, 8 μL) was added. Emission (λ_{ex} = 438 nm): To *o*PyPyBTM′ in ethyl iodide (5×10^{-6} M, 2 mL), TfOH in methanol (1×10^{-2} M, 2 μL) was added.

Computational details

DFT calculations were executed using the Gaussian09 program package.[4] Calculations were performed using the unrestricted Becke three-parameter hybrid functional with Lee–Yang–Parr correlation functional (B3LYP)[5] or unrestricted M06 functional[6] with the 6-31G(d) basis set. Cartesian coordinates of all the optimized geometries are listed in the supporting information. Frequency calculations were carried out to ensure that the optimized geometries were minima on the potential energy surface, in which no imaginary frequencies were observed in any of the compounds. TD-DFT calculations were performed using UB3LYP to calculate the first 15 doublet transitions. The solvent effect (dichloromethane) was considered using the PCM model.[7] The calculations were conducted with grid = ultrafine option without symmetry constraints.

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Table S1. Crystallographic data of $[Nd(tpyPyBTM')(NO_3)_3(H_2O)](CH_3CN)_2$

	$[Nd(tpyPyBTM')(NO_3)_3(H_2O)](CH_3CN)_2$
Empirical formula	$C_{37}\ H_{24}\ Cl_7\ N_9\ Nd\ O_{10}$
Fw / g mol^{-1}	1147.06
Crystal system	triclinic
Space group	*P*-1
Crystal size / mm	0.5×0.2×0.15
Temperature / K	113
a / Å	12.5288(7)
b / Å	13.8891(10)
c / Å	14.9538(11)
α / º	86.929(3)
β / º	67.150(3)
γ / º	68.829(3)
V / Å^3	2224.7(3)
Z	2
ρ_{calcd} / g cm^{-3}	1.712
λ / Å	0.7107
μ / mm^{-1}	1.652
Reflections collected	16291
Independent reflections	8891
Parameters	562
R_{int}	0.0133
[a]*R*1	0.0375
[b]*wR*2	0.1031
[c]GoF	1.070
CCDC No.	1535850

[a]$R_1 = \Sigma||F^o|-|F^c||/\Sigma|F^o|$ ($I>2\sigma(I)$). [b]$wR_2 = [\Sigma(w(F^{o2}-F^{c2})^2/\Sigma w(F^{o2})^2]^{1/2}$ ($I>2\sigma(I)$). [c]GOF = $[\Sigma(w(F^{o2}-F^{c2})^2/\Sigma(N^r-N^p)^2]$.

Table S2. Photophysical properties of *o*PyPyBTM′ and tpyPyBTM′ in dichloromethane

	ϕ	τ / ns	k_f / 10^7 s^{-1}	k_{nr} / 10^7 s^{-1}
*o*PyPyBTM′	0.0035 (2)	4.7	0.08	21
*o*PyPyBTM′ + H^+	0.037 (1)	4.9	0.75	20
tpyPyBTM′	0.009 (1)	7.8	0.12	13
tpyPyBTM′ + Zn^{2+}	0.030 (1)	7.5	0.41	13
tpyPyBTM′ + La^{3+}	0.0413 (6)	8.1	0.51	12

ϕ: absolute photoluminescence quantum yield

τ: fluorescence lifetime

k_f: rate of fluorescence (ϕ/τ)

k_{nr}: rate of non-radiative decay ($1/\tau - k_f$)

Table S3. Photophysical properties of Rhodamine 6G

Solvent	ϕ	τ / ns	k_f / 10^7 s^{-1}	k_{nr} / 10^7 s^{-1}
Ethanol	0.913 (1)	4.0	23	2.2
Ethyl iodide	0.217 (1)	1.7	13	46
Dichloromethane	0.830 (2)	3.6	23	4.7

ϕ: absolute photoluminescence quantum yield

τ: fluorescence lifetime

k_f: rate of fluorescence (ϕ/τ)

k_{nr}: rate of non-radiative decay ($1/\tau - k_f$)

Table S4. Photophysical properties of *o*PyPyBTM′ and tpyPyBTM′ in ethyl iodide

	ϕ	τ / ns	k_f / 10^7 s^{-1}	k_{nr} / 10^7 s^{-1}
*o*PyPyBTM′	0.0050 (5)	5.0	0.10	20
*o*PyPyBTM′ + H^+	0.0202 (3)	4.9	0.42	20
tpyPyBTM′	0.0054 (2)	7.9	0.07	13
tpyPyBTM′ + Zn^{2+}	0.017 (2)	7.4	0.23	13

ϕ: absolute photoluminescence quantum yield

τ: fluorescence lifetime

k_f: rate of fluorescence (ϕ/τ)

k_{nr}: rate of non-radiative decay ($1/\tau - k_f$)

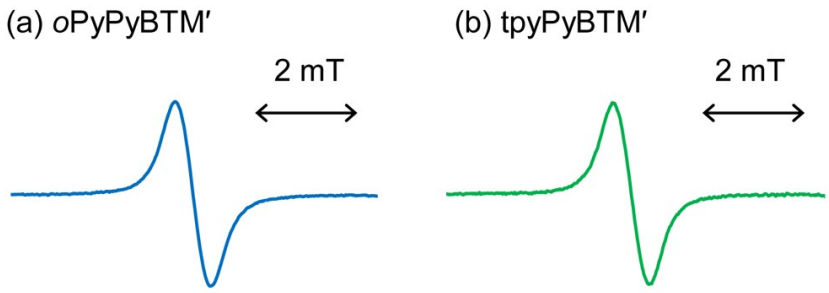

Fig. S1 ESR spectrum of (a) *o*PyPyBTM′ and (b) tpyPyBTM′ in toluene at room temperature.

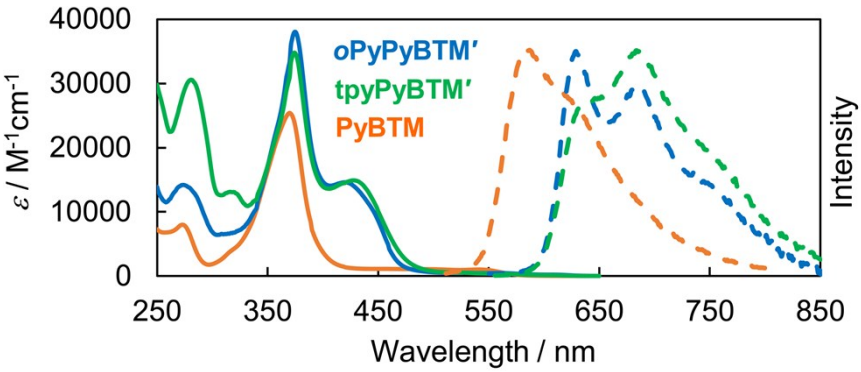

Fig. S2 Absorption and emission spectra of PyBTM (orange line), *o*PyPyBTM′ (blue line), and tpyPyBTM′ (green line) in dichloromethane.

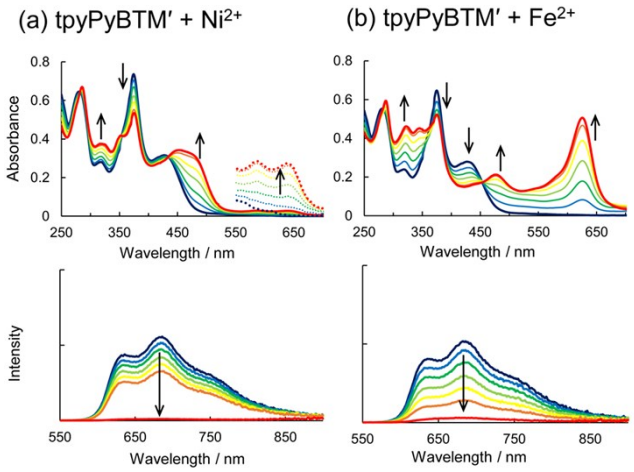

Fig. S3 Changes in the absorption and emission spectra of (a) tpyPyBTM′ during titration with $Ni^{II}(AcO)_2$, and (b) tpyPyBTM′ during titration with $Fe^{II}SO_4$ in dichloromethane. (navy: original spectra.; blue: 0.2 eq.; green: 0.4 eq.; yellow green: 0.6 eq.; yellow: 0.8 eq.; orange: 1.0 eq.; red: final spectra). In all emission spectra, excitation light was irradiated at the longest wavelength isosbestic point.

