Supporting Information

Optical Nature of Non-Substituted Triphenylmethyl Cation: Crystalline State Emission, Thermochromism, and Phosphorescence

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Contents

1. General Information S2
2. Synthesis S2
3. Differential scanning calorimetry (DSC) measurement S3
4. UV-vis spectra measurements S3
5. X-ray crystallographic analysis S4
6. Variable-temperature X-ray analyses in O-crystal S8
7. Quantum chemical calculations S9
8. Excitation and emission spectra of Y-crystal S12
9. TD-DFT calculations S13
10. Emission spectra of trityl cation in frozen state S26
11. Emission decay curves of trityl cation S27
12. Evaluation of spin-orbit coupling between singlet and triplet states S29
General Information

Hexafluorophosphate (60%) and acetic anhydride were purchased from Fujifilm Wako chemicals and used without purification for reaction. For measurements, dried chloroform was purchased. Data collection for X-ray crystal analysis was performed on Rigaku R-AXIS RAPID II Imaging Plate or Rigaku XtaLAB Synergy Custom (Mo-Kα, λ = 0.71069 Å). The structure was solved with direct methods and refined with full-matrix least squares. The UV-vis spectra were recorded on JASCO V-570 spectrophotometer. The Solid state UV-vis spectra were recorded on JASCO V-570 spectrophotometer with ISN-470 integral sphere unit (Jasco). The emission spectra and emission quantum yields were recorded on FP-8500 spectrofluorometer with ILFC-847 fluorescence integral sphere unit (Jasco).

Measurement for emission lifetime. The emission profiles in the millisecond region as shown in Figure S23 were measured with a home-built setup. A commercially available camera flash was converted to UV flash by replacing its plastic window with a UV transmission filter (HOYA, U330). The UV flash was irradiated to the sample. The emission was guided into a monochromator and detected by a photomultiplier tube equipped with a digital oscilloscope. The sample cell was filled in liquid nitrogen and its temperature was kept at 77 K during the measurement. The emission lifetimes in the nanosecond region as shown in Figure S24 were measured with another home-built time-correlated single-photon counting (TCSPC) apparatus. The pulsed light source was a Ti:sapphire oscillator (Spectra-Physics, Tsunami, 900 nm, 100 fs, 80 MHz) and its output was divided into two portions. One was used for the start pulse of TCSPC and the other was converted to the second harmonics at 450 nm with a beta-barium borate crystal for the excitation pulse. The repetition rate of the pulsed irradiation was reduced to 8 MHz using an electro-optic modulator (Conoptics, Model 350). The polarization of the excitation pulse was set to the magic angle with respect to that of the fluorescence detection by using a film polarizer and Babinet-Soleil compensator. The emission signals were detected by a photomultiplier tube with a pre-amplifier and a TCSPC module (PicoQuamt, PicoHarp 300) after the spectral selection with a monochromator. The instrumental response function was 43 ps and the validity of the measurement was confirmed by measuring a fluorescence lifetime of a standard sample (coumarin 153 in methanol). The nano-–microsecond emission decay curves in Figure S25 were recorded with the other setup. Nanosecond UV pulses (355 nm, 10 Hz) from a frequency-tripled nanosecond YAG laser irradiated to sample in glass tube immersed in liquid nitrogen. The pulse energy employed was 0.4 mJ/pulse or less. The emission from the sample was collected in perpendicular direction by a high-NA lens and coupled to an optical fiber bundle. Excitation-cut filter (L39) was used to ensure to block the scattering of the excitation. The fiber bundle was connected to a monochromator (Jovin-Yvon HR-10) and detected by a photomultiplier tube (Hamamatsu R926). The signal from the photomultiplier was acquired and averaged by a digital oscilloscope (500 MHz, 5 GS/s).

Computational Methods. MP2 and TD-DFT calculations were performed with the Gaussian 16 program. The calculations of spin-orbit coupling (SOC) were performed with ORCA program (program version 4.2.1). The molecular geometries from X-ray crystallographic analysis were used for the calculations.

