Electronic Supplementary Material (ESI) for Journal of Materials Chemistry C.

Supporting Information

Donor Engineering of Diphenylamine-Substituted Tris(2,4,6-trichlorophenyl)methyl Radicals for Controlling the Intramolecular Charge Transfer and Near-Infrared Photothermal Conversion

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Contents

1. General experimental information.

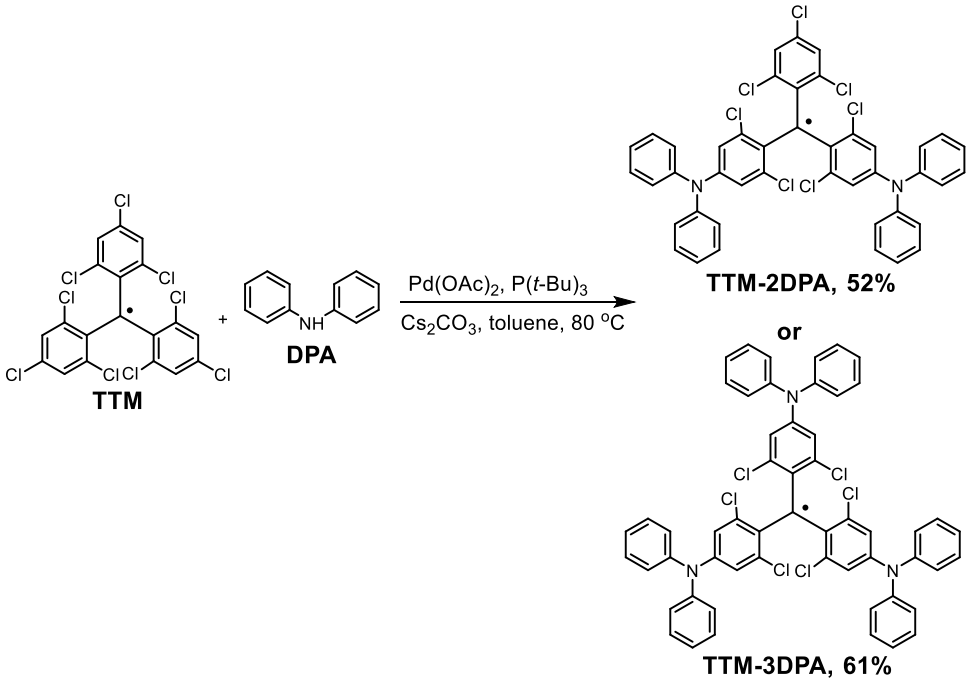
All chemicals and reagents were purchased from commercial sources and used as received unless specified. Anhydrous tetrahydrofuran (THF) and toluene were distilled from sodium benzophenone ketyl. Dichloromethane (DCM) and chloroform were distilled from CaH_2. All reactions and manipulations were carried out with the use of standard inert atmosphere and Schlenk techniques.

High resolution mass spectroscopies (HRMS) were recorded on a Bruker McriOTOF11 Fourier Transform IonCyclotron Resonance Mass Spectrometer. ^{1}H NMR (400 MHz) spectra were recorded on a Varian Mercury Plus-400 spectrometer. The purity was further confirmed on a high performance liquid chromatography (HPLC, Japan Analytical Industry LC-9160NEXT) with a UV-Vis spectrophotometric detector (200 nm) and chloroform as eluent. Electron paramagnetic resonance (EPR) spectra of radicals were recorded with Bruker EMXnano at ambient temperature. Single crystal X-ray diffraction data was collected on a Bruker D8 VENTURE MetalJet diffractometer. UV-Vis-NIR absorption spectra were recorded on a PerkinElmer Lambda-750 spectrophotometer. Photoluminescence (PL) spectra were measured on a HORIBA fluorescence spectrometer (Duetta). Electrochemical measurements were performed using a CHI760 electrochemical analyzer with a glass carbon disk as the working electrode, a platinum wire as the counter electrode and an Ag/Ag^+ electrode as the reference electrode at the rate of 100 mV s^{-1}, while 0.1 M tetrabutylammonium hexafluorophosphate ($TBAPF_6$) in dichloromethane was the electrolyte. Redox couple ferrocenium/ferrocene was used as a standard. Thermal stability measurements were performed on a PerkinElmer Pyris 1 TGA analyzer. Density functional theory (DFT) calculations were conducted with the Gaussian 16 program.[1] The geometries were optimized using UB3LYP method and 6-31G(d) basis set. Time-dependent density functional theory (TD-DFT) calculations were carried out using the same program with m06 method.[2] The Measurement of Photothermal Performance was conducted by A NIR laser (Changchun New Industries Optoelectronics Tech. Co., Ltd, MDL-XF-760 nm/MDL-N-980 nm) was used in the measurement of photothermal performance.

2. Synthesis.

TTM, arylamines **BDPA**, and **TDPA** were synthesized according to references.[3-6]

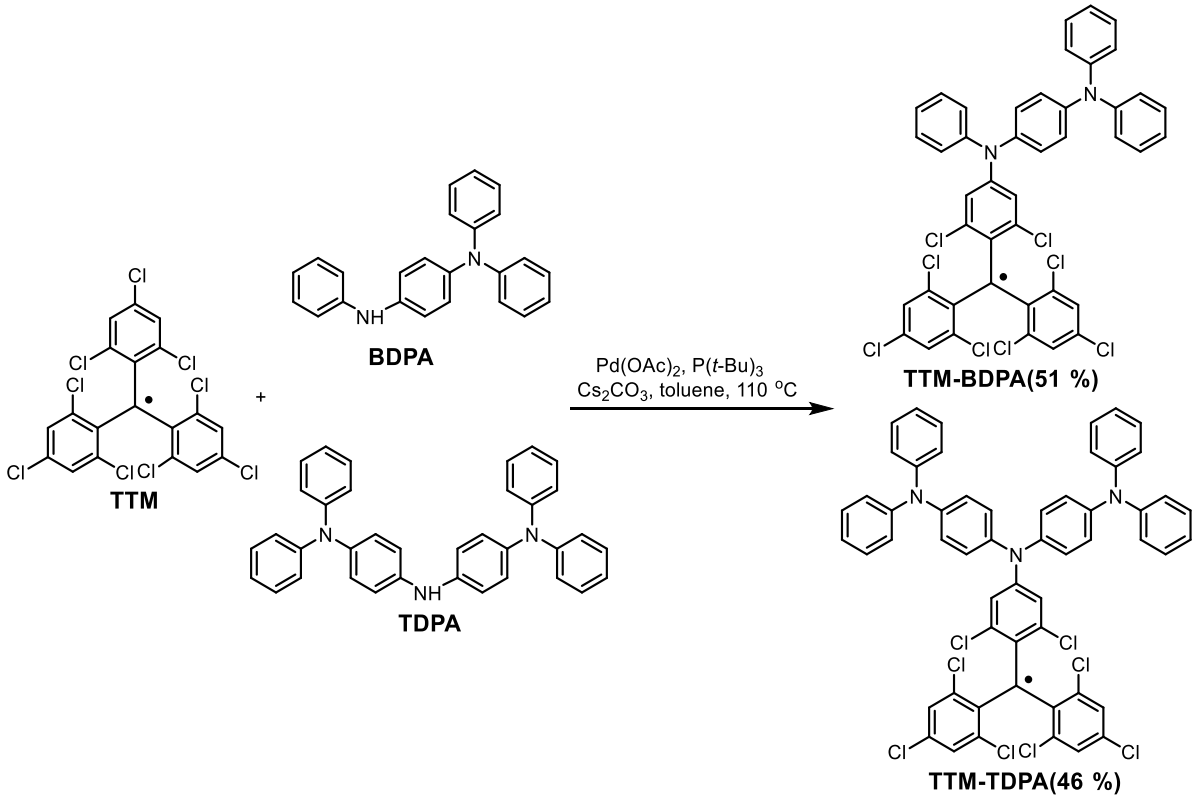
Synthesis of TTM-2DPA and TTM-3DPA.



Scheme S1. Synthetic routes for **TTM-2DPA** and **TTM-3DPA**.

Under nitrogen atmosphere and in the dark, radical **TTM** (1.00 g, 1.80 mmol), diphenylamine (2.70 mmol or 7.20 mmol), Cs_2CO_3 (1.76 g, 5.40 mmol), $Pd(OAc)_2$ (0.05 g, 0.22 mmol), and P(*t*-Bu)$_3$ (1.34 g, 0.66 mmol, 10% in toluene) were dissolved in 20 mL dry toluene. Then the mixture was stirred at 80 ℃ for 48 h. After cooling, the solvent was removed under vacuum. The crude product was purified by silica gel column chromatography (PE: EA = 6:1 v/v) to afford the desired radicals **TTM-2DPA** (0.76 g, yield: 52%) or **TTM-3DPA** (1.04 g, yield: 61%) as the dark green solids. **TTM-2DPA**. HRMS (ESI, m/z): $[M]^+$ calcd for $C_{43}H_{26}Cl_7N_2$, 816.9886; found 816.9911. **TTM-3DPA**. HRMS (ESI, m/z): $[M]^+$ calcd for $C_{55}H_{36}Cl_6N_3$, 950.1011; found 950.1039.

Synthesis of TTM-BDPA and TTM-TDPA.



Scheme S2. Synthetic routes for **TTM-BDPA** and **TTM-TDPA**.

Under nitrogen atmosphere and in the dark, radical **TTM** (1.00 g, 1.80 mmol), arylphenylamine (1.20 mmol), Cs_2CO_3 (1.76 g, 5.40 mmol), $Pd(OAc)_2$ (0.05 g, 0.22 mmol), and P(*t*-Bu)$_3$ (1.34 g, 0.66 mmol, 10% in toluene) were dissolved in 20 mL dry toluene. Then the mixture was stirred at 110 ℃ for 36 h. After cooling, the solvent was removed under vacuum. The crude product was purified by silica gel column chromatography (PE: DCM = 8:1 v/v) to afford the desired radicals **TTM-BDPA** (0.52 g, yield: 51%) or **TTM-TDPA** (0.56 g, yield: 46%) as the dark green solids. **TTM-BDPA**. HRMS (ESI, m/z): $[M]^+$ calcd for $C_{43}H_{25}Cl_8N_2$, 852.9467; found 852.9460. **TTM-TDPA**. HRMS (ESI, m/z): $[M]^+$ calcd for $C_{55}H_{34}Cl_8N_3$, 1020.0202; found 1020.0237.

3. Fig. S1-S4. HRMS spectra of the target neutral radicals.

Fig. S1. HRMS spectrum (ESI) of compound **TTM-2DPA**.

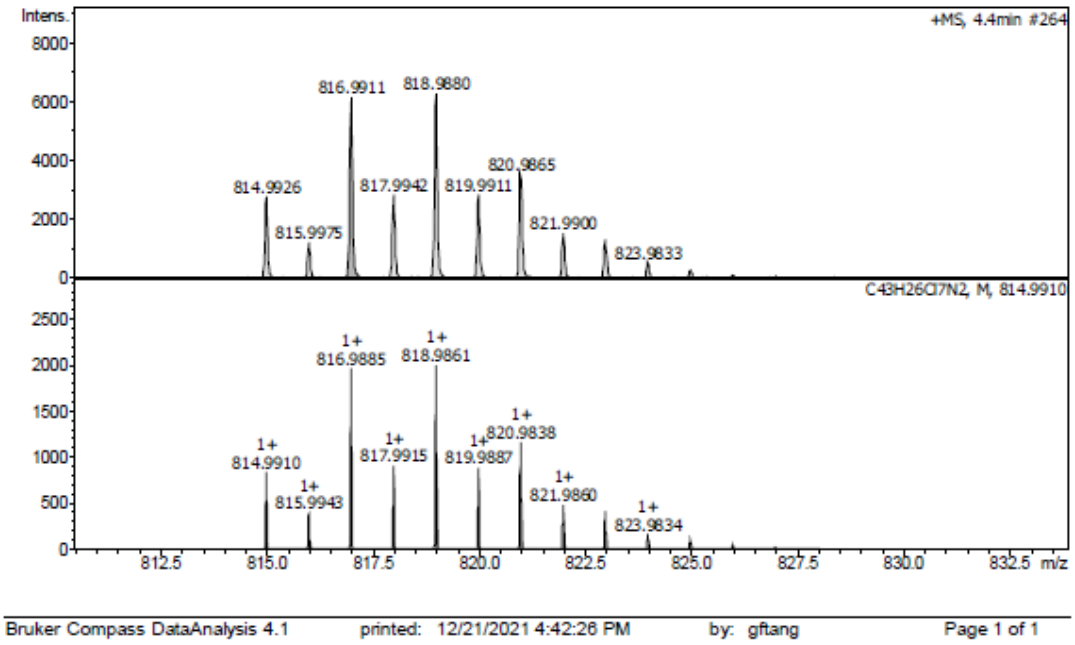


Fig. S2. HRMS spectrum (ESI) of compound **TTM-3DPA**.

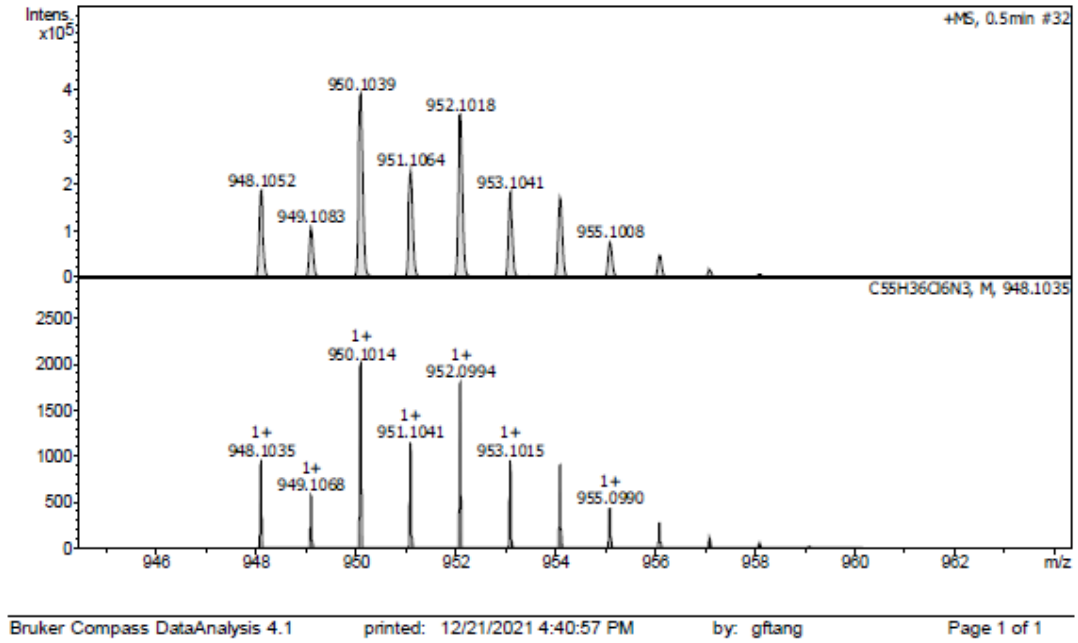


Fig. S3. HRMS spectrum (ESI) of compound **TTM-BDPA**.