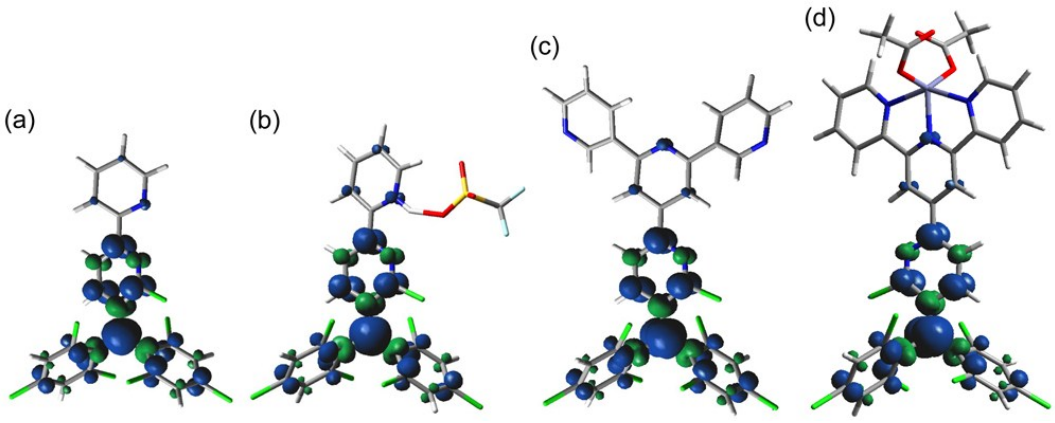

Fig. S4 Calculated spin density distributions of (a) *o*PyPyBTM′ (b) *o*PyPyBTM′·TfOH, (c) tpyPyBTM′, and (d) tpyPyBTM′·$Zn(OAc)_2$ using UB3LYP/6-31G. They are mainly on the central methyl group similar to those of the other PyBTM derivatives.

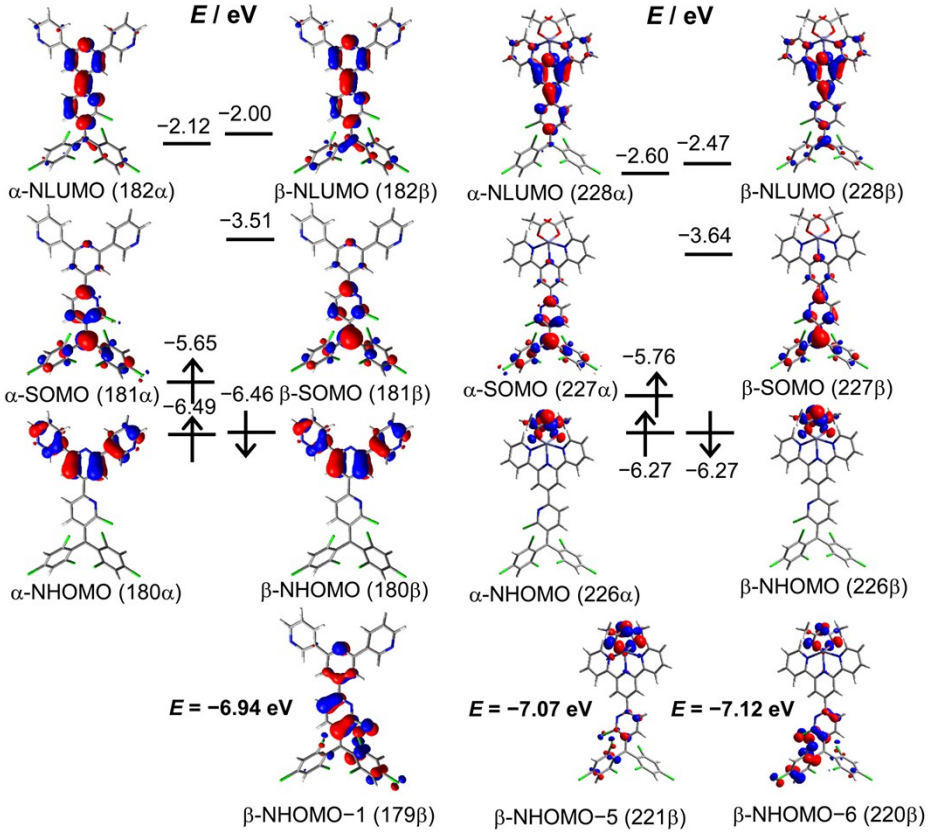

Fig. S5 Molecular orbitals of tpyPyBTM′ (left), and tpyPyBTM′·$Zn(OAc)_2$ (right) in dichloromethane calculated using DFT (UB3LYP/6-31G(d)). The solvent effect was treated with the PCM.

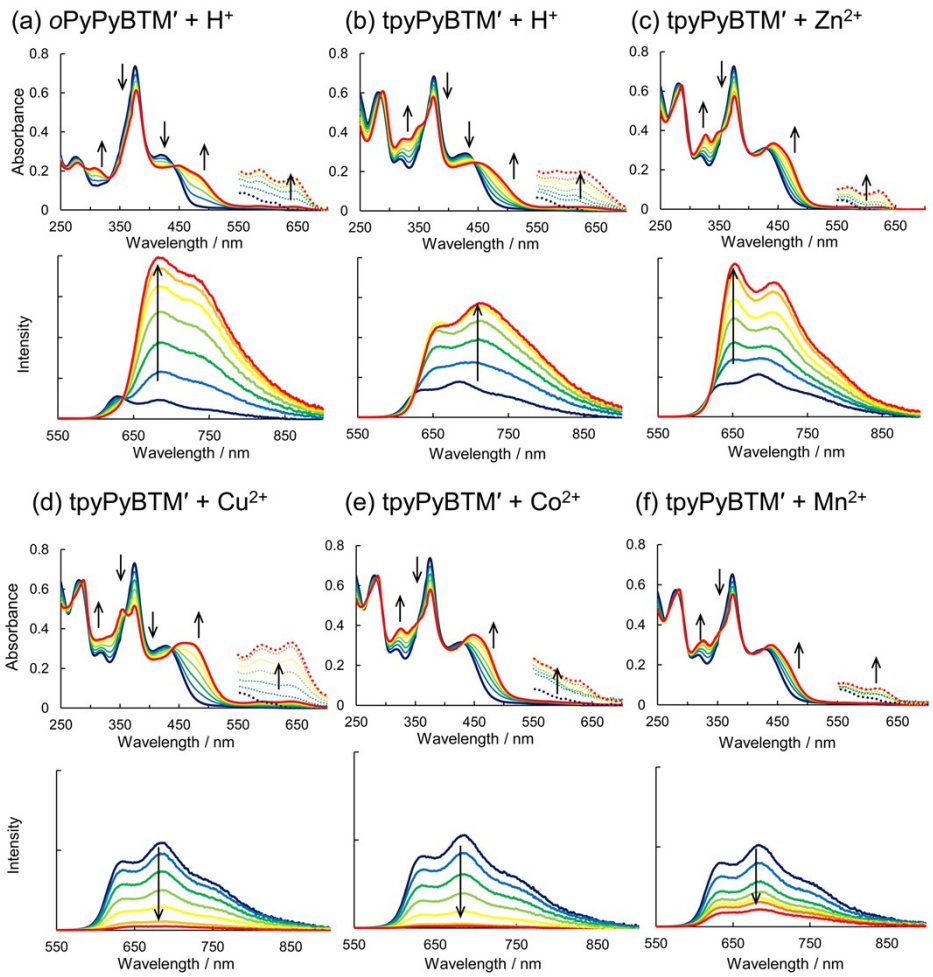

Fig. S6 (Enlarged **Fig. 2**) Changes in the absorption and emission spectra of (a) *o*PyPyBTM′ during titration with TfOH, (b) tpyPyBTM′ during titration with TfOH, (c) tpyPyBTM′ during titration with $Zn(OAc)_2$, (d) tpyPyBTM′ during titration with $Cu^{II}(OAc)_2$, (e) tpyPyBTM′ during titration with $Co^{II}(OAc)_2$, and (f) tpyPyBTM′ during titration with $Mn^{II}(OAc)_2$ in dichloromethane (navy: original spectra.; blue: 0.2 eq.; green: 0.4 eq.; yellow-green: 0.6 eq.; yellow: 0.8 eq.; orange: 1.0 eq.; red: final spectra). In all emission spectra, excitation light was irradiated at the longest wavelength isosbestic point. Details of the experiments are provided in the ESI†.