Synthesis

Synthesis of triphenylmethyl hexafluorophosphate (trityl PF₆)

To a solution of triphenylmethyl alcohol (100 mg, 0.38 mmol) in acetic anhydride (2 ml) was slowly added hexafluorophosphoric acid solution (60%, 0.5 ml) at room temperature (Caution! This reaction is exothermic and the solution is splashed.). For collecting yellow crystal (Y-crystal), the reaction vial was putted in a fridge to keep 4–5 °C for several hours whereas, for collecting orange crystal (O-crystal), the reaction vial was left at room temperature for several days to over a week with absence of light. Y- or O-crystal was collected by filtration and washed by acetic anhydride and dried diethyl ether. The obtained yield was 115 mg (0.29 mmol, 78%) or 122 mg (0.31 mmol, 83%), respectively. To avoid hydration reaction by air moisture, both crystals were stored in vacuumed glass tube. Mp: 183 °C (Y-crystal), 259 °C (O-crystal, decomp.). MS (DI): m/z 243 [M – PF₆].

S2
• Differential scanning calorimetry (DSC) measurement

Figure S1. DSC measurements (a) Y-crystal, (b) O-crystal. Heating scan rate was 20 °C/min because a slow decomposition below its melting point or decomposition point occurs during the measurement.

• UV-vis spectra measurements

Figure S2. (a) UV-vis spectrum of trityl cation (2% TFA in CHCl₃) and solid state diffuse reflection spectra of Y- and O-crystals after applying Kubelka-Munk function. (b) Solid-state diffuse reflectance spectrum of Y-crystal (Normalized intensity range: 0 to 1.0 a.u.) and translucent solution spectrum of trityl cation (Normalized intensity range: 0 to 0.12 a.u.).
X-ray crystallographic analysis

X-ray crystallography of Y-crystal

Crystal date for Y-crystal_170K: CCDC 2063283. C_{19}H_{15}PF_{6}, M_W = 388.29, Cubic, space group F 4_3 2 (no 210), a = b = c = 19.280(4) Å, V = 7166(5) Å^3, Z = 16, D = 1.440 g cm^3, T = 170 K, Data collection with MoKα radiation (multi-layer mirror monochromated). 17648 measured reflection, 697 unique reflections; structure solution by direct methods (Shelxs), refinement by fullmatrix least squares on F with anisotropic temperature factors for the non-H atoms. Final R1 = 0.0626, wR2 = 0.1698, GOF = 1.061.

Crystal date for Y-crystal_273K: CCDC 2063286. C_{19}H_{15}PF_{6}, M_W = 388.29, Cubic, space group F 4_3 2 (no 210), a = b = c = 19.401(6) Å, V = 7302(7) Å^3, Z = 16, D = 1.413 g cm^3, T = 273 K, Data collection with MoKα radiation (multi-layer mirror monochromated). 18004 measured reflection, 707 unique reflections; structure solution by direct methods (Shelxs), refinement by fullmatrix least squares on F with anisotropic temperature factors for the non-H atoms. Final R1 = 0.0701, wR2 = 0.2088, GOF = 1.147.