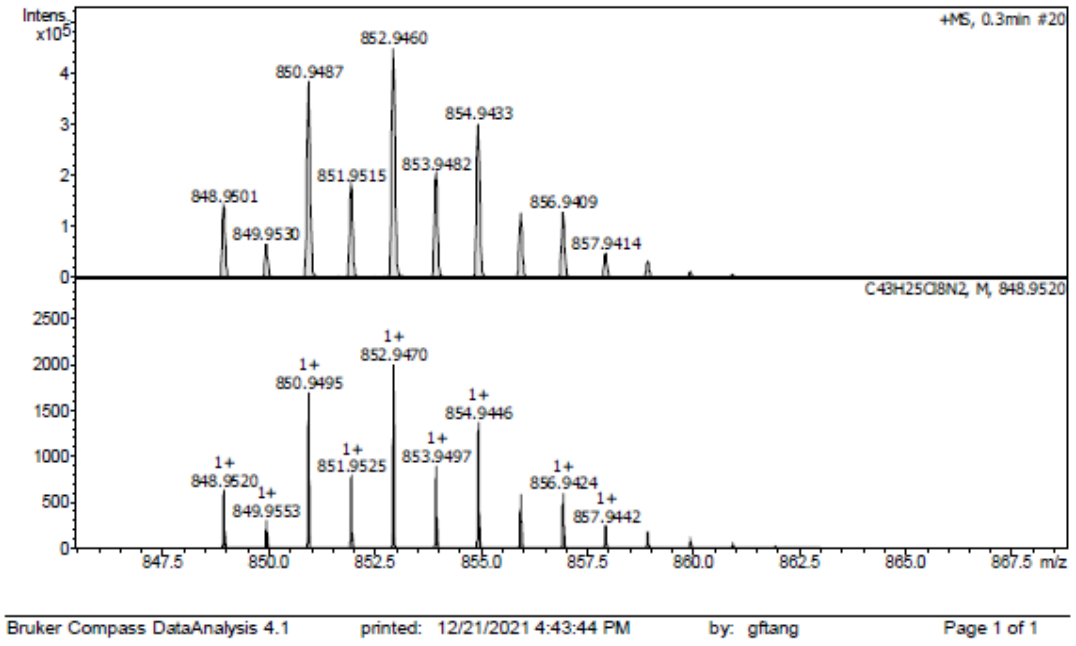
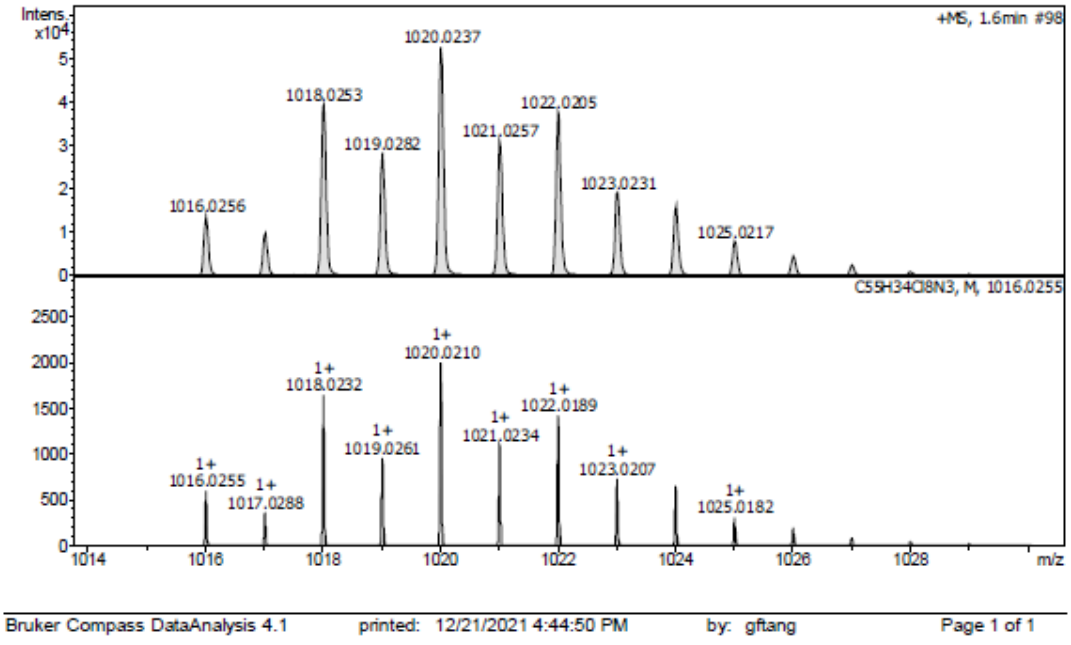
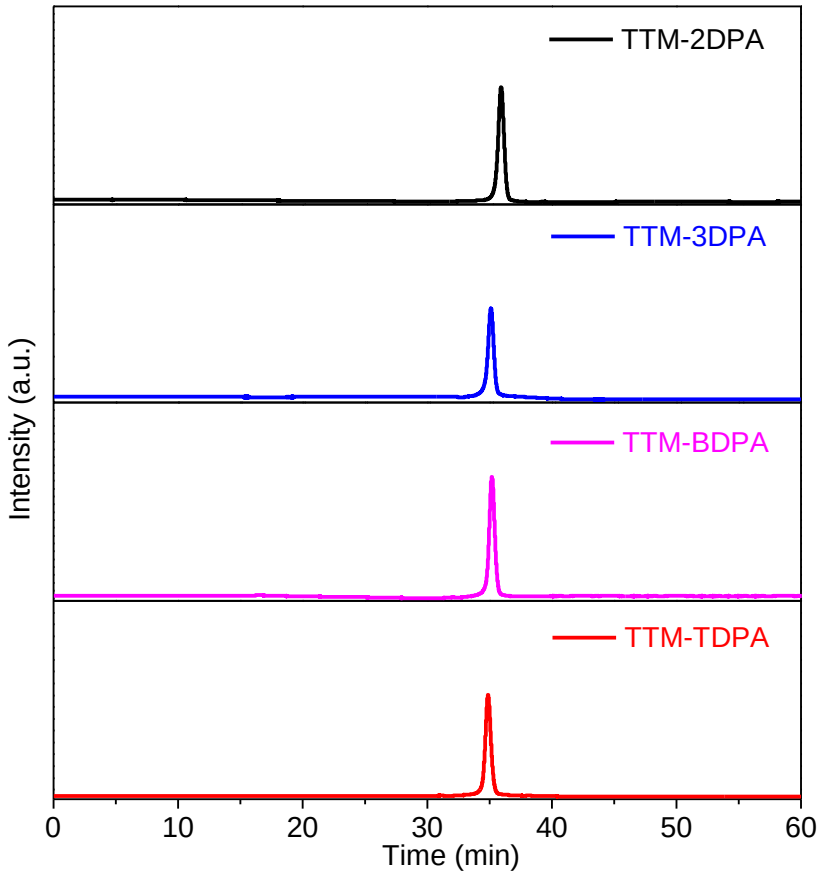


Fig. S4. HRMS spectrum (ESI) of compound **TTM-TDPA**.



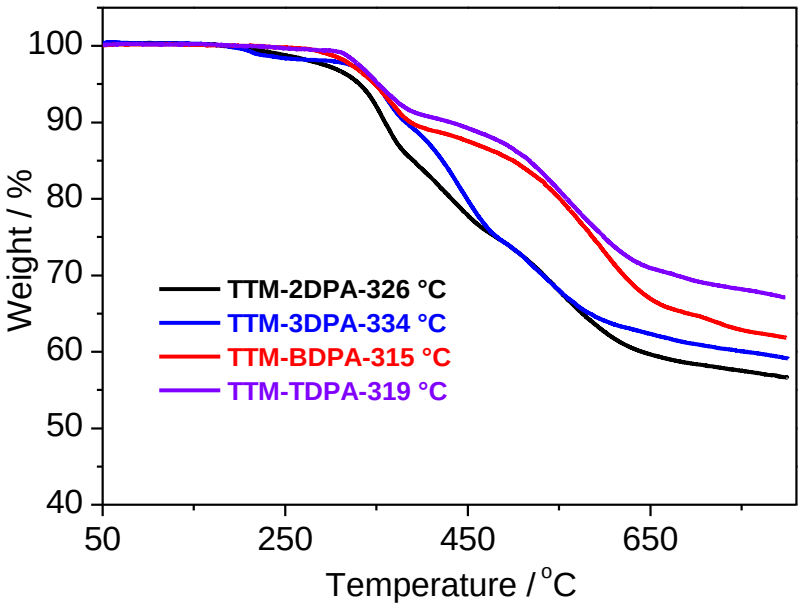
4. Fig. S5. HPLC curves of the target neutral radicals.

Fig. S5. HPLC curves of **TTM-2DPA**, **TTM-3DPA**, **TTM-BDPA**, and **TTM-TDPA**.



5. Fig. S6. TGA curves of the target neutral radicals.

Fig. S6. TGA curves of **TTM-2DPA**, **TTM-3DPA**, **TTM-BDPA**, and **TTM-TDPA**.



6. Fig. S7-S8. Single crystal structure of TTM-BDPA.

Fig. S7. Structure diagram for **TTM-BDPA** with an ellipsoid contour probability level of 50%.

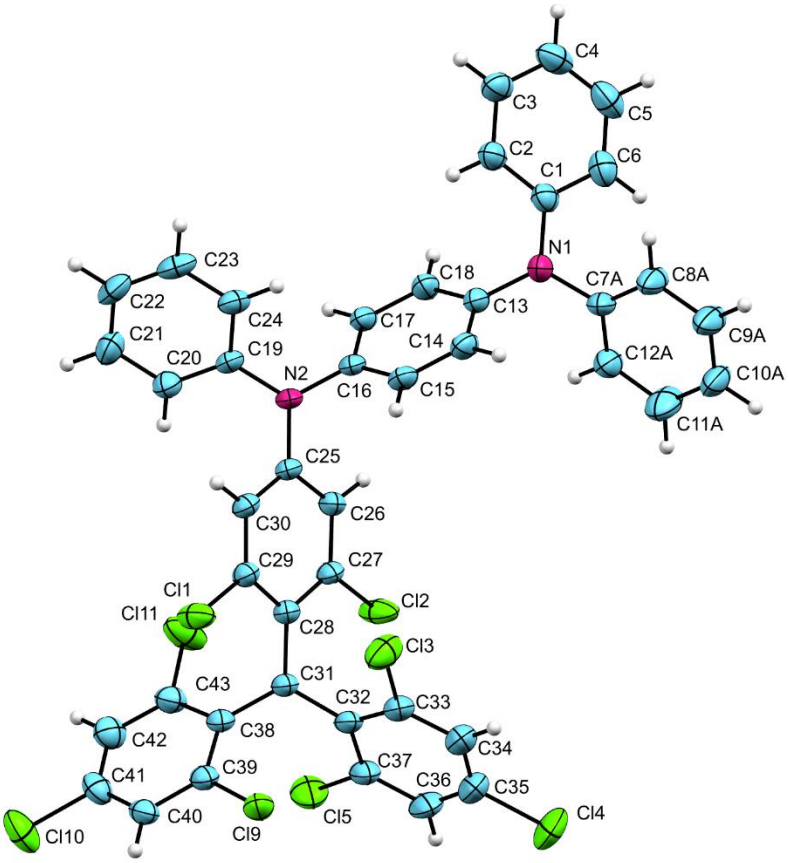
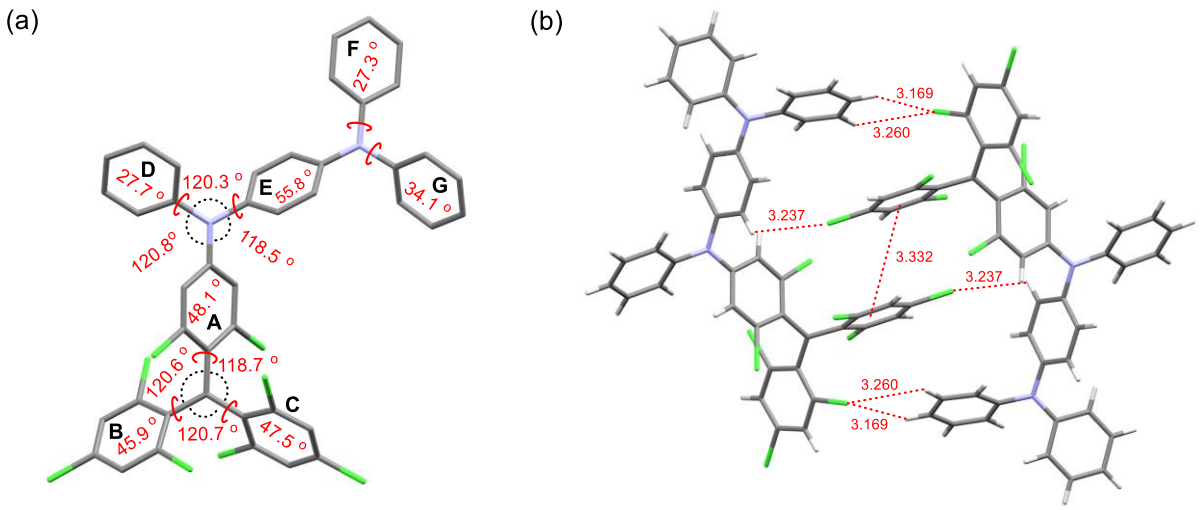
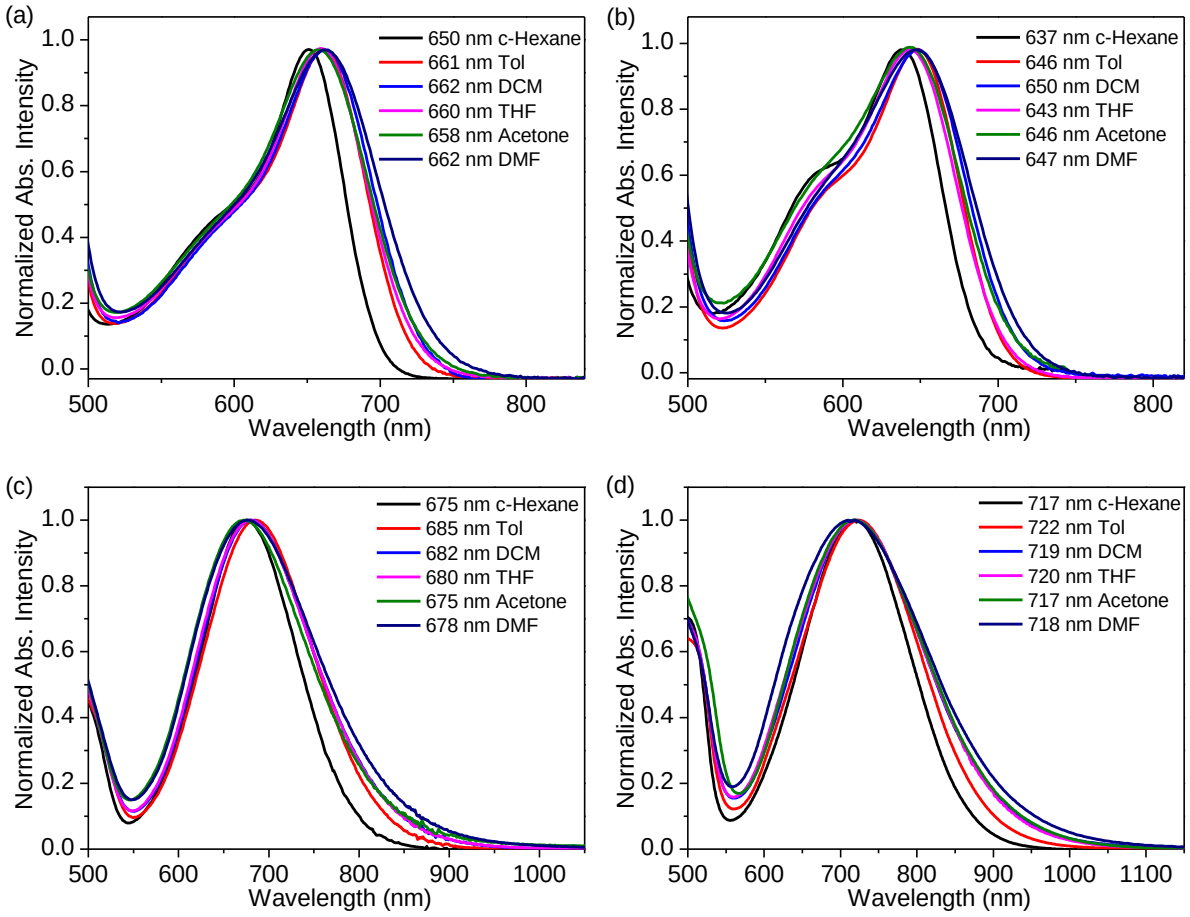


Fig. S8. X-ray crystallographic structure, bond angles, and torsion angles of **TTM-BDPA.**



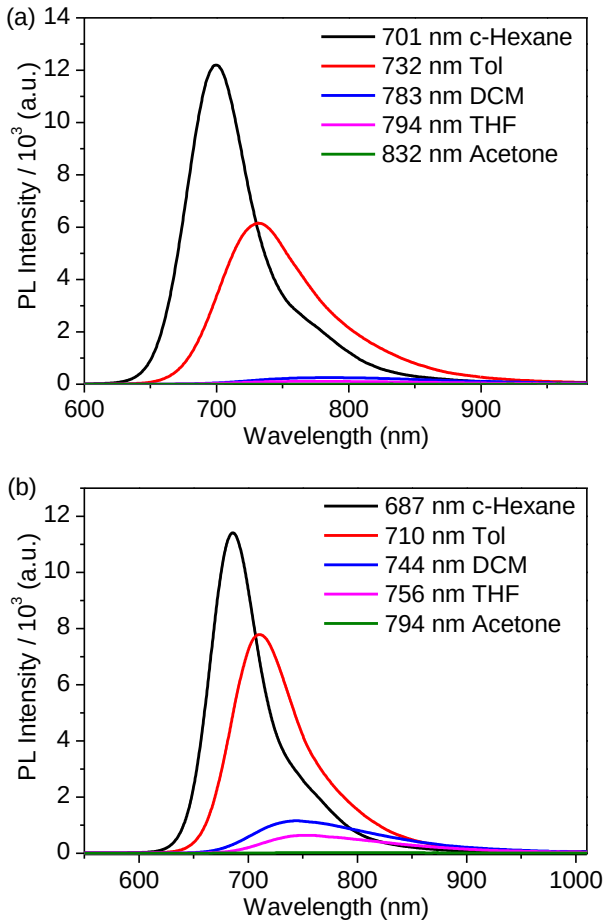
7. Fig. S9. UV-vis-NIR absorption spectra of the target neutral radicals in different organic solvents.