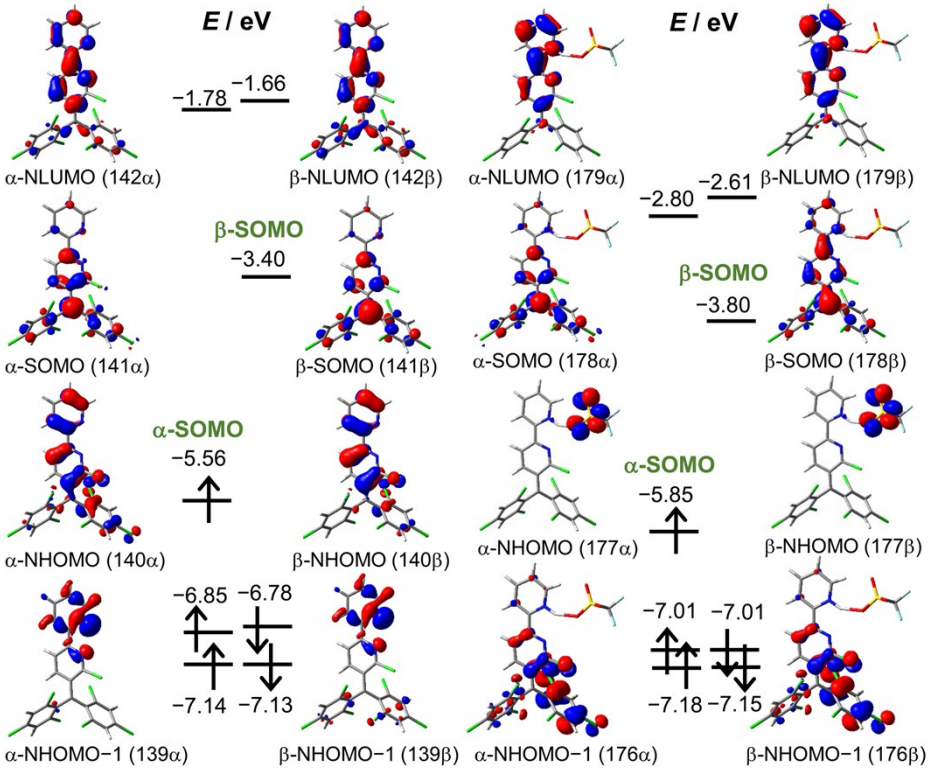

Fig. S7 (Enlarged **Fig. 3**) Molecular orbitals of *o*PyPyBTM′ (left), and *o*PyPyBTM′·TfOH (right) in dichloromethane calculated using DFT (UB3LYP/6-31G(d)). The solvent (dichloromethane) effect was treated with the PCM.

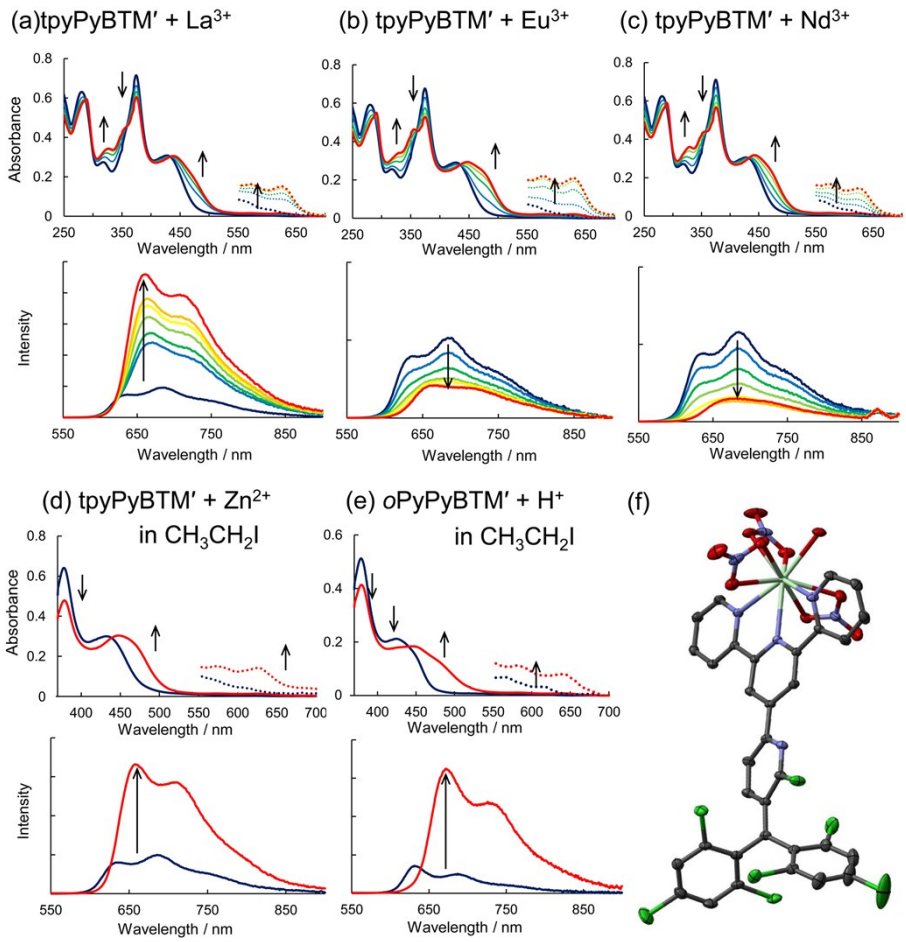

Fig. S8 (Enlarged **Fig. 4)** Changes in the absorption and emission spectra of (a) tpyPyBTM′ during titration with $La^{III}(TfO)_3$, (b) tpyPyBTM′ during titration with $Eu^{III}(TfO)_3$, (c) tpyPyBTM′ during titration with $Nd^{III}(NO_3)_3$ in dichloromethane, and change of absorption and emission spectra of (d) tpyPyBTM′ during titration with $Zn(OAc)_2$, and (e) *o*PyPyBTM′ during titration with TfOH in ethyl iodide. (navy: original spectra.; blue: 0.2 eq.; green: 0.4 eq.; yellow-green: 0.6 eq.; yellow: 0.8 eq.; orange: 1.0 eq.; red: final spectra). In all emission spectra, excitation light was irradiated at the longest wavelength isosbestic point. In ethyl iodide, absorption below 370 nm was not measured because of the solvent absorption. Details of the experiments are provided in the ESI†. (f) Molecular structure of $[Nd(tpyPyBTM′)(NO_3)_3(H_2O)]$ in crystalline $[Nd(tpyPyBTM′)(NO_3)_3(H_2O)](CH_3CN)_2$ with thermal ellipsoids at the 50% probability level. Hydrogen atoms are omitted for clarity.

Cartesian coordinates of all the optimized geometries by DFT calculation

*o*PyPyBTM′ in dichloromethane
UB3LYP / 6-31G(d)

Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	17	0	-0.045831	2.221734	2.185442
2	17	0	-2.853887	-0.260154	2.129084
3	17	0	-2.584545	0.465842	-2.399214
4	17	0	-3.567704	5.357057	-0.396609
5	17	0	1.093510	-1.972446	1.796058
6	17	0	0.176979	-2.110520	-2.114384
7	17	0	-3.737676	-5.116234	0.004411
8	6	0	-1.793545	3.637150	0.739693
9	1	0	-1.611823	4.407663	1.478442
10	6	0	-2.273704	1.633467	-1.125293
11	6	0	-1.069202	-2.260824	-0.885854
12	6	0	2.904874	1.179943	-0.815524
13	1	0	3.387302	1.933870	-1.426702
14	6	0	0.853969	0.122256	-0.014777
15	6	0	-1.781597	-3.454787	-0.896730
16	1	0	-1.533110	-4.231966	-1.608467
17	6	0	-2.827382	-3.620290	0.006039
18	6	0	-1.124300	2.420293	0.815068
19	6	0	-2.426169	-1.435039	0.896522
20	6	0	-3.161083	-2.616661	0.908562
21	1	0	-3.964418	-2.752828	1.621627
22	6	0	-2.963700	2.839029	-1.226069
23	1	0	-3.667234	2.999799	-2.033306
24	6	0	-1.350036	-1.194029	0.006859
25	6	0	-1.329863	1.360562	-0.105743
26	6	0	1.735417	-0.758338	0.675285
27	6	0	-2.713425	3.832588	-0.286383
28	6	0	-0.598004	0.075586	-0.005264
29	6	0	1.523691	1.125574	-0.754244
30	1	0	0.934538	1.840627	-1.318416
31	6	0	5.144114	0.190324	-0.164511
32	6	0	5.884193	1.356449	-0.416683
33	6	0	7.066793	-1.056991	0.014736
34	6	0	7.274852	1.280273	-0.451855
35	1	0	5.387464	2.310133	-0.558295
36	6	0	3.657307	0.219818	-0.121922
37	7	0	3.043430	-0.723324	0.620882
38	1	0	7.867524	2.171145	-0.637829
39	1	0	7.507747	-2.036851	0.190711
40	7	0	5.733086	-1.001106	0.053699
41	6	0	7.886164	0.047214	-0.235013
42	1	0	8.965853	-0.061712	-0.252595