Figure S3. X-ray crystallography of Y-crystal at 170 K. (a) D_3 symmetric trityl cation in Y-crystal. Torsion angle of three phenyl rings is 32.93°. Bond length between C1 and C2 is 1.434 Å. (b) Depicting with two independent PF_6 anions and shortest distances between trityl cation and PF_6 anions. Inter-atomic distance between C1 and F1 is 3.503 Å, and between C4 and F7 is 3.273 Å. (c) Inter-atomic distance of central sp^2 carbons between neighboring trityl cations is 6.817 Å (Left figure is top view. Right figure is side view.). For clarity, other two trityl cations constructing a tetragonal cage are shown as wireframe and a central PF_6 anion is shown as capped stick. (d) Packing structure of Y-crystal. Protons are omitted for clarity.
Figure S4. X-ray crystallography of Y-crystal at 273 K. (a) $D_3$ symmetric trityl cation in Y-crystal. Torsion angle of three phenyl rings is 33.05°. Bond length between C1 and C2 is 1.431 Å. (b) Depicting with two independent PF$_6$ anions and shortest distances between trityl cation and PF$_6$ anions. Inter-atomic distance between C1 and F1 is 3.529 Å, and between C4 and F7 is 3.357 Å. (c) Inter-atomic distance of central sp$^2$ carbons between neighboring trityl cations is 6.859 Å (Left figure is top view. Right figure is side view.). For clarity, other two trityl cations constructing a tetragonal cage are shown as wireframe and a central PF$_6$ anion is shown as capped stick. (d) Packing structure of Y-crystal. Protons are omitted for clarity.

Table S1. Structural difference of Y-crystal between 273 K and 170 K.

|       | Cell length / Å | Cell volume / Å$^3$ | Torsion angle $\theta / ^\circ$ | C1-C2 / Å | C1-F1 / Å | C4-F7 / Å | C1(A)-C1(B) / Å |
|-------|-----------------|---------------------|---------------------------------|-----------|-----------|-----------|-----------------|
| 273 K | 19.401(6)       | 7302(7)             | 33.05                           | 1.431     | 3.529     | 3.357     | 6.859           |
| 170 K | 19.280(4)       | 7166(5)             | 32.93                           | 1.434     | 3.503     | 3.273     | 6.817           |
X-ray crystallography of Trityl BF$_4$

Crystal data for Trityl BF$_4$: CCDC 2093998. C$_{19}$H$_{15}$BF$_4$, $M_w = 330.13$, Cubic, space group $F$ 23 (no 196), $a = b = c = 18.5320(6)$ Å, $V = 6364.5(6)$ Å$^3$, $Z = 16$, $D = 1.378$ g cm$^{-3}$, $T = 200$ K, Data collection with MoK$\alpha$ radiation (multi-layer mirror monochromated). 2248 measured reflection, 894 unique reflections; structure solution by direct methods (Shelxs), refinement by fullmatrix least squares on $F$ with anisotropic temperature factors for the non-H atoms. Final $R_1 = 0.1303$, $wR_2 = 0.3474$, GOF = 1.630.

**Figure S5.** X-ray crystallography of Trityl BF$_4$ at 200 K. (a) $D_3$ symmetric trityl cation. Torsion angle of three phenyl rings is $30.90^\circ$. Bond length between C1 and C2 is 1.459 Å. (b) Depicting with two independent BF$_4$ anions and shortest distances between trityl cation and BF$_4$ anions. (c) Inter-atomic distance of central sp$^2$ carbons between neighboring trityl cations is 6.694 Å (Left figure is top view. Right figure is side view.). For clarity, other two trityl cations constructing a tetragonal cage are shown as wireframe and a central BF$_4$ anion is shown as capped stick. (d) Packing structure of Trityl BF$_4$. Protons are omitted for clarity.
X-ray crystallography of O-crystal

Crystal date for O-crystal_195K: CCDC 2063287. C_{10}H_{15}·PF_6, M_W = 388.29, Monoclinic, space group P 2_1/n (no 14), a = 9.9081(3), b = 8.6985(2), c = 19.3133(5) Å, β = 90.482(2)°, V = 1664.47(8) Å^3, Z = 4, D = 1.549 g cm^-3, T = 195 K, Data collection with MoKα radiation (multi-layer mirror monochromated). 21205 measured reflection, 4400 unique reflections; structure solution by direct methods (Shelxs), refinement by fullmatrix least squares on F with anisotropic temperature factors for the non-H atoms. Final R1 = 0.0435, wR2 = 0.1227, GOF = 1.070