Fig. S9. UV-vis-NIR absorption spectra of (a) **TTM-2DPA**, (b) **TTM-3DPA**, (c) **TTM-BDPA**, and (d) **TTM-TDPA** in different organic solvents, respectively.



8. Fig. S10. PL spectra of the luminescent radicals in different organic solvents.

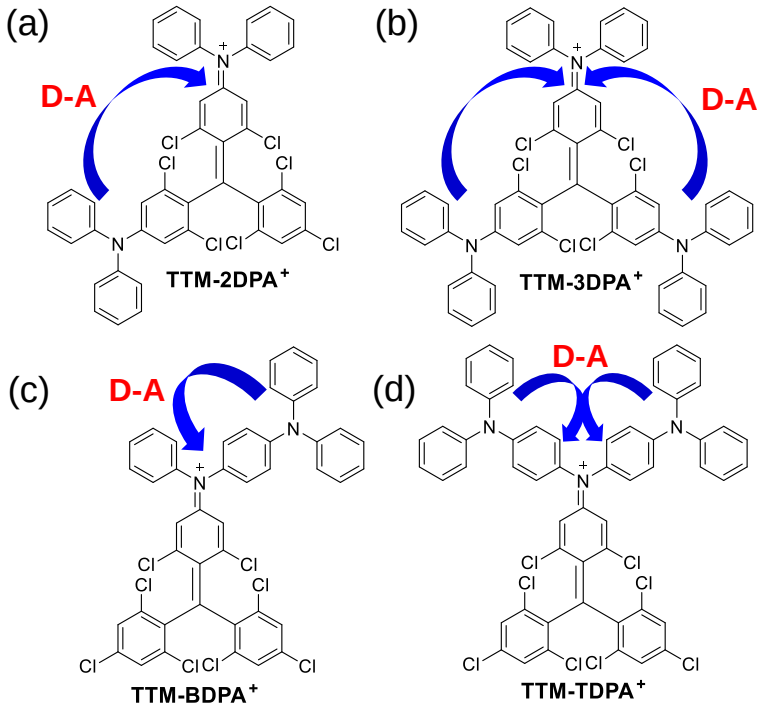
Fig. S10. PL spectra of (a) **TTM-2DPA** and (b) **TTM-3DPA** in different organic solvents, respectively.



The PL intensity of **TTM-2DPA** and **TTM-3DPA** in DMF solution is too weak to be recorded.

9. Fig. S11. Photophysical of the radical cations.

Fig. S11. Illustration diagrams of the D-A interactions for (a) **TTM-2DPA**$^{+}$, (b) **TTM-3DPA**$^{+}$, (c) **TTM-BDPA**$^{+}$, and (d) **TTM-TDPA**$^{+}$, respectively.



10. Fig. S12-S15. ^{1}H NMR spectra of Neutral Radicals and Oxidized Cations.

Fig. S12. ^{1}H NMR spectra for **TTM-2DPA** and **TTM-2DPA**$^+$ in $CDCl_3$.

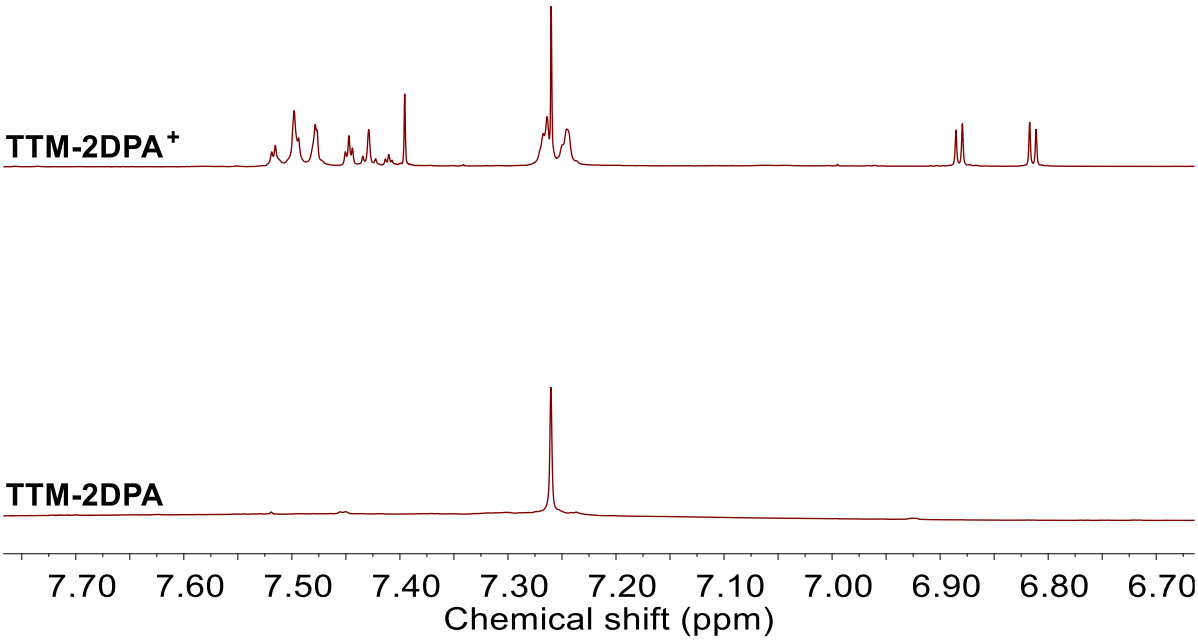


Fig. S13. ^{1}H NMR spectra for **TTM-3DPA** and **TTM-3DPA**$^+$ in $CDCl_3$.

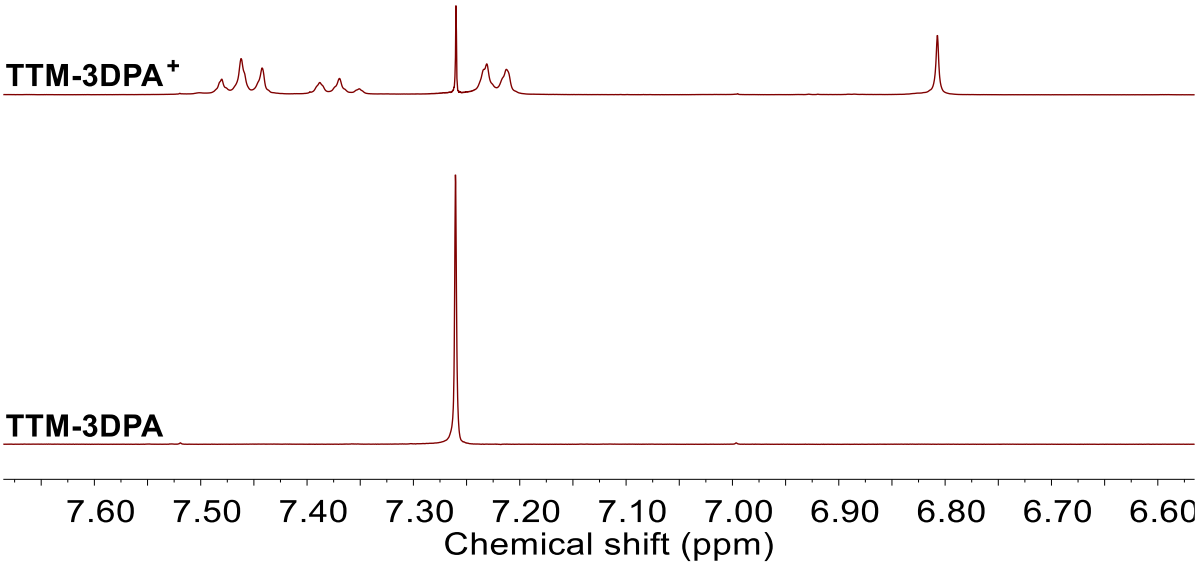


Fig. S14. ^{1}H NMR spectra for **TTM-BDPA** and **TTM-BDPA**$^{+}$ in $CDCl_3$.

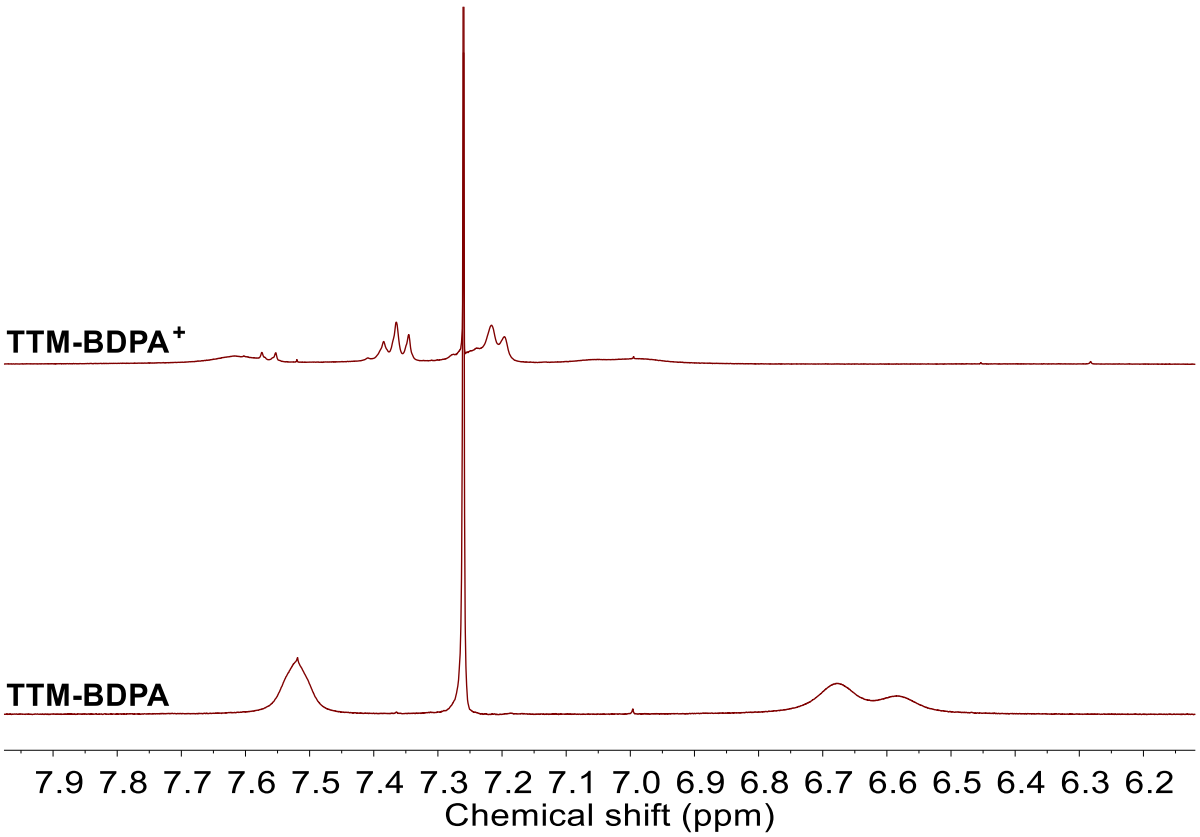
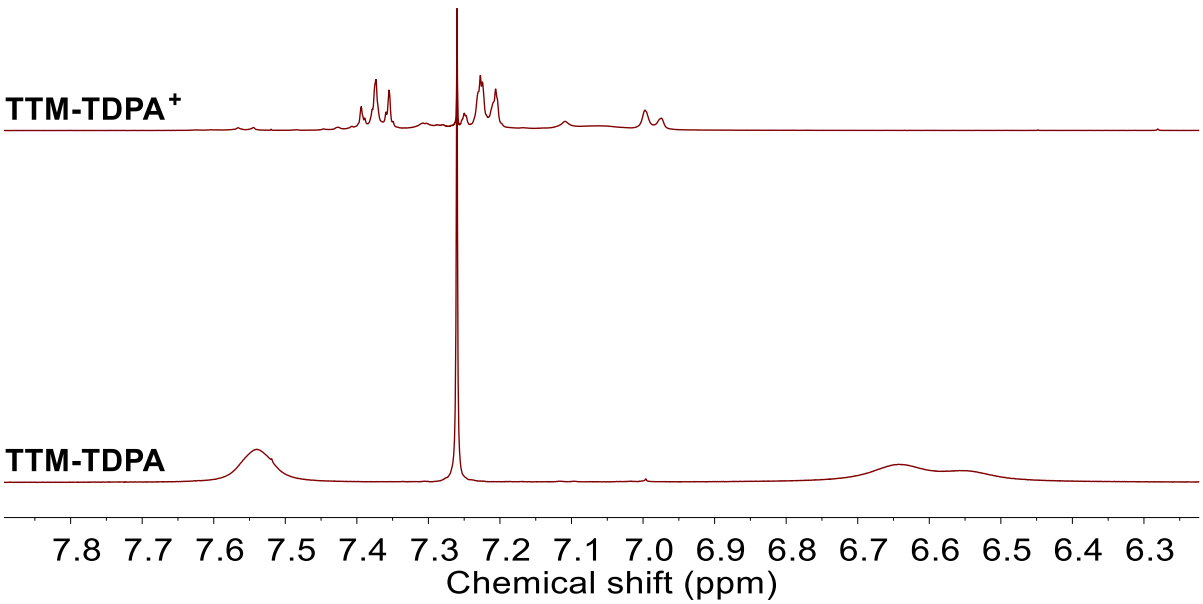


Fig. S15. ^{1}H NMR spectra for **TTM-TDPA** and **TTM-TDPA**$^{+}$ in $CDCl_3$.



11. Fig. S16-S17. Calculated frontier orbitals of the neutral and oxidized monocation species

Fig. S16. Molecular orbitals of (a) **TTM-2DPA**, (b) **TTM-3DPA**, (c) **TTM-BDPA**, and (d) **TTM-TDPA**.