*o*PyPyBTM′ in dichloromethane
UM06 / 6-31G(d)

Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	17	0	-0.067229	2.174184	2.166715
2	17	0	-2.794430	-0.264688	2.114379
3	17	0	-2.529239	0.442629	-2.410359
4	17	0	-3.629186	5.277372	-0.365701
5	17	0	1.044553	-1.851416	1.857948
6	17	0	0.191894	-2.071649	-2.122048
7	17	0	-3.659663	-5.116507	0.014304
8	6	0	-1.831056	3.591028	0.748875
9	1	0	-1.666357	4.359371	1.499128
10	6	0	-2.269165	1.607934	-1.137097
11	6	0	-1.041662	-2.248669	-0.898659
12	6	0	2.889986	1.144770	-0.879235
13	1	0	3.380934	1.865708	-1.527689
14	6	0	0.851052	0.132649	-0.038164
15	6	0	-1.737450	-3.447086	-0.903189
16	1	0	-1.485666	-4.226345	-1.617074
17	6	0	-2.771295	-3.619326	0.005951
18	6	0	-1.141722	2.390310	0.808995
19	6	0	-2.390008	-1.437297	0.886163
20	6	0	-3.109903	-2.622353	0.907992
21	1	0	-3.907743	-2.768545	1.630655
22	6	0	-2.980212	2.796498	-1.226816
23	1	0	-3.686689	2.956329	-2.036575
24	6	0	-1.330224	-1.192151	-0.009155
25	6	0	-1.331197	1.346749	-0.120798
26	6	0	1.719411	-0.709278	0.695123
27	6	0	-2.749928	3.777754	-0.274641
28	6	0	-0.594871	0.076525	-0.024698
29	6	0	1.511630	1.094466	-0.822537
30	1	0	0.915521	1.778927	-1.425036
31	6	0	5.113696	0.202843	-0.165431
32	6	0	5.839016	1.364023	-0.447661
33	6	0	7.036092	-1.014608	0.068271
34	6	0	7.225929	1.300312	-0.468968
35	1	0	5.331185	2.310191	-0.620540
36	6	0	3.633135	0.224080	-0.134334
37	7	0	3.023080	-0.681011	0.648613
38	1	0	7.813207	2.192038	-0.677787
39	1	0	7.488625	-1.985066	0.279818
40	7	0	5.706954	-0.970766	0.095503
41	6	0	7.844679	0.084985	-0.209611
42	1	0	8.927252	-0.013841	-0.215003

tpyPyBTM′ in dichloromethane
UB3LYP / 6-31G(d)

Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	17	0	-2.063037	1.586363	2.705220
2	17	0	-4.866854	-0.775765	1.949367
3	17	0	-4.505566	1.114206	-2.229609
4	17	0	-5.535389	5.307177	0.973413
5	17	0	-0.909889	-2.371562	1.230861
6	17	0	-1.757916	-1.465356	-2.575653
7	17	0	-5.721156	-4.892907	-1.395247
8	6	0	-3.783711	3.340773	1.650944
9	1	0	-3.618095	3.888240	2.570339
10	6	0	-4.223292	1.903028	-0.686976
11	6	0	-3.029398	-1.924120	-1.454056
12	6	0	0.946326	1.357459	-0.410904
13	1	0	1.430548	2.254067	-0.777828
14	6	0	-1.121228	0.134973	0.046412
15	6	0	-3.744426	-3.067466	-1.792249
16	1	0	-3.484496	-3.631426	-2.679229
17	6	0	-4.807700	-3.457360	-0.983632
18	6	0	-3.114761	2.144396	1.415792
19	6	0	-4.418683	-1.586975	0.458795
20	6	0	-5.155911	-2.724895	0.145746
21	1	0	-5.972897	-3.038519	0.783324
22	6	0	-4.911605	3.095794	-0.479799
23	1	0	-5.597818	3.467636	-1.230312
24	6	0	-3.325488	-1.128079	-0.317136
25	6	0	-3.301197	1.366778	0.243947
26	6	0	-0.254368	-0.904512	0.491326
27	6	0	-4.682157	3.804407	0.694236
28	6	0	-2.572188	0.096075	0.017542
29	6	0	-0.435699	1.295430	-0.384545
30	1	0	-1.013683	2.142587	-0.737700
31	6	0	3.169741	0.190245	-0.006894
32	6	0	3.831100	-1.002744	0.310803
33	6	0	3.955622	1.301915	-0.335630
34	6	0	5.230631	-1.040030	0.302335
35	1	0	3.245264	-1.881250	0.546862
36	6	0	5.351440	1.176309	-0.358808
37	1	0	3.502998	2.261947	-0.548094
38	7	0	5.971504	0.029231	-0.037402
39	6	0	1.687171	0.243688	0.011169
40	7	0	1.053852	-0.856895	0.467935
41	6	0	6.229155	2.320216	-0.719774
42	6	0	7.552387	2.382936	-0.259014
43	6	0	5.789017	3.369160	-1.542585
44	6	0	8.345314	3.469815	-0.611545
45	1	0	7.935390	1.585518	0.368693
46	7	0	6.539452	4.421246	-1.890119
47	1	0	4.785480	3.351091	-1.963271
48	6	0	7.794589	4.464833	-1.421118
49	1	0	9.370563	3.550689	-0.263962
50	1	0	8.385975	5.331891	-1.709510
51	6	0	5.980189	-2.276288	0.647227
52	6	0	7.287667	-2.476904	0.181005
53	6	0	5.430208	-3.281240	1.459189
54	6	0	7.959445	-3.646893	0.519041
55	1	0	7.753058	-1.718894	-0.439741
56	7	0	6.064051	-4.411507	1.793366
57	1	0	4.434088	-3.161296	1.880110
58	6	0	7.306439	-4.584961	1.320323
59	1	0	8.969094	-3.834300	0.166818
60	1	0	7.801444	-5.513736	1.598093

*o*PyPyBTM′·HSO_3CF_3 in dichloromethane
UB3LYP / 6-31G(d)

Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	17	0	2.155692	-1.939649	2.368642
2	17	0	3.448233	1.574280	2.192302
3	17	0	4.543341	0.296036	-2.084785
4	17	0	7.203682	-3.197782	1.014774
5	17	0	-0.666973	1.082426	0.957086
6	17	0	0.916262	1.196865	-2.712682
7	17	0	2.452880	5.954688	-0.753685
8	6	0	4.634247	-2.461763	1.510555
9	1	0	4.670812	-3.128997	2.362490
10	6	0	4.535418	-0.714351	-0.650289
11	6	0	1.653811	2.080592	-1.386346
12	6	0	-0.186944	-2.836361	-1.161856
13	1	0	-0.109333	-3.809439	-1.631020
14	6	0	0.907372	-0.818451	-0.318393
15	6	0	1.724654	3.459155	-1.548247
16	1	0	1.310761	3.927047	-2.432561
17	6	0	2.352409	4.218505	-0.565183
18	6	0	3.480022	-1.736513	1.236117
19	6	0	2.813022	2.237310	0.697822
20	6	0	2.900857	3.619370	0.563603
21	1	0	3.373214	4.213512	1.335708
22	6	0	5.706417	-1.425041	-0.400119
23	1	0	6.563949	-1.310510	-1.051177
24	6	0	2.190437	1.400975	-0.261998
25	6	0	3.373915	-0.828506	0.151162
26	6	0	-0.409122	-0.397828	0.045782
27	6	0	5.742115	-2.294749	0.684329
28	6	0	2.131292	-0.066165	-0.117268
29	6	0	0.959456	-2.102324	-0.910774
30	1	0	1.922454	-2.503786	-1.205683
31	6	0	-2.710851	-2.952175	-1.047200
32	6	0	-2.869622	-4.160659	-1.727546
33	6	0	-5.070902	-2.833768	-0.726292
34	6	0	-4.143201	-4.699022	-1.900302
35	1	0	-2.005765	-4.676586	-2.125342
36	6	0	-1.421212	-2.280821	-0.804806
37	7	0	-1.498829	-1.084648	-0.193077
38	1	0	-4.259325	-5.638264	-2.430901
39	1	0	-5.867443	-2.229406	-0.298784
40	6	0	-5.261318	-4.032045	-1.396013
41	1	0	-6.262389	-4.427305	-1.517001
42	7	0	-3.828119	-2.341164	-0.575902
43	8	0	-4.489624	-0.089036	0.914572
44	1	0	-3.748927	-1.440951	-0.060568
45	16	0	-5.905117	0.280175	1.212868
46	8	0	-6.176054	0.577785	2.631909
47	8	0	-6.904955	-0.582570	0.534085
48	6	0	-6.092086	1.919777	0.357799
49	9	0	-5.228120	2.816712	0.856280
50	9	0	-5.857163	1.794675	-0.958621
51	9	0	-7.336554	2.395902	0.519228