Crystal date for O-crystal_273K: CCDC 2063285. C_{19}H_{15}·PF_6, M_W = 388.29, Monoclinic, space group P 2_1/n (no 14), a = 10.0072(3), b = 8.7452(3), c = 19.3379(6) Å, β = 90.121(3)°, V = 1692.35(9) Å^3, Z = 4, D = 1.524 g cm^-3, T = 273 K, Data collection with MoKα radiation (multi-layer mirror monochromated). 21566 measured reflection, 4466 unique reflections; structure solution by direct methods (Shelxs), refinement by fullmatrix least squares on F with anisotropic temperature factors for the non-H atoms. Final R1 = 0.0443, wR2 = 0.1255, GOF = 1.068

Crystal date for O-crystal_83K: CCDC 2063284. C_{19}H_{15}·PF_6, M_W = 388.29, Monoclinic, space group P 2_1/n (no 14), a = 9.8111(2), b = 8.6592(2), c = 19.2629(5) Å, β = 90.665(2)°, V = 1636.39(7) Å^3, Z = 4, D = 1.576 g cm^-3, T = 83 K, Data collection with MoKα radiation (multi-layer mirror monochromated). 31097 measured reflection, 4509 unique reflections; structure solution by direct methods (Shelxs), refinement by fullmatrix least squares on F with anisotropic temperature factors for the non-H atoms. Final R1 = 0.0464, wR2 = 0.1276, GOF = 1.059

Figure S6. X-ray crystallography of O-crystal (273 K). (a) Top view of trityl cation dimer in O-crystal with different colors and without PF_6 anions for clarity. (b) Side view of trityl cation dimer in O-crystal with PF_6 anions. (c) One dimensional alignment of trityl PF_6 (viewing from c axis). (d) The alignment of 1D chains and the distance between neighboring 1D chains is 7.197 Å. Protons are omitted for clarity. Ortep drawing is 50% probability.
Figure S7. X-ray crystallography of O-crystal (83 K). (a) Top view of trityl cation dimer in O-crystal with different colors and without PF₆ anions for clarity. (b) Side view of trityl cation dimer in O-crystal with PF₆ anions. (c) One dimensional alignment of trityl PF₆ (viewing from c axis). (d) The alignment of 1D chains and the distance between neighboring 1D chains is 7.059 Å. Protons are omitted for clarity. Ortep drawing is 50% probability.

· Variable-temperature X-ray analyses in O-crystal

Table S2. Structural comparison of trityl cation scaffold in O-crystal at 273 K, 195 K, and 83 K.

|       | φ₁   | φ₂   | φ₃   | C1-C2 | C1-C3 | C1-C4 |
|-------|------|------|------|-------|-------|-------|
| 273 K | 26.1°| 32.4°| 39.6°| 1.440 Å | 1.447 Å | 1.449 Å |
| 195 K | 25.4°| 31.8°| 40.2°| 1.437 Å | 1.450 Å | 1.450 Å |
| 83 K  | 24.8°| 31.5°| 40.5°| 1.438 Å | 1.450 Å | 1.450 Å |
| Δ(273 K-83 K) | 1.3° | 0.9° | -0.9° | 0.002 Å | -0.003 Å | -0.001 Å |
• Quantum chemical calculations

NBO analysis

**Figure S8.** Natural bond orbital analysis of trityl PF₆ (MP2/6-311+G**) for evaluating charge transfer interaction between trityl cation and PF₆ anion. (a) X-ray structures in O-crystal at both 273 and 83 K. From NBO analysis, lone pairs on F1 (PF₆ anion) act as donor to a vacant orbital on C1 (trityl cation). Upon cooling the temperature from 273 K to 83 K, the charge transfer interaction energies \( E \) are increased due to shorten the C1···F1 distance. (b) X-ray structures in Y-crystal at 170 K. Due to having \( C_3 \) symmetry, three inter-atomic distance C1···F1, C1···F2, and C1···F3 are equal. The charge transfer interactions \( E \) between C1···F1 are weaker than those observed in O-crystal owing to its longer C1···F1 distance.