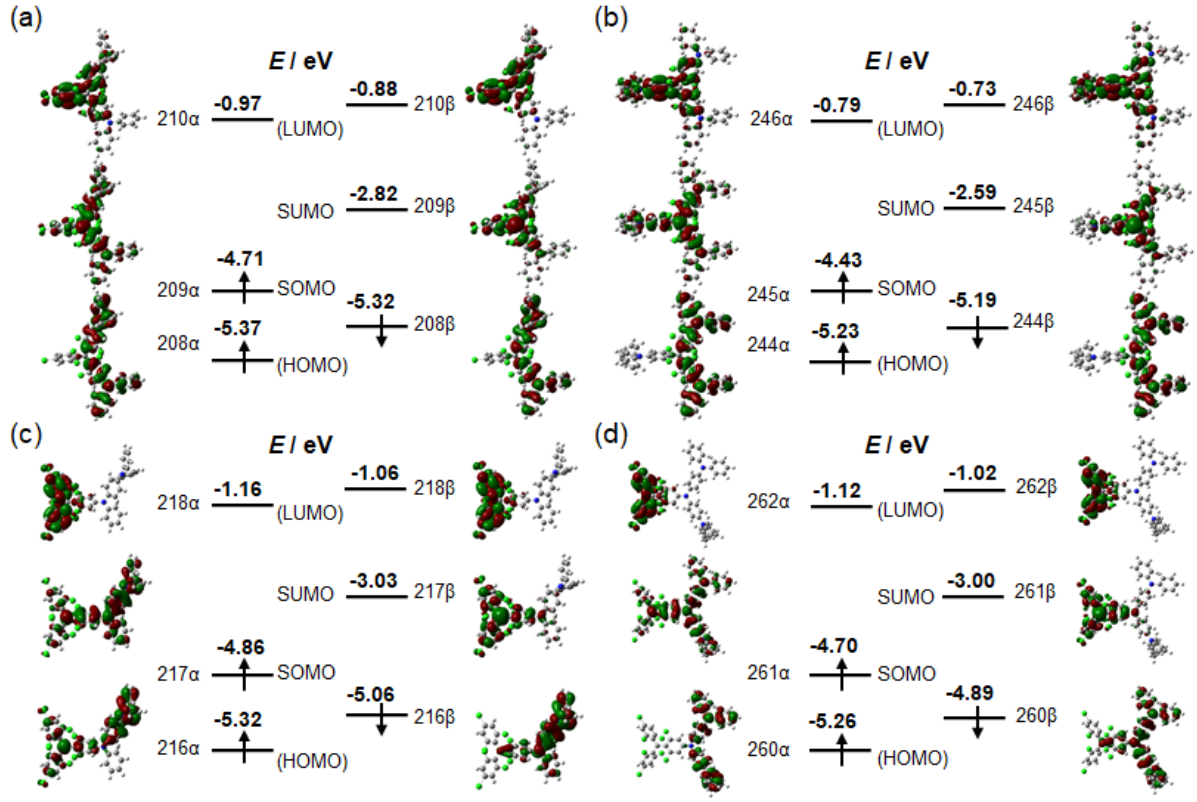
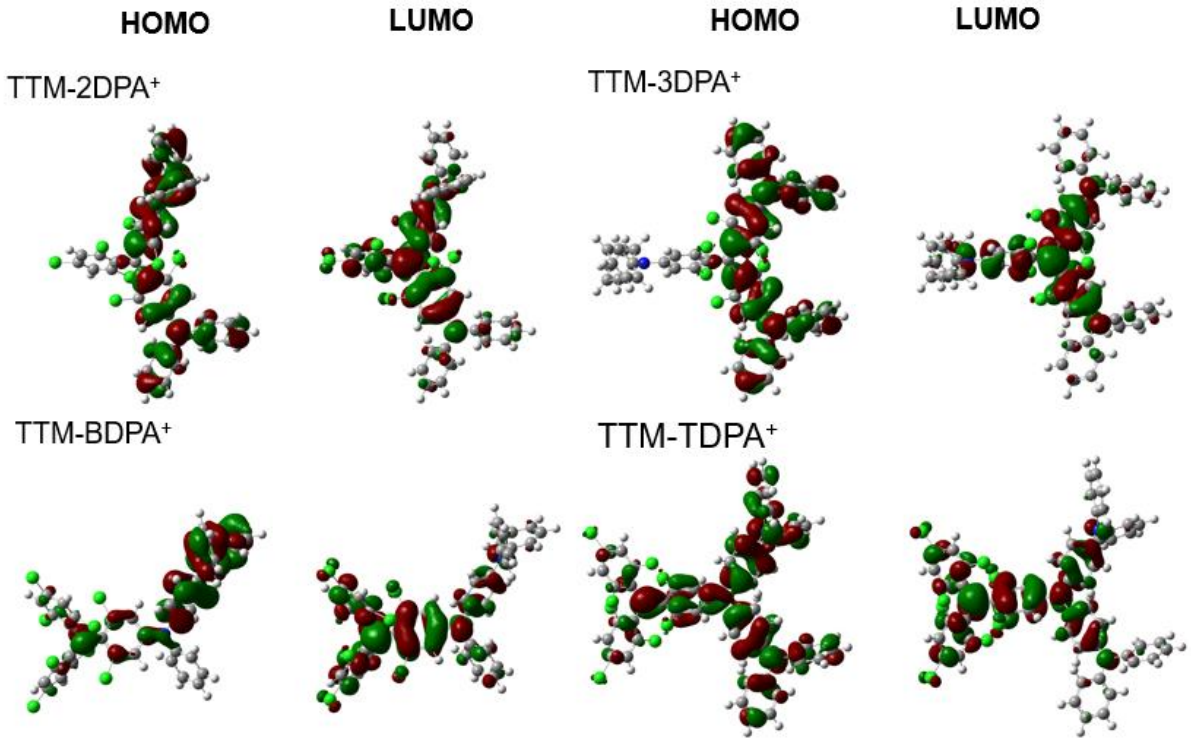


Fig. S17. Molecular orbitals of **TTM-2DPA**$^{+}$, **TTM-3DPA**$^{+}$, **TTM-BDPA**$^{+}$, and **TTM-TDPA**$^{+}$.



12. Fig. S18-S19. Photothermal Conversion Study of Neutral Radicals.

1. Experimental details.

To investigate the photothermal conversion properties, radicals **TTM-DPA**, **TTM-2DPA**, **TTM-3DPA**, **TTM-BDPA**, and **TTM-TDPA** were dissolved in cyclohexane solution with a 50 μM concentration. then 0.4 mL of this solution was taken into a centrifuge tube and irradiated by 760 nm laser at 0.4 W / cm^2. The temperature changes of this solution were monitored by an infrared camera. Related measurements and calculations were conducted according to reference.[7]

The photothermal conversion efficiencies (η) were calculated by the following:

$$\eta = hS(\Delta T_{sample} - \Delta T_{solvent}) / I(1 - 10^{-A}) \quad (1)$$

$$hS = \Sigma mC_p / \tau_s \quad (2)$$

$$\tau_s = -t / \ln\theta \quad (3)$$

$$\theta = (T_{amb} - T) / (T_{amb} - T_{max}) \quad (4)$$

Where h is the heat transfer coefficient, S is the surface area of the container, τ_s is the sample system time constant, m is the mass of the products, C_p is the specific heat capacity of the solvent, and the value of τ_s was obtained from the cooling curves of these solutions.[8]

According to this equation, $\sum mCp = m_{(cyclohexane)} \cdot C_{p(cyclohexane)} = \rho_{(cyclohexane)} \cdot V_{(cyclohexane)} \cdot C_{p(cyclohexane)} = 0.790 \times 0.4 \times 1.85 = 0.5846\ J \cdot K^{-1}$. $\Delta T_{solvent} = 1.7$ °C (Figure 7c in main text), $I = 0.4$ W / cm^2, and the absorbance at 760 nm for **TTM-BDPA** and **TTM-TDPA** were 0.15881 and 0.39776 (Figure 7b in main text), respectively.

2.TTM-BDPA.

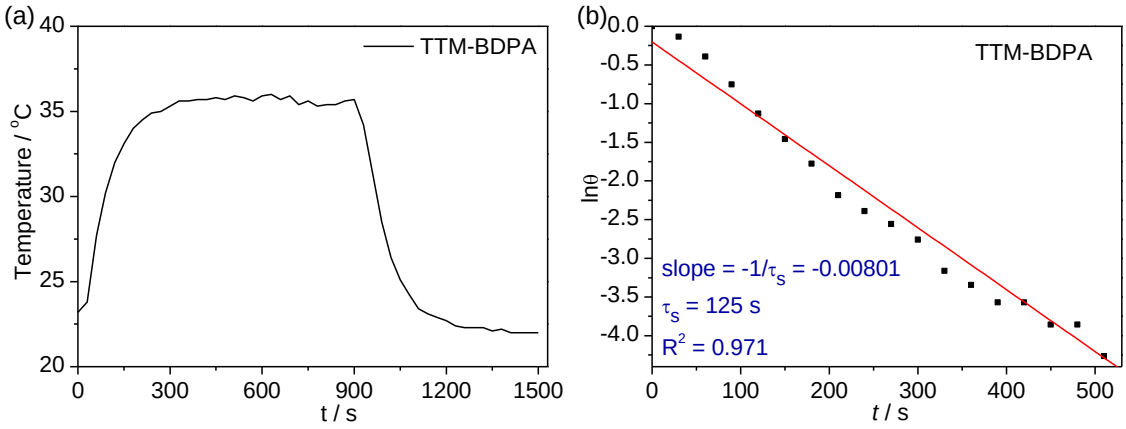


Fig. S18. (a) Heating and cooling curve of **TTM-BDPA**. (b) Fitting linear of lnθ-t.

Photothermal conversion efficiency $\boldsymbol{\eta}$ of **TTM-BDPA** was calculated by equations above. A fitting linear of lnθ-t was obtained by Eqs (**3**) and (**4**), by which **τs** was calculated as 125 s. Thus, $h\mathbf{S}$ = 0.5846 / 125 = 4.68 × 10^{-3} J·K^{-1}·S^{-1}. ΔT_{sample} = 12.5 ℃. $\mathbf{A_1}$ = 0.15881. Eventually, $\boldsymbol{\eta_1}$ = 4.68 × 10^{-3} × (12.5-1.7) / [0.4 × (1 - $10^{-0.15881}$)] = 41%.

3.TTM-TDPA.

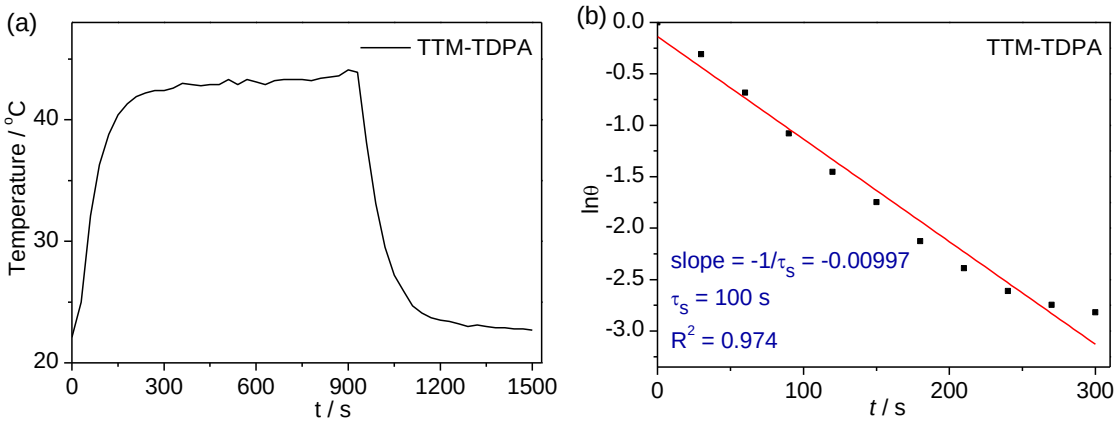


Fig. S19. (a) Heating and cooling curve of **TTM-TDPA**. (b) Fitting linear of lnθ-t.

Photothermal conversion efficiency $\boldsymbol{\eta}$ of **TTM-TDPA** was calculated by equations above. A fitting linear of lnθ-t was obtained by Eqs (**3**) and (**4**), by which **τs** was calculated as 100 s. Thus, $h\mathbf{S}$ = 0.5846 / 100 = 5.85 × 10^{-3} J·K^{-1}·S^{-1}. ΔT_{sample} = 22.0 ℃. $\mathbf{A_1}$ = 0.39776. Eventually, $\boldsymbol{\eta_1}$ = 5.85 × 10^{-3} × (22.0-1.7) / [0.4 × (1 - $10^{-0.39776}$)] = 50%.

13. Fig. S20-S22. Photothermal Conversion Study of Oxidized Cations.

1. Experimental details.

To investigate the photothermal conversion properties of oxidized cations with obvious NIR absorption, **TTM-2DPA**$^+$, **TTM-3DPA**$^+$, **TTM-BDPA**$^+$, and **TTM-TDPA**$^+$ were dissolved in chloroform solution with a 10 μM concentration. then 0.4 mL of this solution was taken into a centrifuge tube and irradiated by 980 nm laser at 0.4 W / cm^2. The temperature changes of this solution were monitored by an infrared camera. Related measurements and calculations were conducted according to reference.[7]

The photothermal conversion efficiencies (η) were calculated by the following:

$$\eta = hS(\Delta T_{sample} - \Delta T_{solvent}) / I(1 - 10^{-A}) \quad (1)$$

$$hS = \Sigma mC_p / \tau_s \quad (2)$$

$$\tau_s = -t / \ln\theta \quad (3)$$

$$\theta = (T_{amb} - T) / (T_{amb} - T_{max}) \quad (4)$$

Where h is the heat transfer coefficient, S is the surface area of the container, τ_s is the sample system time constant, m is the mass of the products, C_p is the specific heat capacity of the solvent, and the value of τ_s was obtained from the cooling curves of these solutions.[8]

According to this equation, $\sum mCp = m_{(chloroform)} \cdot C_{p(chloroform)} = \rho_{(chloroform)} \cdot V_{(chloroform)} \cdot C_{p\ (chloroform)} = 1.480 \times 0.4 \times 0.98 = 0.5802\ J \cdot K^{-1}$. $\Delta T_{solvent} = 0.7$ ℃ (Fig. S20b), $I = 0.4$ W / cm^2, and the absorbance at 980 nm for **TTM-BDPA**$^+$ and **TTM-TDPA**$^+$ were 0.33615 and 0.53555, respectively.

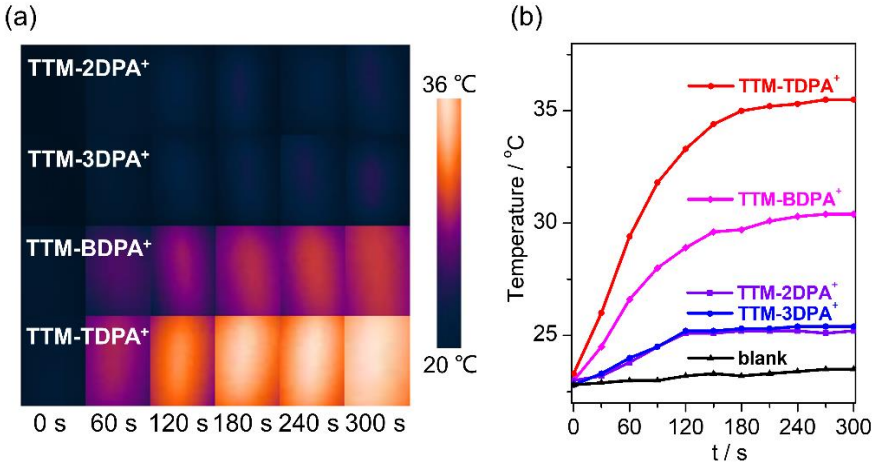


Fig. S20. (a) NIR thermal images and (b) photothermal conversion curves of **TTM-2DPA**$^+$, **TTM-3DPA**$^+$, **TTM-BDPA**$^+$, and **TTM-TDPA**$^+$ under 980 nm laser irradiation (0.4 W / cm^2).

2.TTM-BDPA$^+$.