*o*PyPyBTM′·HSO_3CF_3 in dichloromethane
UM06 / 6-31G(d)

Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	17	0	1.901942	-1.846345	2.359737
2	17	0	3.313023	1.540509	2.139006
3	17	0	4.551034	0.126201	-2.008645
4	17	0	6.983468	-3.243328	1.380595
5	17	0	-0.659581	1.091965	0.859314
6	17	0	0.990344	1.089069	-2.817318
7	17	0	2.572071	5.849441	-0.952011
8	6	0	4.413401	-2.461054	1.689557
9	1	0	4.391386	-3.090787	2.574523
10	6	0	4.470535	-0.818442	-0.544243
11	6	0	1.701390	1.998633	-1.506577
12	6	0	-0.269985	-2.789573	-1.311055
13	1	0	-0.213242	-3.759714	-1.796161
14	6	0	0.849345	-0.828605	-0.411428
15	6	0	1.812808	3.365080	-1.704244
16	1	0	1.443325	3.820390	-2.618681
17	6	0	2.420909	4.132403	-0.720706
18	6	0	3.293584	-1.736666	1.314115
19	6	0	2.778161	2.186387	0.609813
20	6	0	2.907292	3.556760	0.443283
21	1	0	3.362911	4.164390	1.220040
22	6	0	5.610607	-1.529118	-0.196754
23	1	0	6.510174	-1.457667	-0.801685
24	6	0	2.177102	1.345794	-0.349006
25	6	0	3.273020	-0.882520	0.192089
26	6	0	-0.451039	-0.377908	-0.065580
27	6	0	5.565930	-2.344303	0.924341
28	6	0	2.076637	-0.104691	-0.166058
29	6	0	0.888686	-2.093693	-1.022993
30	1	0	1.854370	-2.511454	-1.303112
31	6	0	-2.785785	-2.838832	-1.235652
32	6	0	-2.975497	-3.994903	-1.981314
33	6	0	-5.129533	-2.680256	-0.880467
34	6	0	-4.261354	-4.487065	-2.169787
35	1	0	-2.125519	-4.505819	-2.421938
36	6	0	-1.488239	-2.207063	-0.965337
37	7	0	-1.550937	-1.025836	-0.334331
38	1	0	-4.407974	-5.390924	-2.755429
39	1	0	-5.906547	-2.077974	-0.405468
40	6	0	-5.354821	-3.826900	-1.617741
41	1	0	-6.367462	-4.191384	-1.753551
42	7	0	-3.876953	-2.232004	-0.717226
43	8	0	-4.385824	-0.177141	1.040622
44	1	0	-3.761309	-1.371834	-0.138488
45	16	0	-5.768980	0.285831	1.297180
46	8	0	-6.106520	0.449165	2.711856
47	8	0	-6.784810	-0.382689	0.466095
48	6	0	-5.746024	1.999809	0.644187
49	9	0	-4.837928	2.728683	1.283515
50	9	0	-5.449747	1.997851	-0.652218
51	9	0	-6.936307	2.569282	0.803729

tpyPyBTM′·Zn($OCOCH_3$)$_2$ in dichloromethane
UB3LYP / 6-31G(d)

Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	17	0	4.004144	1.465909	-2.767533
2	17	0	2.803983	-2.401910	-1.156848
3	17	0	6.428823	1.168714	2.189136
4	17	0	6.778422	-0.901159	-1.900054
5	17	0	3.637875	-1.353607	2.632904
6	17	0	7.533405	5.201516	-1.189129
7	17	0	7.555982	-4.884461	1.620394
8	7	0	-5.614394	1.769024	1.274854
9	7	0	-4.024384	0.108291	0.013710
10	7	0	-5.464314	-1.694281	-1.238723
11	7	0	0.854496	-0.849020	-0.438913
12	6	0	-3.316663	-0.839601	-0.621276
13	6	0	5.234945	1.333505	-0.296675
14	6	0	-2.008072	1.201257	0.672126
15	6	0	3.037457	0.139294	-0.054269
16	6	0	-6.505115	2.573792	1.865919
17	6	0	-1.922836	-0.809934	-0.642036
18	6	0	2.364810	1.324390	0.324988
19	6	0	-3.401343	1.110218	0.651670
20	6	0	-6.278831	-2.576242	-1.830037
21	6	0	6.311850	-1.642145	-0.379382
22	6	0	2.162353	-0.908966	-0.464721
23	6	0	0.982678	1.399707	0.351414
24	6	0	6.163329	1.894372	0.613315
25	6	0	-4.782429	4.077650	2.579209
26	6	0	-4.304664	2.081741	1.327291
27	6	0	-4.131561	-1.887543	-1.293524
28	6	0	-6.133296	3.742649	2.530874
29	6	0	0.235977	0.271445	-0.013779
30	6	0	5.221619	-1.135666	0.370923
31	6	0	-5.802777	-3.706360	-2.495440
32	6	0	-4.427029	-3.917236	-2.546450
33	6	0	4.487898	0.083925	-0.018737
34	6	0	6.870856	3.065915	0.356431
35	6	0	-3.851567	3.235893	1.972174
36	6	0	-3.575601	-2.994271	-1.941016
37	6	0	5.751103	3.236910	-1.786062
38	6	0	7.030306	-2.776430	-0.014274
39	6	0	6.655277	3.726752	-0.847825
40	6	0	-1.245621	0.230185	0.009079
41	6	0	5.062558	2.062767	-1.501294
42	6	0	5.604407	-3.016247	1.929010
43	6	0	4.907641	-1.878374	1.538725
44	6	0	6.665871	-3.455196	1.143350
45	1	0	-1.526420	2.002042	1.216715
46	1	0	-7.535618	2.238660	1.812282
47	1	0	-1.345364	-1.567540	-1.153725
48	1	0	2.951505	2.183378	0.631618
49	1	0	-7.335287	-2.335240	-1.777773
50	1	0	0.503942	2.324657	0.649611
51	1	0	-4.451197	4.980417	3.083088
52	1	0	-6.888021	4.367362	2.996222
53	1	0	-6.498438	-4.396742	-2.960085
54	1	0	-4.015961	-4.785610	-3.051952
55	1	0	7.561721	3.458737	1.091789
56	1	0	-2.797637	3.485203	2.000869
57	1	0	-2.502893	-3.142509	-1.973456
58	1	0	5.596235	3.746704	-2.728712
59	1	0	7.845786	-3.128758	-0.633289
60	1	0	5.332207	-3.538184	2.837769
61	30	0	-6.167105	0.008130	0.017712
62	8	0	-6.889849	-1.179192	1.375548
63	8	0	-6.998863	1.139292	-1.322303
64	6	0	-7.953165	-0.831695	2.035159
65	6	0	-8.012606	0.704207	-2.007758
66	8	0	-8.537678	-0.411017	-1.883374
67	8	0	-8.585232	0.221669	1.872695
68	6	0	-8.404403	-1.856896	3.071571
69	1	0	-9.289797	-1.507009	3.606383
70	1	0	-8.629196	-2.809562	2.579269
71	1	0	-7.596695	-2.047764	3.786912
72	6	0	-8.550002	1.705502	-3.026430
73	1	0	-7.763797	1.969049	-3.742893
74	1	0	-9.407125	1.293382	-3.563067
75	1	0	-8.846531	2.630640	-2.520186

Extracted results of TD-DFT calculation.

*o*PyPyBTM′ in dichloromethane
UB3LYP / 6-31G(d)

Excitation energies and oscillator strengths:

Excited State 1: 2.227-A 2.4483 eV 506.41 nm f=0.0397 <S**2>=0.990
141A ->142A -0.39989
140B ->141B 0.86316
This state for optimization and/or second-order correction.
Total Energy, E(TD-HF/TD-KS) = -4213.21682106
Copying the excited state density for this state as the 1-particle RhoCI density.