| Donor NBO (i) | Acceptor NBO (j) | \( E \) (kcal/mol) |
|---------------|------------------|------------------|
| LP (1) F 1   | LP*(1) C 1       | 0.49             |
| LP (3) F 1   | LP*(1) C 1       | 0.68             |
| LP (4) F 1   | LP*(1) C 1       | 0.14             |

| Donor NBO (i) | Acceptor NBO (j) | \( E \) (kcal/mol) |
|---------------|------------------|------------------|
| LP (1) F 1   | LP*(1) C 1       | 0.71             |
| LP (3) F 1   | LP*(1) C 1       | 1.03             |
| LP (4) F 1   | LP*(1) C 1       | 0.19             |

**Figure S9.** Natural bond orbital analysis of trityl PF₆ face-to-face dimer (MP2/6-311+G**) for evaluating charge transfer interaction between trityl cation and PF₆ anion. Compared with those in monomers (Figure S7), the charge transfer interaction energies \( E \) at both 273 K and 83 K are increased probably for reducing the cation-cation repulsive energy in the face-to-face cation dimer structure.

| Donor NBO (i) | Acceptor NBO (j) | \( E \) (kcal/mol) |
|---------------|------------------|------------------|
| LP (1) F 1   | LP*(1) C 1       | 0.56             |
| LP (3) F 1   | LP*(1) C 1       | 0.79             |
| LP (4) F 1   | LP*(1) C 1       | 0.20             |
| LP (1) F 2   | LP*(1) C 2       | 0.56             |
| LP (3) F 2   | LP*(1) C 2       | 0.79             |
| LP (4) F 2   | LP*(1) C 2       | 0.20             |

| Donor NBO (i) | Acceptor NBO (j) | \( E \) (kcal/mol) |
|---------------|------------------|------------------|
| LP (1) F 1   | LP*(1) C 1       | 0.82             |
| LP (3) F 1   | LP*(1) C 1       | 1.17             |
| LP (4) F 1   | LP*(1) C 1       | 0.27             |
| LP (1) F 2   | LP*(1) C 2       | 0.82             |
| LP (3) F 2   | LP*(1) C 2       | 1.17             |
| LP (4) F 2   | LP*(1) C 2       | 0.27             |
Table S3. Hirshfeld atomic population analysis of (a) trityl PF$_6$ monomer and (b) trityl PF$_6$ face-to-face dimer (MP2/6-311+G**) in O-crystal at both 273 and 83 K, and (c) trityl PF$_6$ monomer in Y-crystal at 170K. X-ray structures at both temperatures were used for the calculations as shown in Figure S7 and S8. The absolute value of total net charges both trityl cation and PF$_6$ anion are decreased upon cooling and formation of dimeric structure. This is because that the shortening C1···F1 distance increases the charge transfer from PF$_6$ anion to trityl cation, and the cation-cation repulsive energy in the face-to-face cation dimer structure increases the charge transfer as well, as discussed in Figure S8.

|                  | (a) Trityl PF$_6$ monomer (O-crystal) | (b) Trityl PF$_6$ face-to-face dimer (O-crystal) | (c) Trityl PF$_6$ monomer (Y-crystal) |
|------------------|--------------------------------------|-----------------------------------------------|--------------------------------------|
|                  | Total | Trityl cation | PF$_6$ anion | Total | Trityl cation | PF$_6$ anion | Total | Trityl cation | PF$_6$ anion |
| 273 K            | +0.92237 | -0.92241 |             | 273 K | +0.92043 | -0.92031 | 170 K | +0.92002 | -0.92008 |
| 83 K             | +0.91581 | -0.91589 |             | 83 K  | +0.91373 | -0.91366 |             |             |             |