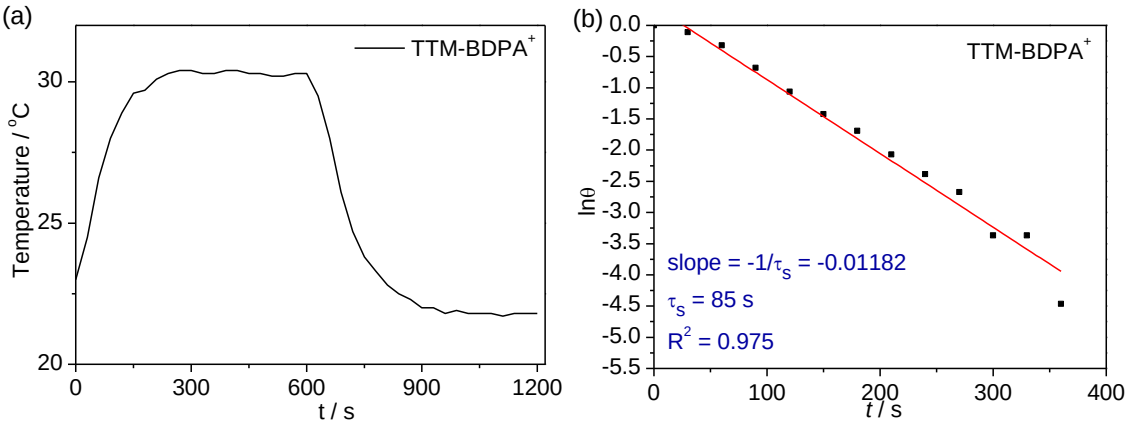


Fig. S21. (a) Heating and cooling curve of **TTM-BDPA**$^+$. (b) Fitting linear of lnθ-t.

Photothermal conversion efficiency $\boldsymbol{\eta}$ of **TTM-BDPA**$^+$ was calculated by equations above. A fitting linear of lnθ-t was obtained by Eqs (**3**) and (**4**), by which **τs** was calculated as 85 s. Thus, $h\mathbf{S} = 0.5802 / 85 = 6.83 \times 10^{-3}$ J·K^{-1}·S^{-1}. $\Delta T_{sample} = 7.4$ ℃. $\mathbf{A_1} = 0.33615$. Eventually, $\boldsymbol{\eta_1} = 6.83 \times 10^{-3} \times (7.4 - 0.7) / [0.4 \times (1 - 10^{-0.33615})] = 21\%$.

3.TTM-TDPA$^+$.

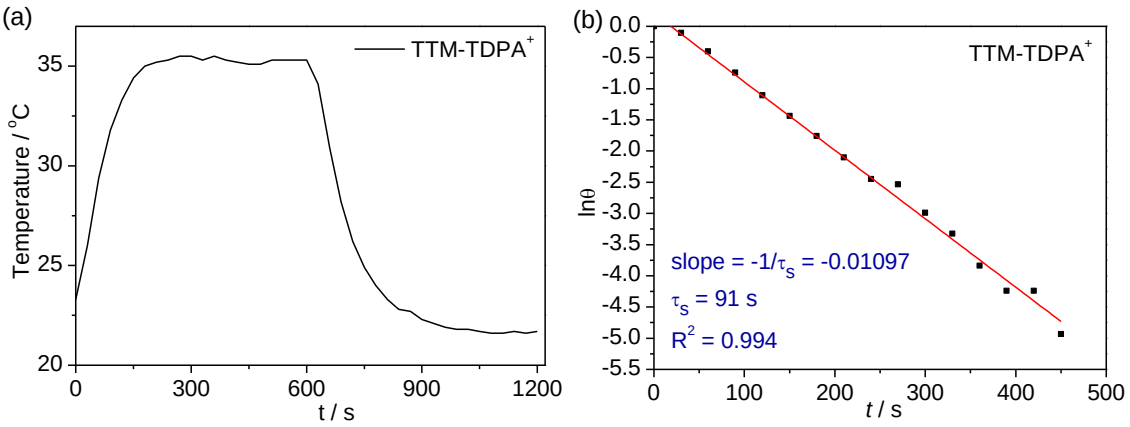


Fig. S22. (a) Heating and cooling curve of **TTM-TDPA**$^+$. (b) Fitting linear of lnθ-t.

Photothermal conversion efficiency $\boldsymbol{\eta}$ of **TTM-TDPA**$^+$ was calculated by equations above. A fitting linear of lnθ-t was obtained by Eqs (**3**) and (**4**), by which **τs** was calculated as 91 s. Thus, $h\mathbf{S} = 0.5802 / 91 = 6.38 \times 10^{-3}$ J·K^{-1}·S^{-1}. $\Delta T_{sample} = 12.2$ ℃. $\mathbf{A_1} = 0.53555$. Eventually, $\boldsymbol{\eta_1} = 6.38 \times 10^{-3} \times (12.2-0.7) / [0.4 \times (1 - 10^{-0.53555})] = 26\%$.

14. Fig. S23-S24. Stability of Neutral Radicals.

Fig. S23. Absorption intensity changes at λ_{max} of **TTM-2DPA**, **TTM-3DPA**, **TTM-BDPA**, and **TTM-TDPA** in dilute DCM solutions exposed in ambient environment.

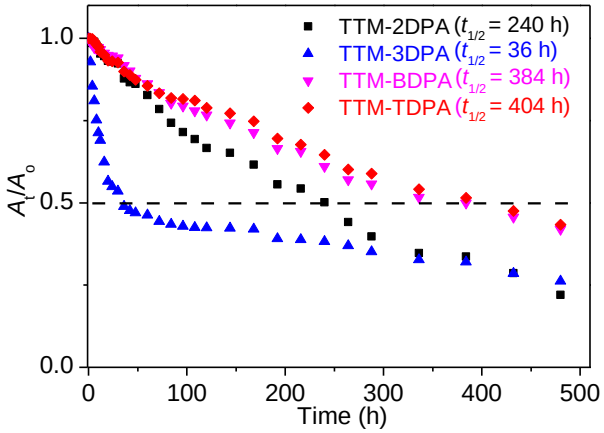
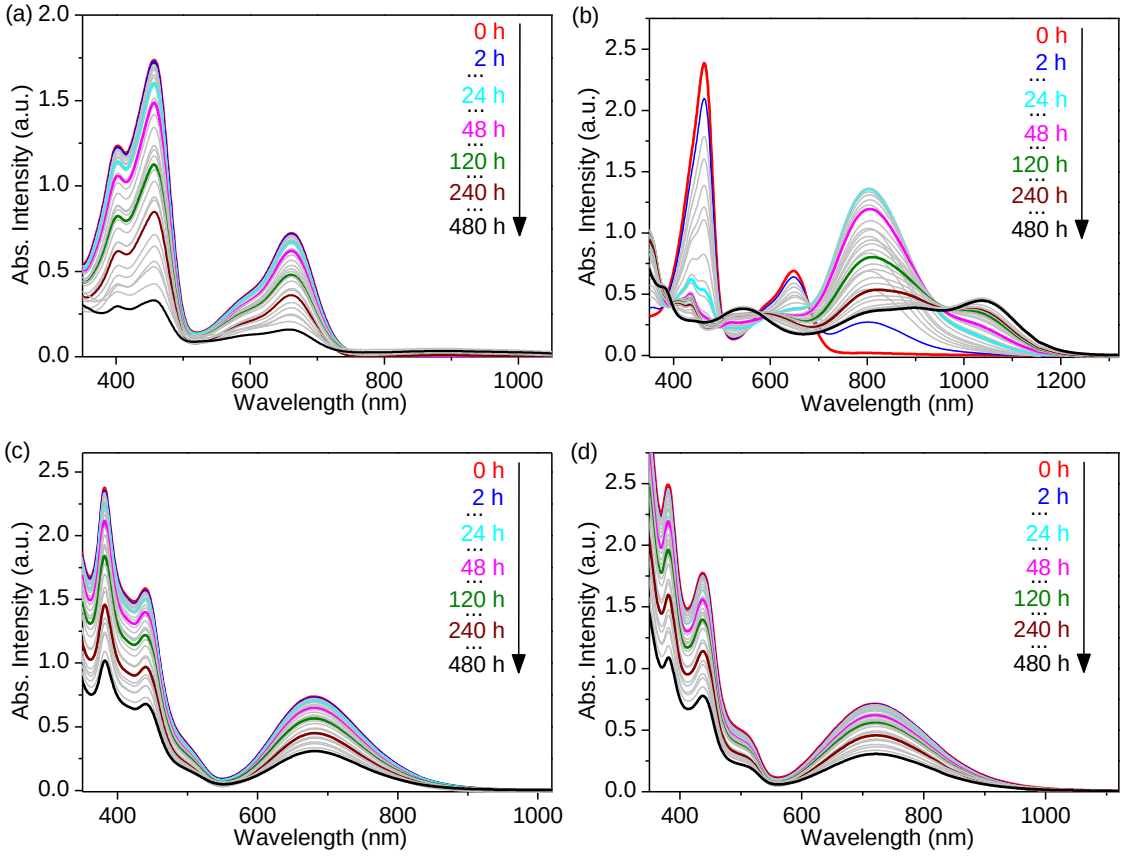


Fig. S24. Absorption spectra of TTM radical derivatives in DCM solution under the continuous natural light irradiation: (a) **TTM-2DPA**, (b) **TTM-3DPA**, (c) **TTM-BDPA**, and (d) **TTM-TDPA** in dilute DCM solutions exposed in ambient environment.



15. Fig. S25-S26. Stability of Oxidized Cations.

Fig. S25. Absorption intensity changes at λ_{max} of **TTM-2DPA**$^+$, **TTM-3DPA**$^+$, **TTM-BDPA**$^+$, and **TTM-TDPA**$^+$ in dilute DCM solutions exposed in ambient environment.

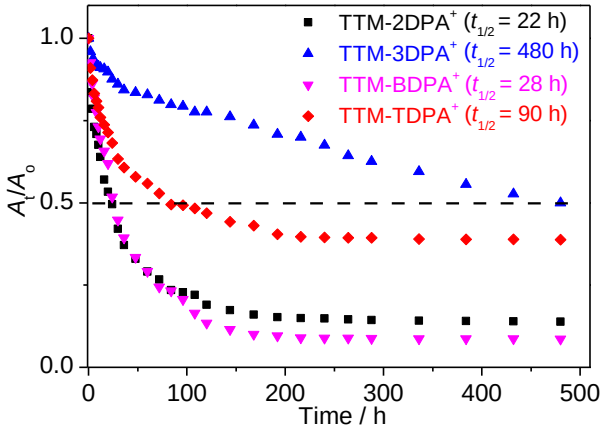
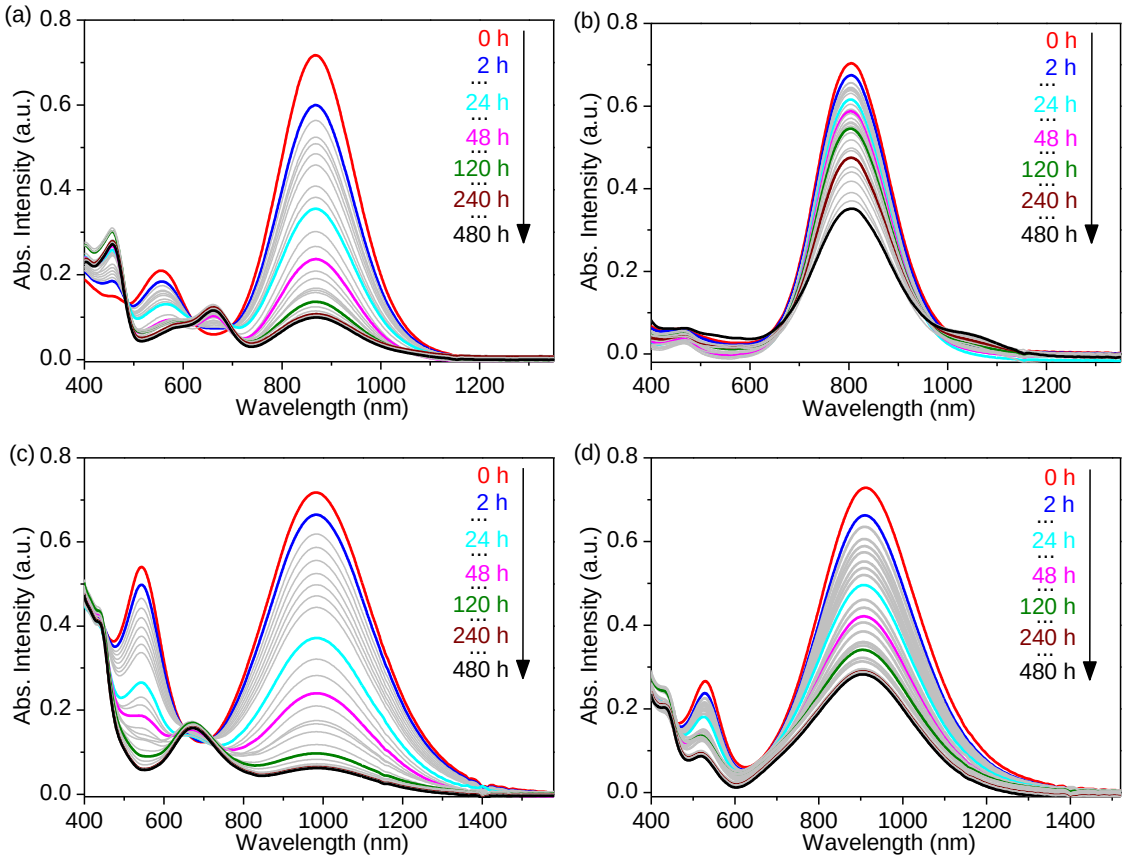
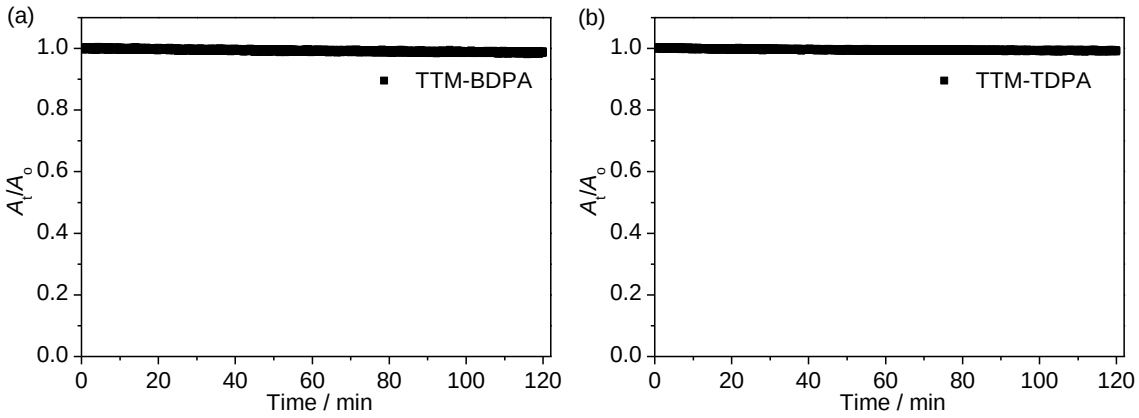


Fig. S26. Absorption spectra of TTM radical derivatives in DCM solution under the continuous natural light irradiation: (a) **TTM-2DPA**$^+$, (b) **TTM-3DPA**$^+$, (c) **TTM-BDPA**$^+$, and (d) **TTM-TDPA**$^+$ in dilute DCM solutions exposed in ambient environment.



16. Fig. S27. Photostability of NIR photothermal conversion materials TTM-BDPA and TTM-TDPA.

Fig. S27. Absorption intensity changes at $\lambda_{irradiation}$ of (a) **TTM-BDPA** and (b) **TTM-TDPA** in dilute DCM solutions under the continuous irradiation of 760 nm NIR light.



17. Table S1-S2. Single crystal data of TTM-BDPA.

Table S1. Single crystal data and structural refinements of **TTM-BDPA**.