Excited State 2: 2.268-A 2.7715 eV 447.35 nm f=0.0219 <S**2>=1.036
140A ->143A -0.10287
141A ->142A 0.14463
141A ->143A 0.35310
135B ->143B -0.10058
136B ->141B -0.18574
137B ->141B 0.78620
138B ->141B -0.14012
139B ->141B 0.25035

Excited State 3: 2.141-A 2.8982 eV 427.80 nm f=0.0643 <S**2>=0.896
141A ->142A 0.44447
135B ->141B -0.10095
137B ->141B 0.14739
138B ->141B 0.75599
139B ->141B -0.29640
140B ->141B 0.22870

Excited State 4: 2.182-A 2.9925 eV 414.32 nm f=0.1601 <S**2>=0.940
141A ->142A 0.50578
133B ->141B 0.15414
135B ->141B 0.21545
136B ->141B -0.18299
137B ->141B -0.32338
139B ->141B 0.59831
140B ->141B 0.26691

Excited State 5: 2.195-A 2.9990 eV 413.42 nm f=0.2035 <S**2>=0.955
140A ->142A -0.10632
141A ->142A -0.45149
141A ->143A 0.14102
135B ->141B 0.51025
136B ->141B -0.20523
138B ->141B 0.52631
139B ->141B 0.21883
140B ->141B -0.20845

Excited State 6: 2.118-A 3.0268 eV 409.62 nm f=0.0038 <S**2>=0.871
141A ->144A -0.13966
135B ->141B 0.16824
136B ->141B 0.89113
137B ->141B 0.18863
138B ->141B 0.11037
139B ->141B 0.24380

Excited State 7: 2.305-A 3.1055 eV 399.24 nm f=0.0360 <S**2>=1.078
137A ->143A 0.11833
141A ->142A 0.20364
141A ->143A 0.13029
141A ->148A -0.13631
133B ->141B 0.15183
134B ->141B -0.12832
135B ->141B 0.58612
138B ->141B -0.25551
139B ->141B -0.55355
139B ->142B -0.14652
140B ->141B 0.12974

Excited State 8: 2.248-A 3.2576 eV 380.60 nm f=0.1906 <S**2>=1.013
140A ->143A -0.10276
141A ->143A 0.79622
135B ->141B -0.20333
136B ->141B 0.20462
137B ->141B -0.39583

Excited State 9: 2.146-A 3.3796 eV 366.86 nm f=0.0576 <S**2>=0.902
141A ->142A 0.11224
141A ->144A -0.39918
141A ->145A 0.16181
141A ->146A -0.17462
133B ->141B -0.43411
134B ->141B 0.69184
140B ->141B 0.10076

Excited State 10: 2.233-A 3.4397 eV 360.46 nm f=0.0627 <S**2>=0.996
141A ->144A 0.61228
141A ->145A -0.16153
141A ->146A 0.15046
132B ->141B -0.19115
133B ->141B 0.24432
134B ->141B 0.58279
140B ->141B -0.13265

Excited State 11: 2.474-A 3.5253 eV 351.70 nm f=0.0188 <S**2>=1.280
135A ->142A 0.12773
140A ->142A 0.18708
141A ->144A -0.54242
141A ->145A -0.14842
132B ->141B -0.11936
133B ->141B 0.62261
134B ->141B 0.13354
140B ->142B -0.20136

*o*PyPyBTM′ in dichloromethane
UM06 / 6-31G(d)

Excitation energies and oscillator strengths:

Excited State 1: 2.387-A 2.5404 eV 488.06 nm f=0.0176 <S**2>=1.174
140A ->142A -0.12840
141A ->142A -0.45517
131B ->141B -0.10418
134B ->141B 0.12607
140B ->141B 0.79075
140B ->142B 0.13920
This state for optimization and/or second-order correction.
Total Energy, E(TD-HF/TD-KS) = -4212.29979082
Copying the excited state density for this state as the 1-particle RhoCI density.

Excited State 2: 2.511-A 2.8193 eV 439.77 nm f=0.0088 <S**2>=1.327
140A ->143A 0.14199
141A ->142A -0.11919
141A ->143A -0.41839
135B ->143B 0.15402
136B ->141B 0.13996
138B ->141B 0.43341
139B ->141B 0.59582
139B ->142B -0.12510

Excited State 3: 2.537-A 3.0249 eV 409.88 nm f=0.0969 <S**2>=1.359
136A ->144A -0.10820
138A ->143A -0.11558
139A ->143A -0.13213
140A ->142A -0.20090
141A ->142A -0.38187
141A ->143A 0.15161
141A ->148A -0.12330
135B ->141B 0.52670
136B ->144B 0.12520
137B ->141B 0.14741
138B ->141B 0.34338
139B ->141B -0.20146
139B ->143B 0.10531
140B ->141B -0.23893
140B ->142B 0.18131

Excited State 4: 2.386-A 3.0715 eV 403.66 nm f=0.2241 <S**2>=1.173
138A ->143A -0.10008
139A ->143A -0.14783
141A ->142A 0.60562
141A ->148A -0.15776
134B ->141B 0.18415
135B ->141B 0.34263
136B ->144B 0.10818
137B ->141B 0.19837
139B ->141B 0.18431
139B ->143B 0.13286
140B ->141B 0.41878

Excited State 5: 2.155-A 3.1620 eV 392.11 nm f=0.1258 <S**2>=0.910
141A ->142A 0.29855
141A ->143A -0.15241
141A ->145A -0.14598
135B ->141B -0.21228
138B ->141B 0.61864
139B ->141B -0.57720
140B ->141B 0.15896

Excited State 6: 2.174-A 3.2404 eV 382.62 nm f=0.0063 <S**2>=0.931
141A ->143A -0.12343
141A ->144A -0.23613
136B ->141B 0.86979
138B ->141B -0.27015
139B ->141B -0.15422

Excited State 7: 2.283-A 3.3441 eV 370.76 nm f=0.1990 <S**2>=1.053
140A ->143A -0.10650
141A ->143A 0.63660
135B ->141B -0.15638
136B ->141B 0.27811
137B ->141B -0.28753
138B ->141B 0.33699
139B ->141B 0.36964

Excited State 8: 2.339-A 3.4143 eV 363.13 nm f=0.0222 <S**2>=1.118
141A ->143A 0.17154
133B ->141B 0.16839
135B ->141B -0.19501
136B ->141B 0.16980
137B ->141B 0.83662
137B ->142B 0.26735
138B ->141B 0.12013

Excited State 9: 2.334-A 3.5230 eV 351.92 nm f=0.0947 <S**2>=1.112
141A ->143A -0.12794
141A ->144A 0.68508
141A ->145A -0.27150
141A ->146A 0.29672
141A ->147A 0.11218
133B ->141B -0.23028
134B ->141B 0.26256
135B ->141B 0.14703
136B ->141B 0.16482
140B ->141B -0.16034

*o*PyPyBTM′·HSO_3CF_3 in dichloromethane
UB3LYP / 6-31G(d)

Excitation energies and oscillator strengths:

Excited State 1: 2.237-A 2.2568 eV 549.38 nm f=0.0491 <S**2>=1.001
178A ->179A 0.80699
178A ->180A 0.13187
172B ->178B 0.19300
173B ->178B 0.16053
174B ->178B -0.13271
176B ->178B 0.42524
This state for optimization and/or second-order correction.
Total Energy, E(TD-HF/TD-KS) = -5175.27634660
Copying the excited state density for this state as the 1-particle RhoCI density.

Excited State 2: 2.102-A 2.5434 eV 487.47 nm f=0.2265 <S**2>=0.855
178A ->179A -0.41277
173B ->178B -0.14558
175B ->178B 0.30439
176B ->178B 0.79919
176B ->179B 0.11350

Excited State 3: 2.122-A 2.6318 eV 471.09 nm f=0.0603 <S**2>=0.876
178A ->179A 0.17106
178A ->181A -0.15186
173B ->178B -0.31497
174B ->178B 0.11395
175B ->178B 0.81767
175B ->179B 0.13292
176B ->178B -0.32349

Excited State 4: 2.126-A 2.7386 eV 452.73 nm f=0.1570 <S**2>=0.880
178A ->179A -0.22273
178A ->181A 0.11936
173B ->178B 0.71827
174B ->178B -0.42007
175B ->178B 0.39304
176B ->178B -0.10865
177B ->178B -0.12076

Excited State 5: 2.156-A 2.7825 eV 445.59 nm f=0.0010 <S**2>=0.912
174B ->178B -0.10357
177B ->178B 0.98520

Excited State 6: 2.086-A 2.7861 eV 445.02 nm f=0.0068 <S**2>=0.838
173B ->178B 0.46824
174B ->178B 0.85369
174B ->179B 0.10455

Excited State 7: 2.365-A 2.9749 eV 416.76 nm f=0.0320 <S**2>=1.148
173A ->179A 0.10806
176A ->179A 0.15736
178A ->179A -0.22243
178A ->180A 0.13200
178A ->182A 0.10308
178A ->185A -0.15452
178A ->188A -0.11166
172B ->178B 0.83291
176B ->179B -0.11211

Excited State 8: 2.419-A 3.2433 eV 382.27 nm f=0.1239 <S**2>=1.213
173A ->179A -0.11307
176A ->179A -0.15933
178A ->180A 0.82407
178A ->181A 0.23305
178A ->182A 0.16447
178A ->185A 0.12843
173B ->178B -0.14291
174B ->178B 0.10413
176B ->179B 0.12718