Evaluation of six-fold phenyl embrace interaction

Figure S10. DFT calculations for evaluating the complexation energies of trityl PF$_6$ dimer in O-crystal at 273 K and 83 K by counterpoise method with BSSE correction (CAM-B3LYP/6-31G**). (a) Calculated results of the complexation energy (CE$_{TP}$) between trityl cation and PF$_6$ anion. (b) Calculated results of the complexation energy (CE$_{T-T}$) between trityl cations. (c) Calculated results of the complexation energy (CE$_{2TP}$) between trityl PF$_6$ dimer. The energy CE$_{2TP}$ is the sum of complexation energy working at between trityl cations (CE$_{TP-TP}$) as well as between trityl cation and PF$_6$ anion (CE$_{TP}$). (d) Calculation of the complexation energy working at between trityl cations (CE$_{TP-TP}$).
Electrostatic potential surfaces

Figure S11. Electrostatic potential (ESP) surfaces calculated by CAM-B3LYP/6-31G**. (a) ESP surfaces of trityl PF$_6$ at 273 K. (b) ESP surfaces of trityl PF$_6$ at 83 K. (c) ESP surfaces of trityl cation dimer at 273 K. (d) ESP surfaces of trityl cation dimer at 83 K. (e) ESP surfaces of trityl PF$_6$ dimer at 273 K. (f) ESP surfaces of trityl PF$_6$ dimer at 83 K. Compared with both temperatures, there is no significant differences on the ESP surfaces.
Excitation and emission spectra of Y-crystal

Figure S12. Excitation (blue line) and emission (yellow line) spectra of Y-crystal. (a) Measured at 293 K. (b) Measured at 77 K. Although there are spectra shifting upon cooling, the degree of shift is relatively small and it is hard to recognize the color changing with naked eye as shown in Movie S3-4.
TD-DFT calculations

Trityl PF$_6$ (face-to-face dimer) in O-crystal.

**Table S4.** TD-DFT calculation results of face-to-face dimer in O-crystal at 273 K. Grayed characters indicated a forbidden transitions (allowed transition wrote as black characters). A yellow highlighted transition as shown in allowed transitions indicated a major contribution for its transition.

The calculation was conducted by CAM-B3LYP/6-311+G(d,p) level with tuned parameters ($\alpha = 0.079$, $\beta = 0.921$, $\mu = 0.15$).

The values for $\alpha$ and $\beta$ indicate the contribution of HF exchange in short-range and long-range, respectively. (For example, in long-range correction (LC) scheme, the parameters of $\alpha$ and $\beta$ are 0 and 1.0, respectively.) The parameter $\mu$ determines the balance of DFT to HF exchange depending on the range distance.

| Excited State 1: 2.8805 eV 430.42 nm $\neq 0.0000$ | Excited State 6: 2.9187 eV 424.80 nm $\neq 0.0116$ |
|-----------------------------------------------|-----------------------------------------------|
| 178 $\rightarrow$ 199 0.10428 |
| 195 $\rightarrow$ 200 0.14651 |
| 196 $\rightarrow$ 199 -0.16366 |
| 197 $\rightarrow$ 197 0.48042 |
| 198 $\rightarrow$ 200 0.43131 |
| 195 $\rightarrow$ 199 0.46835 |
| 196 $\rightarrow$ 200 -0.41615 |
| 197 $\rightarrow$ 200 -0.14209 |
| 198 $\rightarrow$ 199 -0.15822 |

| Excited State 2: 2.8806 eV 430.42 nm $\neq 0.0004$ | Excited State 7: 2.9369 eV 422.16 nm $\neq 0.0000$ |
|-----------------------------------------------|-----------------------------------------------|
| 177 $\rightarrow$ 199 -0.10586 |
| 195 $\rightarrow$ 199 0.15132 |
| 196 $\rightarrow$ 199 -0.13497 |
| 197 $\rightarrow$ 200 0.43275 |
| 198 $\rightarrow$ 199 0.48300 |
| 196 $\rightarrow$ 199 0.50422 |
| 197 $\rightarrow$ 199 -0.37581 |
| 198 $\rightarrow$ 199 -0.10484 |
| 199 $\rightarrow$ 199 -0.21653 |