Sum formula	$C_{43}H_{25}Cl_8N_2$
Formula weight	853.25
Temperature	173 K
Wavelength	1.34138 Å
Bond precision	C-C = 0.0033 Å
Crystal system	Monoclinic
Space group	P121/n1
Cell	a = 14.1818(6) Å, b = 7.9814(4) Å, c = 39.7376(18) Å α = 90°, β = 98.296(2)°, γ = 90°
Volume (Å^3)	4450.9(4)
Z	4
F (000)	1732.0
Tmin,Tmax	0.563, 0.786
Data completeness	0.998
Theta(max)	57.019
R(reflections)	0.0482(7231)
wR2(reflections)	0.1444(9082)

Table S2. Selected bond lengths of **TTM-BDPA.**

Bond	Length/Å	Bond	Length/Å
Cl(1)-C(29)	1.734(2)	C(23)-C(24)	1.380(3)
Cl(2)-C(27)	1.737(3)	C(19)-C(24)	1.393(3)
Cl(3)-C(33)	1.733(3)	C(25)-C(26)	1.391(3)
Cl(4)-C(35)	1.734(3)	C(26)-C(27)	1.373(4)
Cl(5)-C(37)	1.731(3)	C(27)-C(28)	1.408(3)
Cl(6)-C(39)	1.729(2)	C(28)-C(29)	1.405(3)
Cl(7)-C(41)	1.734(2)	C(29)-C(30)	1.374(3)
Cl(8)-C(43)	1.735(3)	C(25)-C(30)	1.394(3)
C(1)-C(2)	1.388(3)	C(31)-C(32)	1.465(3)
C(2)-C(3)	1.385(4)	C(32)-C(33)	1.397(3)
C(3)-C(4)	1.371(4)	C(33)-C(34)	1.383(4)
C(4)-C(5)	1.379(4)	C(34)-C(35)	1.367(4)
C(5)-C(6)	1.381(4)	C(35)-C(36)	1.369(4)
C(7)-C(8)	1.394(3)	C(36)-C(37)	1.383(4)
C(8)-C(9)	1.37	C(32)-C(37)	1.406(4)
C(9)-C(10)	1.39(2)	C(31)-C(38)	1.465(3)
C(10)-C(11)	1.37(2)	C(31)-C(28)	1.456(3)
C(11)-C(12)	1.37(2)	C(38)-C(39)	1.405(3)
C(7)-C(12)	1.39(2)	C(39)-C(40)	1.384(3)
C(13)-C(14)	1.391(3)	C(40)-C(41)	1.378(3)
C(14)-C(15)	1.384(3)	C(41)-C(42)	1.378(4)
C(15)-C(16)	1.383(3)	C(42)-C(43)	1.385(3)
C(16)-C(17)	1.391(3)	C(38)-C(43)	1.404(3)
C(17)-C(18)	1.390(3)	C(1)-N(1)	1.413(3)
C(13)-C(18)	1.392(3)	N(1)-C(13)	1.424(3)
C(19)-C(20)	1.386(3)	C(7)-N(1)	1.422
C(20)-C(21)	1.387(3)	C(16)-N(2)	1.431(3)
C(21)-C(22)	1.377(4)	C(25)-N(2)	1.404(3)
C(22)-C(23)	1.377(3)	C(19)-N(2)	1.420(3)

18. Table S3. Electrochemical data of the target neutral radicals.

Table S3. Electrochemical data of **TTM-DPA**, **TTM-2DPA**, **TTM-3DPA**, **TTM-BDPA**, and **TTM-TDPA**.

Radical	E^{1}_{ox} (V)	E^{2}_{ox} (V)	E^{3}_{ox} (V)	$\Delta E^{1\text{-}2}_{ox}$[a] (V)	E^{1}_{red} (V)	E_{SOMO}[b] (eV)	E_{SUMO}[b] (eV)	E_{g} (eV)
TTM-DPA	0.20	-	-	-	-1.02	-4.92	-3.86	1.06
TTM-2DPA	-0.05	0.74	-	0.79	-1.21	-4.67	-3.70	0.97
TTM-3DPA	-0.21	0.79	1.08	1.00	-1.36	-4.51	-3.55	0.96
TTM-BDPA	-0.02	0.79	-	0.81	-1.12	-4.74	-3.79	0.95
TTM-TDPA	-0.04	0.71	0.97	0.75	-1.09	-4.67	-3.78	0.89

[a] $\Delta E^{1\text{-}2}_{ox} = E^{2}_{ox} - E^{1}_{ox}$.

[b] The SOMO and SUMO levels were determined from the first oxidation and reduction onset potentials which were calibrated with ferrocene.

19. Table S4. Calcualted energy gap of the target neutral radicals.

Table S4. Calculated SOMO and SUMO energy levels, Energy gap, and Diple Moment of the TTM radical derivatives.

Radical	E_{SOMO} (eV)	E_{SUMO} (eV)	$E_g^{calcd.}$ (eV)	Dipole Moment (Debye)
TTM-DPA	-5.05	-3.08	1.97	4.95
TTM-2DPA	-4.71	-2.82	1.89	4.25
TTM-3DPA	-4.43	-2.59	1.84	0.10
TTM-BDPA	-4.86	-3.03	1.83	5.78
TTM-TDPA	-4.70	-3.00	1.70	6.40

20. Table S5. Calculated energies, oscillator strength and compositions of major electronic transitions of the target neutral radicals and their oxidized monocations.

Table S5. Calculated absorption maxima, oscillator strength and compositions of major electronic transitions of the TTM radical derivatives and their oxidized monocations.

Compound	λ_{abs}^{exp} (nm)	λ_{abs}^{calcd} (nm)	Osc. Strength	Major contributions
TTM-2DPA	650	619	0.23	β-HOMO → SUMO (95%)
TTM-3DPA	637	593	0.21	β-HOMO → SUMO (94%)
TTM-BDPA	675	708	0.18	β-HOMO → SUMO (93%)
TTM-TDPA	717	771	0.21	β-HOMO → SUMO (96%)
TTM-2DPA$^+$	864	758	1.03	HOMO → LUMO (71%)
TTM-3DPA$^+$	801	731	0.77	HOMO → LUMO (70%)
TTM-BDPA$^+$	988	1015	0.72	HOMO → LUMO (71%)
TTM-TDPA$^+$	907	970	0.97	HOMO → LUMO (71%)

21. Table S6-S13. Computational data of the neutral radicals and the oxidized monocations.

Table S6. Computational data for **TTM-2DPA**. (E = -4985.06 hartree).

Centre Number	Atomic Symbol	Coordinates (Angstroms)		
		X	Y	Z
1	C	3.81614300	-0.71090400	0.06334300
2	C	3.55517900	0.33024200	-0.84141200
3	C	2.31297500	0.94476700	-0.86342700
4	C	1.24354800	0.60039000	0.00622300
5	C	1.56200800	-0.45102200	0.90783900
6	C	2.78912100	-1.09460900	0.94035100
7	H	4.31748900	0.65115900	-1.53969400
8	H	2.95287900	-1.88691400	1.65945100
9	C	-0.06501000	1.26694100	-0.01950200
10	C	-0.13829100	2.74040100	-0.04076700
11	C	0.58726200	3.55936300	0.86282000
12	C	-0.93983600	3.45627100	-0.96754400
13	C	0.53248600	4.94947400	0.85130200
14	C	-1.02130300	4.84478700	-0.99860000
15	C	-0.27795800	5.58273200	-0.08426200
16	H	1.09726500	5.52252400	1.57592000
17	H	-1.63839000	5.33741100	-1.73952400
18	C	-1.29870000	0.47416500	-0.02435800
19	C	-2.40511300	0.74458500	0.82634600
20	C	-1.50388300	-0.63990500	-0.88383400
21	C	-3.57330300	-0.00046500	0.83483100
22	C	-2.66511300	-1.39525300	-0.90417400
23	C	-3.72673500	-1.09009300	-0.03719500
24	H	-4.35501200	0.24669600	1.54173800
25	H	-2.75863900	-2.20529800	-1.61616100
26	C	-6.16299300	-1.24623000	0.26099900
27	C	-7.05212000	-1.87564800	1.14433000
28	C	-6.52754200	-0.02709000	-0.32991700
29	C	-8.28703400	-1.29405700	1.42601400
30	H	-6.76988800	-2.81746100	1.60421800
31	C	-7.75724600	0.55568000	-0.02823100
32	H	-5.84585900	0.45741800	-1.02197700
33	C	-8.64461700	-0.07485400	0.84654200
34	H	-8.96651200	-1.79188900	2.11255900
35	H	-8.02667900	1.50086300	-0.49166200
36	H	-9.60488200	0.37905400	1.07386300
37	C	-4.86842100	-3.24551900	-0.34959200
38	C	-5.80301000	-3.79594200	-1.23878200
39	C	-3.90935000	-4.07984800	0.24421700
40	C	-5.77844800	-5.16014800	-1.52324700
41	H	-6.54363200	-3.15088900	-1.70089300
42	C	-3.88162000	-5.43977300	-0.06013000

43	H	-3.19091300	-3.65872500	0.94056900
44	C	-4.81659500	-5.98815900	-0.94066800
45	H	-6.50807100	-5.57377000	-2.21422800
46	H	-3.13290300	-6.07455700	0.40596800
47	H	-4.79616400	-7.04970200	-1.16992700
48	C	5.83115500	-1.50127300	-1.10652200
49	C	5.22493500	-1.96178800	-2.28494100
50	C	7.20174800	-1.20395500	-1.10914000
51	C	5.97892900	-2.10781100	-3.44814300
52	H	4.16638600	-2.20249300	-2.28325000
53	C	7.95132000	-1.37030900	-2.27238600
54	H	7.67131300	-0.84483100	-0.19880000
55	C	7.34494800	-1.81762600	-3.44810200
56	H	5.49651800	-2.46374300	-4.35443100
57	H	9.01233900	-1.13578500	-2.26090200
58	H	7.93067500	-1.93907500	-4.35474900
59	C	5.59656800	-1.85972200	1.31408900
60	C	6.15834000	-3.14408300	1.35724600
61	C	5.57473000	-1.07911900	2.47963600
62	C	6.69270300	-3.63422600	2.54757500
63	H	6.17362700	-3.74990000	0.45672500
64	C	6.09514900	-1.58476900	3.66973400
65	H	5.15043400	-0.08044100	2.44671500
66	C	6.66006600	-2.86128400	3.71015700
67	H	7.12490500	-4.63109300	2.56724600
68	H	6.07065700	-0.97007600	4.56545700
69	H	7.07111200	-3.24915900	4.63775500
70	Cl	0.40834200	-0.97343500	2.13036000
71	Cl	2.09973100	2.16364700	-2.11455300
72	Cl	-0.36381400	7.33271900	-0.11119100
73	Cl	-1.83385900	2.62168500	-2.22762000
74	Cl	1.55520400	2.85492200	2.14734300
75	Cl	-0.31059700	-1.06886900	-2.10451800
76	Cl	-2.31127200	2.00519500	2.05043100
77	N	5.06778800	-1.35009700	0.09019300
78	N	-4.90664200	-1.85203000	-0.04285100

Table S7. Computational data for **TTM-3DPA**. (E = -5042.91 hartree).

Centre Number	Atomic Symbol	Coordinates (Angstroms)		
		X	Y	Z
1	C	4.35610900	0.00032100	-0.00002500
2	C	3.63404600	0.80271600	-0.89625300
3	C	2.24760000	0.78505800	-0.89170500
4	C	1.46888700	0.00007500	-0.00003600
5	C	2.24773100	-0.78478000	0.89163400
6	C	3.63418100	-0.80217900	0.89620800
7	H	4.15445800	1.42933700	-1.60933900
8	H	4.15470100	-1.42866300	1.60933700
9	C	-0.00133300	-0.00001700	-0.00000900
10	C	-0.73554700	1.27141300	-0.00946200
11	C	-0.43052300	2.35431400	0.85869400
12	C	-1.81997500	1.53839300	-0.88831000
13	C	-1.11787600	3.55796300	0.86367900
14	C	-2.51737600	2.73604100	-0.91312200
15	C	-2.17818800	3.77238400	-0.02998600
16	H	-0.84823200	4.32093700	1.58289300
17	H	-3.30779300	2.87574900	-1.63965200
18	C	-0.73543900	-1.27150600	0.00945400
19	C	-1.81970900	-1.53869200	0.88842400
20	C	-0.43037000	-2.35430000	-0.85882700
21	C	-2.51697700	-2.73641600	0.91318900
22	C	-1.11761900	-3.55800200	-0.86387800
23	C	-2.17784100	-3.77260400	0.02985000
24	H	-3.30724900	-2.87630400	1.63984400
25	H	-0.84794300	-4.32090300	-1.58316600
26	C	-4.27499300	-5.01865100	0.33955300
27	C	-4.78856400	-5.98238300	1.22021300
28	C	-5.14877100	-4.09263300	-0.25058700
29	C	-6.15370500	-6.01963500	1.49850900
30	H	-4.11394000	-6.69708700	1.68085800
31	C	-6.50978000	-4.12666200	0.04788700
32	H	-4.75676700	-3.35101800	-0.93952000
33	C	-7.02094800	-5.09100400	0.91910900
34	H	-6.53758800	-6.77145200	2.18293000
35	H	-7.17453300	-3.40284000	-0.41590500
36	H	-8.08334400	-5.11867900	1.14376200
37	C	-2.20856500	-6.21554000	-0.25075700
38	C	-2.79342700	-7.15334000	-1.11480300
39	C	-0.96389600	-6.50067600	0.33124000
40	C	-2.14418600	-8.35668100	-1.38478400
41	H	-3.75418900	-6.93314100	-1.56929400
42	C	-0.31404500	-7.69899000	0.04086000
43	H	-0.51201200	-5.78162700	1.00728400
44	C	-0.90055000	-8.63490900	-0.81374400
45	H	-2.60882500	-9.07373300	-2.05633400
46	H	0.64994200	-7.90586300	0.49781600

47	H	-0.39409200	-9.57071600	-1.03207300
48	C	6.48689000	0.16647000	-1.21844000
49	C	6.11643800	-0.54557600	-2.36947900
50	C	7.58559600	1.03704100	-1.27420300
51	C	6.82768200	-0.37666100	-3.55616300
52	H	5.27268400	-1.22727800	-2.32810600
53	C	8.30199400	1.18531200	-2.46049100
54	H	7.87180900	1.59187300	-0.38629900
55	C	7.92567000	0.48470000	-3.60837400
56	H	6.52822600	-0.93347900	-4.43999700
57	H	9.15079300	1.86339900	-2.48901400
58	H	8.48173400	0.60842700	-4.53324200
59	C	6.48678500	-0.16556400	1.21853100
60	C	7.58542800	-1.03619300	1.27437700
61	C	6.11621700	0.54649400	2.36951700
62	C	8.30167700	-1.18451900	2.46074900
63	H	7.87169100	-1.59101000	0.38647900
64	C	6.82731500	0.37752800	3.55628800
65	H	5.27250100	1.22823200	2.32802700
66	C	7.92524700	-0.48389500	3.60859300
67	H	9.15043900	-1.86264600	2.48939300
68	H	6.52780000	0.93434700	4.44009900
69	H	8.48121200	-0.60768000	4.53351300
70	Cl	1.48047000	-1.76481800	2.13676900
71	Cl	1.48018100	1.76501500	-2.13681500
72	Cl	-2.28348000	0.37595500	-2.12675100
73	Cl	0.79765800	2.18795500	2.10898300
74	Cl	0.79773800	-2.18770700	-2.10915500
75	Cl	-2.28307500	-0.37647700	2.12709400
76	N	5.76445600	0.00047900	0.00000700
77	N	-2.88081200	-4.99168600	0.04001900
78	C	-4.27556700	5.01804700	-0.33959700
79	C	-4.78948100	5.98159000	-1.22027200
80	C	-5.14904800	4.09187600	0.25073300
81	C	-6.15465600	6.01847100	-1.49841800
82	H	-4.11508400	6.69643900	-1.68102900
83	C	-6.51009900	4.12553000	-0.04758900
84	H	-4.75676400	3.35044800	0.93972100
85	C	-7.02160200	5.08965800	-0.91885000
86	H	-6.53881300	6.77013800	-2.18285200
87	H	-7.17460500	3.40157800	0.41635400
88	H	-8.08402300	5.11705000	-1.14341400
89	C	-2.20943400	6.21541200	0.25054000
90	C	-0.96483900	6.50093000	-0.33144200
91	C	-2.79459100	7.15307700	1.11454200
92	C	-0.31535700	7.69943500	-0.04105800
93	H	-0.51272400	5.78202700	-1.00748900
94	C	-2.14571700	8.35661200	1.38453000
95	H	-3.75532500	6.93262100	1.56898000
96	C	-0.90214300	8.63519700	0.81353200

97	H	0.64857600	7.90657700	-0.49800600
98	H	-2.61060300	9.07353400	2.05604800
99	H	-0.39594400	9.57113900	1.03188400
100	N	-2.88136800	4.99139300	-0.04020600

Table S8. Computational data for **TTM-BDPA**. (E = -5444.65 hartree).