Excited State 9: 2.616-A 3.2932 eV 376.49 nm f=0.1180 <S**2>=1.461
174A ->184A 0.11410
175A ->183A 0.10167
178A ->180A -0.16859
178A ->181A 0.71559
178A ->182A -0.27270
172B ->181B -0.10812
173B ->178B -0.20878
175B ->178B 0.18521
175B ->179B -0.10245
176B ->178B 0.11279
176B ->181B 0.12795

Excited State 10: 2.599-A 3.4041 eV 364.22 nm f=0.0018 <S**2>=1.439
173A ->179A -0.15353
176A ->179A -0.26961
178A ->179A 0.13526
178A ->180A -0.32854
178A ->181A 0.20704
178A ->182A 0.49473
178A ->183A 0.14604
167B ->178B -0.15823
168B ->178B -0.39197
172B ->178B 0.20719
172B ->179B 0.10299
176B ->179B 0.19461

Excited State 11: 2.622-A 3.4920 eV 355.05 nm f=0.0299 <S**2>=1.469
167A ->179A 0.10591
173A ->179A 0.17414
176A ->179A 0.26195
178A ->181A 0.16485
178A ->182A 0.40061
165B ->178B -0.17346
166B ->178B -0.10918
167B ->178B 0.33964
168B ->178B -0.33923
169B ->178B 0.24717
171B ->178B 0.15165
172B ->178B -0.30036
172B ->179B -0.12511
173B ->179B -0.16122
174B ->179B 0.10517
176B ->179B -0.25778

*o*PyPyBTM′·HSO_3CF_3 in dichloromethane
UM06 / 6-31G(d)

Excitation energies and oscillator strengths:

Excited State 1: 2.386-A 2.3530 eV 526.91 nm f=0.0359 <S**2>=1.173
177A ->179A 0.13542
178A ->179A 0.75332
178A ->180A 0.16106
172B ->178B 0.21236
173B ->178B -0.10428
174B ->178B -0.19525
177B ->178B -0.44174
This state for optimization and/or second-order correction.
Total Energy, E(TD-HF/TD-KS) = -5174.14794121
Copying the excited state density for this state as the 1-particle RhoCI density.

Excited State 2: 2.242-A 2.6738 eV 463.71 nm f=0.1509 <S**2>=1.006
178A ->179A 0.34625
178A ->181A 0.17009
178A ->182A -0.12980
173B ->178B -0.18556
176B ->178B -0.43829
176B ->179B -0.12648
177B ->178B 0.66336
177B ->179B 0.15874

Excited State 3: 2.238-A 2.7768 eV 446.50 nm f=0.2066 <S**2>=1.003
178A ->179A 0.37595
178A ->181A -0.21849
173B ->178B 0.30083
174B ->178B 0.31869
176B ->178B 0.55230
176B ->179B 0.13609
177B ->178B 0.43901

Excited State 4: 2.160-A 2.9446 eV 421.06 nm f=0.0591 <S**2>=0.917
178A ->179A -0.12868
178A ->181A 0.10699
173B ->178B -0.46437
174B ->178B -0.51704
175B ->178B -0.10529
176B ->178B 0.57978
176B ->179B 0.10797
177B ->178B 0.20621

Excited State 5: 2.660-A 2.9957 eV 413.87 nm f=0.0630 <S**2>=1.519
173A ->181A -0.10573
174A ->179A -0.10331
176A ->181A -0.13295
177A ->179A 0.18544
178A ->179A -0.25942
178A ->185A 0.19261
178A ->188A -0.11440
172B ->178B 0.70344
173B ->178B 0.11755
176B ->181B 0.10951
177B ->179B 0.17203

Excited State 6: 2.143-A 3.0283 eV 409.41 nm f=0.0049 <S**2>=0.898
172B ->178B -0.10697
173B ->178B 0.67485
173B ->179B 0.12067
174B ->178B -0.65333
174B ->179B -0.13220
177B ->178B 0.10988

Excited State 7: 2.680-A 3.2983 eV 375.90 nm f=0.1479 <S**2>=1.545
173A ->184A -0.12494
174A ->183A -0.12949
174A ->184A 0.11882
176A ->183A 0.10226
177A ->182A 0.10843
178A ->180A 0.10978
178A ->181A 0.61752
178A ->182A -0.19656
172B ->181B -0.10800
173B ->178B 0.31170
173B ->184B -0.12710
174B ->178B 0.20152
176B ->178B 0.28274
177B ->178B -0.13461
177B ->182B 0.10459

Excited State 8: 2.569-A 3.3643 eV 368.53 nm f=0.0624 <S**2>=1.400
177A ->179A -0.19184
177A ->181A 0.10102
178A ->180A 0.64304
178A ->181A 0.10675
178A ->182A 0.38055
178A ->183A 0.16545
178A ->185A -0.13251
172B ->178B 0.21603
172B ->179B 0.10079
174B ->178B 0.13978
177B ->178B 0.16797
177B ->179B -0.15385

Excited State 9: 2.235-A 3.3793 eV 366.89 nm f=0.0004 <S**2>=0.998
175B ->178B 0.97969
175B ->179B -0.13265

tpyPyBTM′ in dichloromethane
UB3LYP / 6-31G(d)

Excitation energies and oscillator strengths:

Excited State 1: 2.312-A 2.4190 eV 512.54 nm f=0.0057 <S**2>=1.087
179A ->182A 0.11645
181A ->182A 0.52424
181A ->186A 0.11564
174B ->181B -0.12768
179B ->181B 0.74721
This state for optimization and/or second-order correction.
Total Energy, E(TD-HF/TD-KS) = -4707.41737881
Copying the excited state density for this state as the 1-particle RhoCI density.

Excited State 2: 2.214-A 2.4711 eV 501.74 nm f=0.0047 <S**2>=0.975
180A ->182A -0.11204
180B ->181B 0.97199
180B ->182B 0.14475

Excited State 3: 2.248-A 2.7285 eV 454.40 nm f=0.0820 <S**2>=1.013
181A ->182A 0.31236
181A ->184A 0.26899
173B ->181B -0.27767
174B ->181B -0.43123
176B ->181B 0.54824
177B ->181B 0.20904
178B ->181B -0.15490
179B ->181B -0.25988

Excited State 4: 2.156-A 2.8078 eV 441.58 nm f=0.2027 <S**2>=0.912
181A ->182A -0.48957
181A ->184A 0.12336
171B ->181B 0.16721
176B ->181B 0.56347
177B ->181B -0.31102
178B ->181B 0.16366
179B ->181B 0.43306

Excited State 5: 2.113-A 2.9159 eV 425.20 nm f=0.2392 <S**2>=0.866
181A ->182A 0.36331
181A ->184A -0.11290
181A ->187A 0.10138
171B ->181B -0.17328
173B ->181B 0.25852
174B ->181B 0.56768
176B ->181B 0.46603
177B ->181B -0.31603
178B ->181B 0.10079
179B ->181B -0.18202

Excited State 6: 2.102-A 2.9621 eV 418.56 nm f=0.0081 <S**2>=0.854
181A ->185A -0.12147
173B ->181B 0.85540
174B ->181B -0.42652
176B ->181B 0.11314

Excited State 7: 2.698-A 3.0132 eV 411.47 nm f=0.0950 <S**2>=1.569
179A ->182A -0.17127
180A ->183A -0.30022
181A ->182A 0.37162
181A ->186A 0.17229
181A ->193A 0.13301
171B ->181B 0.51906
172B ->181B 0.10936
174B ->181B -0.18378
177B ->181B -0.20840
178B ->181B 0.16048
179B ->181B -0.16161
179B ->182B -0.14662
180B ->183B 0.28147

Excited State 8: 2.947-A 3.1175 eV 397.71 nm f=0.0002 <S**2>=1.920
177A ->182A -0.10533
180A ->183A 0.40949
180A ->185A -0.11386
181A ->193A 0.10124
169B ->181B 0.15692
171B ->181B 0.56363
172B ->181B 0.14910
177B ->182B 0.10309
180B ->183B -0.43025

Excited State 9: 2.364-A 3.2520 eV 381.26 nm f=0.0287 <S**2>=1.148
172A ->182A -0.11054
181A ->183A 0.13528
181A ->184A -0.30923
172B ->181B 0.54581
172B ->182B 0.20116
175B ->181B 0.37258
176B ->181B 0.13763
178B ->181B -0.50867
179B ->181B 0.12422
180B ->183B 0.10068

Excited State 10: 2.311-A 3.2656 eV 379.67 nm f=0.0144 <S**2>=1.085
181A ->183A -0.15303
181A ->184A 0.20370
168B ->181B -0.12660
171B ->181B -0.23533
172B ->181B 0.45921
172B ->182B 0.17582
175B ->181B 0.32208
176B ->181B -0.15069
177B ->181B -0.20086
178B ->181B 0.55980
179B ->181B -0.16841