Centre Number	Atomic Symbol	Coordinates (Angstroms)		
		X	Y	Z
1	C	3.55075800	4.70024300	-0.34643900
2	C	4.18435500	4.06813800	0.71765400
3	C	4.10125900	2.68341300	0.82359100
4	C	3.40558900	1.86896100	-0.10678500
5	C	2.78767800	2.58199200	-1.16720800
6	C	2.84717100	3.96599200	-1.29494200
7	H	4.71712100	4.64031100	1.46681800
8	H	2.36915000	4.45598500	-2.13389200
9	C	3.33444900	0.39988000	0.01012200
10	C	4.57150800	-0.37235900	0.23382600
11	C	5.74502800	-0.19010000	-0.54255700
12	C	4.68565000	-1.35508300	1.25170800
13	C	6.92049400	-0.90446800	-0.33378600
14	C	5.84476500	-2.08997000	1.47894100
15	C	6.95862000	-1.85499000	0.68025100
16	H	7.78116000	-0.73352000	-0.96820600
17	H	5.87968200	-2.81689500	2.28068100
18	C	2.04687000	-0.28568100	-0.09485300
19	C	1.84486200	-1.45296700	-0.88419400
20	C	0.87256200	0.14843800	0.58210800
21	C	0.63137500	-2.10954300	-0.99563200
22	C	-0.35051000	-0.49416700	0.49606600
23	C	-0.49819800	-1.64340300	-0.29999200
24	H	0.55239800	-2.96728100	-1.65099600
25	H	-1.18599600	-0.12248100	1.07495700
26	C	-1.80421500	-3.69717200	-0.66528200
27	C	-2.70008500	-4.18406700	-1.62792600
28	C	-1.00304200	-4.60039100	0.04932300
29	C	-2.79081000	-5.55373000	-1.86910400
30	H	-3.32002700	-3.48524900	-2.18057100
31	C	-1.08898000	-5.96715900	-0.21052900
32	H	-0.31852400	-4.22771000	0.80493900
33	C	-1.98398200	-6.45152700	-1.16683100
34	H	-3.48813500	-5.91825600	-2.61853400
35	H	-0.46231700	-6.65619100	0.34910000
36	H	-2.05301900	-7.51785600	-1.36156100
37	C	-2.95245900	-1.56911400	-0.23847000
38	C	-3.94680800	-2.03874400	0.63071900
39	C	-3.18795800	-0.38683200	-0.95480200
40	C	-5.14768200	-1.35303700	0.77195500
41	H	-3.78187000	-2.95782200	1.18462800
42	C	-4.37422100	0.31890300	-0.78875200
43	H	-2.42793700	-0.00979500	-1.63241600
44	C	-5.38002500	-0.15545300	0.07217100
45	H	-5.91129800	-1.73909200	1.43889700
46	H	-4.53187400	1.24024500	-1.33934700

47	Cl	1.96368600	1.74050000	-2.46894100
48	Cl	4.84324600	1.99039000	2.25505100
49	Cl	8.42753700	-2.76791500	0.95518200
50	Cl	3.37210600	-1.65435200	2.37735800
51	Cl	5.76350300	0.90904000	-1.91050300
52	Cl	0.93034900	1.49741700	1.71044100
53	Cl	3.13238800	-2.08305900	-1.90452100
54	N	-1.73221800	-2.29548700	-0.40177000
55	Cl	3.63973600	6.44295000	-0.49422100
56	N	-6.59488500	0.55300600	0.23013400
57	C	-7.19935400	1.19953900	-0.88521700
58	C	-7.28035900	0.55209800	-2.12825400
59	C	-7.72862900	2.49302400	-0.75426200
60	C	-7.86865400	1.19298400	-3.21711200
61	H	-6.88182500	-0.45210400	-2.23352200
62	C	-8.33171000	3.11855300	-1.84388100
63	H	-7.66440200	3.00062000	0.20296300
64	C	-8.40161100	2.47668300	-3.08214600
65	H	-7.92319700	0.67761500	-4.17247200
66	H	-8.73637900	4.12024300	-1.72539800
67	H	-8.86583900	2.97034500	-3.93103900
68	C	-7.22005700	0.62770100	1.50759500
69	C	-6.46108000	0.88578600	2.65999600
70	C	-8.60698100	0.44948300	1.62964700
71	C	-7.07899900	0.95192400	3.90750000
72	H	-5.38957800	1.03495400	2.57105800
73	C	-9.21862300	0.53588400	2.87897300
74	H	-9.19805200	0.24534200	0.74246000
75	C	-8.46012900	0.78211200	4.02537600
76	H	-6.47690500	1.15305200	4.78966700
77	H	-10.29364200	0.39585300	2.95613000
78	H	-8.93934800	0.84190800	4.99832400

Table S9. Computational data for **TTM-TDPA**. (E = -5062.10 hartree).

Centre Number	Atomic Symbol	Coordinates (Angstroms)		
		X	Y	Z
1	C	6.12917200	-4.01524900	0.98137000
2	C	6.51697300	-3.31575400	-0.15594000
3	C	5.87902200	-2.11694800	-0.45849200
4	C	4.84896200	-1.55634500	0.34002700
5	C	4.50956600	-2.32255700	1.48573500
6	C	5.12392000	-3.52801500	1.80947700
7	H	7.28701100	-3.70302700	-0.81132100
8	H	4.83436500	-4.06289300	2.70529800
9	C	4.18803900	-0.27783300	0.01512400
10	C	5.01102400	0.90417700	-0.30492000
11	C	6.09981100	1.32701900	0.50048600
12	C	4.78110200	1.70747000	-1.45242100
13	C	6.88976000	2.43284700	0.20241300
14	C	5.54866700	2.82289600	-1.77187600
15	C	6.60331000	3.17606900	-0.93719700
16	H	7.69928700	2.71734700	0.86287000
17	H	5.33662600	3.39029100	-2.66939200
18	C	2.72975500	-0.18287000	0.01040800
19	C	2.01280200	0.88607100	0.61955300
20	C	1.88413200	-1.14994400	-0.60379200
21	C	0.63272600	0.98649900	0.62609900
22	C	0.50261900	-1.07035300	-0.61958500
23	C	-0.15775600	0.00556000	0.00050000
24	H	0.16440000	1.81070000	1.14820500
25	H	-0.06512600	-1.82733300	-1.14485900
26	C	-2.20107500	1.36836700	0.07100200
27	C	-3.23891500	1.58219600	0.98837700
28	C	-1.83140100	2.41685000	-0.78368000
29	C	-3.88433700	2.81167100	1.05646500
30	H	-3.53012000	0.78158000	1.66131100
31	C	-2.47606900	3.64697700	-0.71758600
32	H	-1.04289900	2.26108400	-1.51370400
33	C	-3.51388600	3.86747300	0.20502000
34	H	-4.67481100	2.96374100	1.78384700
35	H	-2.18515100	4.44241000	-1.39556300
36	C	-2.36424900	-1.07511800	-0.08564800
37	C	-3.42611800	-1.13996300	-0.99876200
38	C	-2.13505400	-2.17218200	0.75781500
39	C	-4.24218600	-2.26341800	-1.06048900
40	H	-3.62142500	-0.29455800	-1.65121800
41	C	-2.92890400	-3.31035900	0.67332200
42	H	-1.31832500	-2.13825300	1.47240200
43	C	-4.00296400	-3.37420300	-0.23200800
44	H	-5.06739200	-2.28976000	-1.76434000
45	H	-2.72624800	-4.15486100	1.32349100
46	Cl	3.32718300	-1.74462400	2.64763200

47	Cl	6.36518300	-1.36375500	-1.96733500
48	Cl	7.58294300	4.57486900	-1.32647300
49	Cl	3.54094600	1.28744500	-2.62188700
50	Cl	6.47430100	0.51829600	2.01242200
51	Cl	2.56572000	-2.48542200	-1.52532000
52	Cl	2.85599300	2.12208000	1.54648700
53	N	-1.55260200	0.09736600	-0.00383500
54	Cl	6.91664000	-5.52906300	1.37621600
55	N	-4.82335400	-4.52552700	-0.30677700
56	C	-5.16981300	-5.23747900	0.87639500
57	C	-5.55689600	-4.54872100	2.03694700
58	C	-5.13380000	-6.64065900	0.89647500
59	C	-5.88897700	-5.25198800	3.19345100
60	H	-5.59604700	-3.46398900	2.02538400
61	C	-5.48556100	-7.33574100	2.05204700
62	H	-4.83013000	-7.17866600	0.00407400
63	C	-5.86016400	-6.64810100	3.20833100
64	H	-6.18639600	-4.70324100	4.08324200
65	H	-5.45198300	-8.42205300	2.05047400
66	H	-6.12645500	-7.19311700	4.10937800
67	C	-5.30582800	-4.98037000	-1.56683300
68	C	-4.45543400	-5.02620500	-2.68292800
69	C	-6.63971200	-5.39427700	-1.70826200
70	C	-4.93627900	-5.46679600	-3.91463400
71	H	-3.42015200	-4.71725200	-2.57812700
72	C	-7.10651000	-5.85086900	-2.93949400
73	H	-7.30302200	-5.35666900	-0.84992500
74	C	-6.26152000	-5.88567600	-4.05079900
75	H	-4.26436200	-5.49663000	-4.76836300
76	H	-8.14192100	-6.16819500	-3.03167300
77	H	-6.63068300	-6.23571700	-5.01051600
78	N	-4.16904600	5.12050500	0.27400600
79	C	-5.57105900	5.18487400	0.51207700
80	C	-6.09579400	6.12596700	1.41195200
81	C	-6.44922500	4.31427900	-0.15291500
82	C	-7.46997800	6.19584200	1.63324400
83	H	-5.42168600	6.79874600	1.93251500
84	C	-7.82020800	4.37940100	0.08881000
85	H	-6.05119900	3.59098200	-0.85766500
86	C	-8.34036300	5.32166600	0.97867100
87	H	-7.85943500	6.93049800	2.33313600
88	H	-8.48590800	3.69820600	-0.43477800
89	H	-9.41020500	5.37457800	1.15895200
90	C	-3.42855400	6.32576900	0.10786400
91	C	-3.93571000	7.36602900	-0.68648200
92	C	-2.18572700	6.49279000	0.73894900
93	C	-3.21494600	8.54926900	-0.83757600
94	H	-4.89392700	7.24064200	-1.18069500
95	C	-1.46348400	7.67221200	0.56665700
96	H	-1.79198000	5.69616300	1.36231400

97	C	-1.97379200	8.70883900	-0.21771300
98	H	-3.62188000	9.34498700	-1.45602600
99	H	-0.50254400	7.78482800	1.06165200
100	H	-1.41136300	9.62947300	-0.34393900

Table S10. Computational data for **TTM-2DPA**$^{+}$. (E = -4984.86 hartree).

Centre Number	Atomic Symbol	Coordinates (Angstroms)		
		X	Y	Z
1	C	-0.19260800	5.45698600	0.03827900
2	C	0.59547000	4.79310400	0.97618300
3	C	0.64450200	3.40481700	0.95389000
4	C	-0.09173400	2.62700800	0.02295200
5	C	-0.88193800	3.36039200	-0.89973500
6	C	-0.93185300	4.74896600	-0.90690200
7	H	1.15227700	5.34691900	1.72174800
8	H	-1.52638800	5.26989400	-1.64701700
9	C	-0.03875500	1.14883700	0.01440400
10	C	1.23896100	0.49008500	-0.01418100
11	C	2.35097200	0.94272000	-0.80613600
12	C	1.54220300	-0.65544500	0.80337300
13	C	3.58710800	0.34136900	-0.79736700
14	C	2.78600400	-1.23799200	0.86067100
15	C	3.85052800	-0.76203800	0.05309900
16	H	4.36297000	0.72292600	-1.44650400
17	H	2.94724200	-2.07067400	1.53105900
18	C	-1.26509700	0.40521100	0.03415100
19	C	-1.48791000	-0.75338100	-0.79364800
20	C	-2.40962300	0.77870100	0.82439100
21	C	-2.68804900	-1.41881900	-0.85608600
22	C	-3.60789800	0.10825700	0.79181800
23	C	-3.79018800	-1.00862200	-0.06285000
24	H	-2.80466700	-2.23368100	-1.55766500
25	H	-4.40145200	0.40889100	1.46264600
26	C	-5.08665900	-3.00586800	-0.64286800
27	C	-6.01472600	-3.28302600	-1.65348700
28	C	-4.28622500	-4.02806200	-0.11685900
29	C	-6.13110600	-4.58269400	-2.14260000
30	H	-6.63534600	-2.48511700	-2.04866600
31	C	-4.40679000	-5.32377300	-0.61777900
32	H	-3.58641500	-3.80879900	0.68393100
33	C	-5.32766400	-5.60413000	-1.62945100
34	H	-6.84851200	-4.79589300	-2.92930500
35	H	-3.78922700	-6.11638400	-0.20594300
36	H	-5.42299700	-6.61542500	-2.01299200
37	C	-6.20530600	-1.05440500	0.34436100
38	C	-7.00643800	-1.72512600	1.27581600
39	C	-6.60114900	0.18879900	-0.16558200
40	C	-8.19827500	-1.14280200	1.70293400
41	H	-6.69385300	-2.69131000	1.65899000
42	C	-7.79266900	0.76498500	0.27324000
43	H	-5.98524000	0.69078400	-0.90568100
44	C	-8.59276200	0.10217600	1.20635100
45	H	-8.81712700	-1.66162200	2.42879600
46	H	-8.10071300	1.72684500	-0.12561000

47	Cl	-1.76797800	2.56265700	-2.18388900
48	Cl	1.58591300	2.65762300	2.22830400
49	Cl	0.37085500	-1.32090600	1.92666100
50	Cl	2.16583000	2.23144000	-1.97800400
51	Cl	-2.29178700	2.02392400	2.04956200
52	Cl	-0.28760100	-1.29819600	-1.94952200
53	N	-4.98873700	-1.66964000	-0.11768800
54	Cl	-0.25440300	7.19502600	0.04758600
55	H	-9.52255700	0.55143900	1.54177000
56	N	5.08843800	-1.34974100	0.09146200
57	C	5.49192400	-2.18744700	1.19137900
58	C	5.45495700	-1.69269200	2.50109600
59	C	5.96154900	-3.48079600	0.93693700
60	C	5.87278700	-2.50360300	3.55582800
61	H	5.11153900	-0.67929600	2.68651000
62	C	6.38331200	-4.28065900	1.99766200
63	H	5.99511000	-3.85066100	-0.08297000
64	C	6.33743600	-3.79690400	3.30742400
65	H	5.84738000	-2.11742300	4.57045500
66	H	6.74510700	-5.28511400	1.79938900
67	H	6.66799700	-4.42323200	4.13045700
68	C	6.04890900	-1.15315400	-0.96400400
69	C	5.71438000	-1.47327700	-2.28572300
70	C	7.32870800	-0.68075200	-0.65276600
71	C	6.65973900	-1.30175200	-3.29642100
72	H	4.72598400	-1.86080700	-2.51431600
73	C	8.26838100	-0.51937300	-1.66949400
74	H	7.58007700	-0.44377300	0.37620500
75	C	7.93666200	-0.82564100	-2.99152700
76	H	6.40024800	-1.55302100	-4.32051100
77	H	9.26007200	-0.14912200	-1.42755200
78	H	8.67204300	-0.69838800	-3.78014900

Table S11. Computational data for **TTM-3DPA**$^{+}$. (E = -5042.73 hartree).

Centre Number	Atomic Symbol	Coordinates (Angstroms)		
		X	Y	Z
1	C	4.32942600	-0.06291600	-0.00048900
2	C	3.60883000	0.79866500	-0.86119300
3	C	2.23156400	0.82368700	-0.83913300
4	C	1.43742800	-0.02216000	-0.00037000
5	C	2.20744300	-0.89039300	0.83798400
6	C	3.58486900	-0.90417000	0.85993500
7	H	4.13700000	1.44776000	-1.54591000
8	H	4.09460400	-1.56805700	1.54444500
9	C	-0.01233700	-0.00107700	0.00029300
10	C	-0.71683300	1.26227500	0.00604800
11	C	-0.34503500	2.36148300	0.84695600
12	C	-1.84823600	1.53118400	-0.83126400
13	C	-1.01240700	3.56529600	0.86482700
14	C	-2.51255500	2.73702000	-0.84809400
15	C	-2.11518300	3.79225100	0.00719300
16	H	-0.71284400	4.32636300	1.57269800
17	H	-3.31722100	2.88828000	-1.55496900
18	C	-0.75362000	-1.24315800	-0.00488700
19	C	-1.89190700	-1.47865200	0.83316200
20	C	-0.41521200	-2.35267800	-0.84637800
21	C	-2.59192500	-2.66410900	0.84987200
22	C	-1.11842800	-3.53590400	-0.86458800
23	C	-2.22709600	-3.73017800	-0.00650300
24	H	-3.40021500	-2.79166300	1.55728500
25	H	-0.84216600	-4.30519500	-1.57304500
26	C	-4.26318700	-4.99588300	0.51727100
27	C	-4.57090200	-5.96022600	1.48425000
28	C	-5.26118700	-4.13946700	0.03454300
29	C	-5.87349900	-6.05972700	1.97002100
30	H	-3.79283000	-6.62409000	1.84763700
31	C	-6.55934000	-4.24115200	0.53345800
32	H	-5.01993600	-3.40786900	-0.73072400
33	C	-6.86934900	-5.20033400	1.49983500
34	H	-6.10838500	-6.80745600	2.72173700
35	H	-7.33164000	-3.57819400	0.15448600
36	H	-7.88277700	-5.28116100	1.88131500
37	C	-2.34803500	-6.12551700	-0.52441700
38	C	-3.04312600	-6.86584100	-1.48796800
39	C	-1.11412000	-6.58058300	-0.04181400
40	C	-2.49838100	-8.05455900	-1.97051600
41	H	-4.00166700	-6.50902600	-1.85136600
42	C	-0.57343000	-7.76644700	-0.53759800
43	H	-0.59024900	-6.01175600	0.72046500
44	C	-1.26291600	-8.50632600	-1.50053000
45	H	-3.03903700	-8.62541500	-2.71962600
46	H	0.38187400	-8.11817400	-0.15916000

47	H	-0.84196600	-9.43270000	-1.87963600
48	C	6.46522500	0.43334700	-1.10865200
49	C	6.24394800	-0.05607700	-2.40228400
50	C	7.45362600	1.39777500	-0.88135600
51	C	7.00074100	0.43455900	-3.46587200
52	H	5.48918500	-0.81904000	-2.56812500
53	C	8.21188300	1.87476000	-1.94943400
54	H	7.62393100	1.76529500	0.12571500
55	C	7.98607200	1.39870800	-3.24301500
56	H	6.82790500	0.05136800	-4.46729600
57	H	8.97720100	2.62404100	-1.76967900
58	H	8.57827900	1.77360200	-4.07238700
59	C	6.45018900	-0.61778500	1.10877200
60	C	7.41263900	-1.60827800	0.88217000
61	C	6.24099800	-0.12278600	2.40230100
62	C	8.15695000	-2.10550800	1.95082300
63	H	7.57392400	-1.98009700	-0.12480500
64	C	6.98347300	-0.63363400	3.46645700
65	H	5.50679300	0.66009400	2.56761100
66	C	7.94285000	-1.62376900	3.24428800
67	H	8.90210600	-2.87497000	1.77160600
68	H	6.82009400	-0.24608300	4.46779100
69	H	8.52410200	-2.01449900	4.07410100
70	Cl	1.43890300	-1.93050600	2.02597400
71	Cl	1.49253800	1.88465700	-2.02745100
72	Cl	-2.37052500	0.38153200	-2.05087700
73	Cl	0.90406700	2.18897500	2.06791400
74	Cl	0.83815600	-2.21720200	-2.06761700
75	Cl	-2.37867600	-0.31457100	2.05380400
76	N	5.70685100	-0.08206700	-0.00021400
77	N	-2.92626400	-4.91582700	-0.00529300
78	C	-4.11270700	5.11812700	-0.51577800
79	C	-4.39232500	6.08969800	-1.48405200
80	C	-5.13551400	4.29301500	-0.03045500
81	C	-5.69190700	6.22764100	-1.96850900
82	H	-3.59499900	6.72915200	-1.84947000
83	C	-6.43060200	4.43298900	-0.52804900
84	H	-4.91548200	3.55573300	0.73576000
85	C	-6.71266800	5.39947500	-1.49571000
86	H	-5.90502100	6.98085100	-2.72123900
87	H	-7.22210100	3.79426900	-0.14707200
88	H	-7.72364700	5.51020400	-1.87617900
89	C	-2.16290900	6.19079700	0.52204400
90	C	-0.91589600	6.60694600	0.03796900
91	C	-2.83432200	6.95378200	1.48471300
92	C	-0.33867000	7.77642500	0.53145500
93	H	-0.41021700	6.02104400	-0.72366100
94	C	-2.25297000	8.12598800	1.96494400
95	H	-3.80315900	6.62725600	1.84927500
96	C	-1.00446400	8.53875600	1.49355100

97	H	0.62675600	8.09797500	0.15186000
98	H	-2.77536600	8.71444600	2.71339100
99	H	-0.55498100	9.45236100	1.87088300
100	N	-2.77822200	4.99849500	0.00539500

Table S12. Computational data for **TTM-BDPA**$^{+}$. (E = -5444.44 hartree).

Centre Number	Atomic Symbol	Coordinates (Angstroms)		
		X	Y	Z
1	C	-3.72525800	-4.63158300	0.02545800
2	C	-4.32817900	-3.89559800	1.04277100
3	C	-4.17644700	-2.51436900	1.05745100
4	C	-3.41989900	-1.81304000	0.08179700
5	C	-2.81408200	-2.62253600	-0.91782500
6	C	-2.96647900	-4.00228400	-0.95985900
7	H	-4.89510200	-4.38937900	1.82223400
8	H	-2.51225700	-4.57679100	-1.75743400
9	C	-3.31727000	-0.34040800	0.05518700
10	C	-4.57006200	0.43458900	0.14939300
11	C	-5.70414100	0.16469600	-0.66096300
12	C	-4.73986700	1.46635500	1.11274700
13	C	-6.90562500	0.84977900	-0.52664300
14	C	-5.93679100	2.15160000	1.27444300
15	C	-7.01554900	1.83742600	0.44943600
16	H	-7.73654800	0.62607700	-1.18414300
17	H	-6.03134800	2.91008900	2.04144100
18	C	-2.06527100	0.30118200	-0.05629100
19	C	-1.86058100	1.54076400	-0.78911400
20	C	-0.84719700	-0.21157500	0.55241200
21	C	-0.64224000	2.15260600	-0.91398600
22	C	0.37050000	0.40233000	0.44012300
23	C	0.51886500	1.60281000	-0.30605900
24	H	-0.55372900	3.03007100	-1.54062300
25	H	1.21659500	0.00658700	0.98652300
26	C	1.82140500	3.61423600	-0.74636400
27	C	2.59132400	4.03219000	-1.83815900
28	C	1.15683700	4.54784700	0.05858000
29	C	2.68385700	5.39160500	-2.12885800
30	H	3.10095400	3.29645700	-2.45197800
31	C	1.25656800	5.90545200	-0.24249900
32	H	0.58230400	4.21203900	0.91644400
33	C	2.01770200	6.32896100	-1.33441600
34	H	3.27290800	5.71842600	-2.98028500
35	H	0.74781700	6.63179700	0.38385100
36	H	2.09483600	7.38729300	-1.56411600
37	C	2.95693900	1.49328300	-0.27635700
38	C	4.01992600	2.06289900	0.44788300
39	C	3.13990900	0.23021500	-0.86934400
40	C	5.21468800	1.38430900	0.59683300
41	H	3.90188800	3.04390300	0.89639900
42	C	4.33580300	-0.45045400	-0.72674500
43	H	2.34201900	-0.21394700	-1.45621300
44	C	5.40698500	0.10468100	0.01627700
45	H	6.01934800	1.84257900	1.15888700
46	H	4.45355900	-1.42009600	-1.19491700

47	Cl	-1.90333200	-1.92496300	-2.24388200
48	Cl	-4.86993700	-1.68801100	2.43362800
49	Cl	-8.51585700	2.69487900	0.63783100
50	Cl	-3.47058200	1.88750300	2.24624600
51	Cl	-5.62163900	-0.97490900	-1.98486300
52	Cl	-0.88768300	-1.55287000	1.67414200
53	Cl	-3.13189700	2.24480900	-1.76106700
54	N	1.73671100	2.20949400	-0.43460000
55	Cl	-3.91573700	-6.35920200	-0.01313900
56	N	6.60777300	-0.57443700	0.16313500
57	C	7.00933000	-1.58862300	-0.76934900
58	C	7.04296500	-1.31382400	-2.14337600
59	C	7.40315900	-2.84770400	-0.29904900
60	C	7.45299800	-2.30082600	-3.03864600
61	H	6.75845700	-0.32900600	-2.50177100
62	C	7.82225100	-3.82466600	-1.20069400
63	H	7.38144700	-3.05263700	0.76669400
64	C	7.84491500	-3.55735800	-2.57143500
65	H	7.48170600	-2.08065100	-4.10192500
66	H	8.12623200	-4.79922500	-0.83000700
67	H	8.17144000	-4.32128700	-3.27063700
68	C	7.49632000	-0.28797900	1.25280600
69	C	7.02654600	-0.30850700	2.57331400
70	C	8.84705400	-0.02069500	0.99613700
71	C	7.90258500	-0.04639500	3.62572900
72	H	5.98343000	-0.53805600	2.76945800
73	C	9.71778500	0.22916300	2.05549100
74	H	9.20672700	-0.01181300	-0.02796400
75	C	9.24950600	0.22147100	3.37143400
76	H	7.53379700	-0.06770000	4.64718800
77	H	10.76384200	0.43682100	1.85011200
78	H	9.93086100	0.41785100	4.19377600

Table S13. Computational data for **TTM-TDPA**$^{+}$. (E = -5961.90 hartree).

Centre Number	Atomic Symbol	Coordinates (Angstroms)		
		X	Y	Z
1	C	-6.27054300	-3.90580600	-0.48780500
2	C	-6.58701300	-3.07288100	0.58205500
3	C	-5.87903100	-1.88788700	0.74631300
4	C	-4.83572400	-1.48533600	-0.12680300
5	C	-4.55107600	-2.38687600	-1.18737200
6	C	-5.25269900	-3.57068800	-1.37806600
7	H	-7.36108700	-3.34714400	1.28797200
8	H	-5.01853900	-4.21411600	-2.21688500
9	C	-4.13305800	-0.19112400	0.00422700
10	C	-4.96385300	1.02528500	0.13009700
11	C	-6.03694200	1.32016600	-0.74984200
12	C	-4.77902900	1.95054300	1.19226100
13	C	-6.86317500	2.42665000	-0.58997300
14	C	-5.59907100	3.05638000	1.37872700
15	C	-6.64022900	3.28650000	0.48211300
16	H	-7.65664200	2.62104600	-1.30085000
17	H	-5.43716300	3.71962200	2.21917500
18	C	-2.72489100	-0.12041600	0.00785300
19	C	-1.97334500	0.98061400	-0.57570900
20	C	-1.87068200	-1.14293900	0.59330800
21	C	-0.60634100	1.04658000	-0.58147200
22	C	-0.50361800	-1.07850400	0.59641300
23	C	0.17797700	0.01865400	0.00613400
24	H	-0.11678500	1.85724100	-1.10520400
25	H	0.06216600	-1.83891900	1.11877600
26	C	2.22325000	1.33297400	-0.06926800
27	C	3.31771400	1.49982300	-0.93579700
28	C	1.82739300	2.41122600	0.74237000
29	C	3.98324500	2.71003900	-1.00451700
30	H	3.62299800	0.68078800	-1.57895200
31	C	2.49334900	3.62214400	0.68038800
32	H	1.01442900	2.28323700	1.45055000
33	C	3.58826600	3.80719500	-0.19905400
34	H	4.80429900	2.82749200	-1.70161500
35	H	2.19149900	4.43039400	1.33579200
36	C	2.33403300	-1.10688500	0.06772500
37	C	3.43590700	-1.17873300	0.93739300
38	C	2.03990600	-2.21222900	-0.74989900
39	C	4.20820500	-2.32417500	1.00256000
40	H	3.68037400	-0.32914500	1.56678800
41	C	2.81130600	-3.35968900	-0.68969100
42	H	1.20491000	-2.16605700	-1.44209800
43	C	3.91583700	-3.45006400	0.19243800
44	H	5.05186300	-2.35863600	1.68119200
45	H	2.56590100	-4.19860200	-1.32947300
46	Cl	-3.33927200	-2.02509100	-2.40318100

47	Cl	-6.26606200	-0.96305600	2.18024100
48	Cl	-7.67130700	4.67183300	0.70220300
49	Cl	-3.54324600	1.71402000	2.41465700
50	Cl	-6.31812800	0.36209800	-2.18657500
51	Cl	-2.54098600	-2.45065200	1.54421500
52	Cl	-2.76669700	2.22120500	-1.52242700
53	N	1.54727200	0.08112100	0.00124600
54	Cl	-7.15344400	-5.38901700	-0.71327600
55	N	4.69124000	-4.60040100	0.25764900
56	C	4.73493700	-5.53230000	-0.83272500
57	C	5.05352900	-5.09570300	-2.12585500
58	C	4.49150400	-6.89096400	-0.59595100
59	C	5.11074600	-6.01284600	-3.17450900
60	H	5.26169600	-4.04449000	-2.30177200
61	C	4.56314200	-7.80281900	-1.64801300
62	H	4.25146600	-7.22488900	0.40865700
63	C	4.86805000	-7.36803700	-2.93973600
64	H	5.36158200	-5.66854800	-4.17378200
65	H	4.37340800	-8.85512300	-1.45734300
66	H	4.92128000	-8.08106500	-3.75700400
67	C	5.47574100	-4.90476100	1.41975300
68	C	4.88312000	-4.92593800	2.68978000
69	C	6.83386300	-5.21674000	1.27920900
70	C	5.65133600	-5.24099800	3.80989700
71	H	3.82506000	-4.70419000	2.79276900
72	C	7.59133300	-5.54293900	2.40310400
73	H	7.28655600	-5.20565300	0.29265000
74	C	7.00574600	-5.55210300	3.67103900
75	H	5.18501000	-5.25915000	4.79081200
76	H	8.64390500	-5.78437300	2.28678500
77	H	7.59939300	-5.80528600	4.54433900
78	N	4.25632100	5.02253700	-0.26552600
79	C	5.61083500	5.10219800	-0.73076400
80	C	5.94822900	6.01956400	-1.73402800
81	C	6.60392000	4.29149700	-0.16392100
82	C	7.26931100	6.11950400	-2.16739300
83	H	5.17651200	6.64907900	-2.16582600
84	C	7.92048800	4.38996400	-0.61206400
85	H	6.34248600	3.59670800	0.62862400
86	C	8.25822600	5.30404100	-1.61251400
87	H	7.52399900	6.83266200	-2.94597500
88	H	8.68623000	3.76192600	-0.16573000
89	H	9.28599500	5.38402600	-1.95375400
90	C	3.61738500	6.24361200	0.13199700
91	C	4.25577300	7.09958100	1.03852700
92	C	2.37356800	6.60041200	-0.40705100
93	C	3.64959500	8.30045100	1.40397400
94	H	5.22151400	6.82157400	1.44880200
95	C	1.76940000	7.79791100	-0.02667400
96	H	1.89167700	5.94479200	-1.12616700

97	C	2.40465000	8.65210400	0.87743800
98	H	4.14991500	8.95933800	2.10768300
99	H	0.80754000	8.07062500	-0.45144200
100	H	1.93518200	9.58789400	1.16561100

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