Excited State 11: 2.279-A 3.2689 eV 379.29 nm f=0.1355 <S**2>=1.048
181A ->183A -0.17190
181A ->184A 0.66179
173B ->181B 0.21890
174B ->181B 0.25059
176B ->181B -0.19340
177B ->181B -0.18915
178B ->181B -0.45759

Excited State 12: 2.197-A 3.2976 eV 375.98 nm f=0.0112 <S**2>=0.957
180A ->183A -0.12610
181A ->184A 0.18752
171B ->181B 0.10760

172B ->181B 0.15256
173B ->181B 0.13841
174B ->181B 0.33995
176B ->181B 0.13442
177B ->181B 0.76402
178B ->181B 0.29125
179B ->181B 0.17622
180B ->183B 0.13699

Excited State 13: 3.328-A 3.3268 eV 372.69 nm f=0.0021 <S**2>=2.520
177A ->183A -0.14368
180A ->182A 0.62084
180A ->186A -0.20803
181A ->183A 0.10313
172B ->181B -0.15825
177B ->183B 0.13991
179B ->183B 0.10177
180B ->181B 0.17971
180B ->182B -0.50999
180B ->186B 0.19568

Excited State 14: 2.227-A 3.3655 eV 368.40 nm f=0.0885 <S**2>=0.990
181A ->182A -0.10308
181A ->183A 0.61423
181A ->184A 0.15917
181A ->185A 0.42211
181A ->186A -0.10216
181A ->187A 0.19467
181A ->188A 0.22027
167B ->181B 0.11966
168B ->181B 0.33115
174B ->181B -0.13341
175B ->181B 0.17412
177B ->181B -0.11634
178B ->181B 0.13284

Excited State 15: 2.149-A 3.3872 eV 366.04 nm f=0.0051 <S**2>=0.905
181A ->183A -0.12006
172B ->181B -0.46860
172B ->182B -0.12090
174B ->181B 0.10905
175B ->181B 0.83297

Excited State 16: 2.236-A 3.4578 eV 358.57 nm f=0.0119 <S**2>=1.000
181A ->183A -0.20800
181A ->184A -0.11486
181A ->185A -0.14425
181A ->186A 0.11087
167B ->181B -0.11625
168B ->181B 0.86124
170B ->181B -0.12175
171B ->181B -0.13554

tpyPyBTM′·Zn(OCOCH$_3$)$_2$ in dichloromethane
UB3LYP / 6-31G(d)

Excitation energies and oscillator strengths:

Excited State 1: 2.134-A 2.3546 eV 526.55 nm f=0.0001 <S**2>=0.889
227A ->228A -0.10216
226B ->227B 0.98573
This state for optimization and/or second-order correction.
Total Energy, E(TD-HF/TD-KS) = -6943.68456371
Copying the excited state density for this state as the 1-particle RhoCI density.

Excited State 2: 2.298-A 2.3657 eV 524.09 nm f=0.0245 <S**2>=1.071
227A ->228A 0.70841
227A ->230A -0.20428
214B ->227B -0.15110
217B ->227B -0.16803
220B ->227B -0.39362
221B ->227B 0.34165
226B ->227B 0.14437

Excited State 3: 2.132-A 2.4185 eV 512.65 nm f=0.0000 <S**2>=0.886
225B ->227B 0.99571

Excited State 4: 2.130-A 2.6436 eV 468.99 nm f=0.2801 <S**2>=0.884
227A ->228A 0.46850
227A ->231A 0.14132
216B ->227B -0.17620
217B ->227B -0.15373
218B ->227B -0.30423
220B ->227B 0.58822
221B ->227B -0.40231
222B ->227B 0.12859

Excited State 5: 2.421-A 2.7096 eV 457.57 nm f=0.0046 <S**2>=1.215
222A ->228A -0.19585
227A ->229A -0.10203
217B ->227B 0.10759
218B ->227B 0.20344
222B ->227B 0.82449
222B ->228B 0.20731
223B ->227B -0.18604
224B ->227B -0.29433

Excited State 6: 2.166-A 2.7273 eV 454.61 nm f=0.1388 <S**2>=0.923
227A ->228A 0.27179
227A ->231A -0.19681
216B ->227B 0.27243
217B ->227B 0.27371
218B ->227B 0.69490
218B ->228B -0.10568
220B ->227B 0.26577
221B ->227B -0.23366
222B ->227B -0.19511
223B ->227B 0.10787

Excited State 7: 2.127-A 2.8401 eV 436.55 nm f=0.1529 <S**2>=0.881
227A ->228A 0.22526
227A ->231A -0.10506
216B ->227B 0.39503
217B ->227B 0.62365
218B ->227B -0.51994
220B ->227B -0.17188
223B ->227B 0.14955

Excited State 8: 2.178-A 2.8808 eV 430.38 nm f=0.0003 <S**2>=0.936
219B ->227B -0.12291
222B ->227B 0.37835
223B ->227B 0.38480
224B ->227B 0.81534
224B ->228B 0.10804

Excited State 9: 2.193-A 2.8959 eV 428.14 nm f=0.0021 <S**2>=0.953
216B ->227B -0.45988
217B ->227B 0.13077
218B ->227B 0.11292
223B ->227B 0.74210
224B ->227B -0.35002

Excited State 10: 2.111-A 2.8989 eV 427.70 nm f=0.0045 <S**2>=0.864
216B ->227B 0.63495
217B ->227B -0.58410
223B ->227B 0.40344
224B ->227B -0.21029

Excited State 11: 3.171-A 2.9595 eV 418.93 nm f=0.0185 <S**2>=2.264
215A ->228A -0.17183
222A ->229A 0.49000
227A ->228A -0.20477
214B ->227B -0.26055
215B ->227B 0.22540
215B ->228B 0.15885
217B ->227B 0.10584
222B ->229B -0.45542
223B ->227B 0.19100
223B ->229B 0.10101
224B ->227B -0.15548
224B ->229B 0.14181

Excited State 12: 2.470-A 3.0663 eV 404.34 nm f=0.0136 <S**2>=1.275
222A ->229A 0.23294
227A ->229A -0.40219
227A ->230A -0.13788
227A ->232A -0.10436
227A ->237A 0.10536
214B ->227B 0.65748
215B ->227B -0.16549
215B ->228B 0.10359
220B ->227B -0.11601
221B ->227B -0.20179
222B ->229B -0.23438

Excited State 13: 2.255-A 3.1179 eV 397.65 nm f=0.0002 <S**2>=1.021
213B ->227B 0.11948
219B ->227B 0.93197
219B ->228B 0.18546
221B ->227B 0.15213
224B ->227B 0.11876

Excited State 14: 2.233-A 3.1280 eV 396.37

nm f=0.0339 <S**2>=0.997

222A ->228A -0.11098

227A ->229A 0.68836

227A ->232A 0.13414

214B ->227B 0.12324

219B ->227B 0.14158

220B ->227B -0.33154

221B ->227B -0.51740

Excited State 15: 2.230-A 3.1518 eV 393.38 nm f=0.0178 <S**2>=0.993

227A ->229A 0.47501

214B ->227B 0.37625

217B ->227B 0.12853

220B ->227B 0.44957

221B ->227B 0.54461

Excited State 16: 2.867-A 3.2016 eV 387.25 nm f=0.0004 <S**2>=1.806

226A ->228A 0.99062

226A ->230A 0.10955

Excited State 17: 3.136-A 3.2454 eV 382.03 nm f=0.0048 <S**2>=2.209

215A ->229A -0.17017

222A ->228A 0.53032

222A ->230A 0.12826

224A ->228A -0.10617

225A ->228A -0.49657

227A ->229A 0.12449

215B ->229B 0.17303

222B ->227B 0.27003

222B ->228B -0.39254

222B ->230B -0.11211

224B ->228B 0.13006

Excited State 18: 2.931-A 3.2631 eV 379.96 nm f=0.0016 <S**2>=1.898

222A ->228A 0.33208

225A ->228A 0.85169

215B ->229B 0.10064

222B ->227B 0.15367

222B ->228B -0.23938

Excited State 19: 2.442-A 3.2813 eV 377.85 nm f=0.1582 <S**2>=1.241

216A ->235A 0.10229

227A ->230A 0.18093

227A ->231A 0.78533

216B ->227B 0.24540

217B ->227B 0.16994

218B ->227B 0.21224

Excited State 20: 2.763-A 3.3406 eV 371.15 nm f=0.0006 <S**2>=1.658

226B ->228B 0.98475

226B ->230B 0.11675