| Excited State 3: 2.8851 eV 429.74 nm $\neq 0.0000$ | Excited State 8: 2.9666 eV 418.22 nm $\neq 0.0421$ |
|-----------------------------------------------|-----------------------------------------------|
| 193 $\rightarrow$ 199 0.50367 |
| 194 $\rightarrow$ 200 0.45281 |
| 197 $\rightarrow$ 199 0.50739 |
| 198 $\rightarrow$ 200 0.50739 |
| 199 $\rightarrow$ 199 0.50739 |
| 196 $\rightarrow$ 199 0.50739 |
| 197 $\rightarrow$ 199 0.50739 |
| 198 $\rightarrow$ 199 0.50739 |

| Excited State 4: 2.8861 eV 429.59 nm $\neq 0.0035$ | Excited State 9: 3.0883 eV 401.46 nm $\neq 0.0000$ |
|-----------------------------------------------|-----------------------------------------------|
| 195 $\rightarrow$ 199 0.45384 |
| 196 $\rightarrow$ 199 0.45384 |
| 197 $\rightarrow$ 199 0.45384 |
| 198 $\rightarrow$ 199 0.45384 |
| 199 $\rightarrow$ 199 0.45384 |
| 196 $\rightarrow$ 199 0.45384 |
| 197 $\rightarrow$ 199 0.45384 |
| 198 $\rightarrow$ 199 0.45384 |

| Excited State 5: 2.9154 eV 425.28 nm $\neq 0.0000$ | Excited State 10: 3.1339 eV 395.62 nm $\neq 0.0490$ |
|-----------------------------------------------|-----------------------------------------------|
| 175 $\rightarrow$ 199 0.11628 |
| 176 $\rightarrow$ 199 -0.10961 |
| 192 $\rightarrow$ 199 -0.13212 |
| 195 $\rightarrow$ 199 -0.40230 |
| 196 $\rightarrow$ 199 0.45322 |
| 197 $\rightarrow$ 199 0.15849 |
| 198 $\rightarrow$ 199 0.14978 |
| 175 $\rightarrow$ 199 0.11628 |
| 176 $\rightarrow$ 199 -0.20649 |
| 185 $\rightarrow$ 199 0.29158 |
| 187 $\rightarrow$ 199 0.19401 |
| 188 $\rightarrow$ 199 -0.13540 |
| 189 $\rightarrow$ 199 0.55665 |
| 190 $\rightarrow$ 199 -0.24895 |
Figure S13. Kohm-Sham molecular orbitals (no. 189-200) of face-to-face trityl PF₆ dimer at 273 K (upper) and its energy diagram (lower). The calculation was conducted by CAM-B3LYP/6-311+G(d,p) level with tuned parameters ($\mu = 0.15$, $\alpha = 0.079$, $\beta = 0.921$).
Table S5. TD-DFT calculation results of face-to-face dimer in O-crystal at 83 K. Grayed characters indicated a forbidden transitions (allowed transition wrote as black characters). A yellow highlighted transition as shown in allowed transitions indicated a major contribution for its transition.

The calculation was conducted by CAM-B3LYP/6-311+G(d,p) level with tuned parameters ($\mu = 0.15$, $\alpha = 0.079$, $\beta = 0.921$).

| Excited State 1 | 2.9073 eV 428.46 nm f=0.0000 |
|-----------------|---------------------------------|
| 187 -> 199      | 0.13065                         |
| 188 -> 200      | 0.15170                         |
| 189 -> 200      | -0.10990                        |
| 190 -> 199      | -0.10338                        |
| 191 -> 200      | -0.36546                        |
| 192 -> 199      | 0.53036                         |

| Excited State 2 | 2.9378 eV 422.02 nm f=0.0441 |
|-----------------|-------------------------------|
| 186 -> 200      | 0.10410                       |
| 187 -> 200      | -0.19258                      |
| 188 -> 199      | -0.22698                      |
| 191 -> 199      | 0.47966                       |
| 192 -> 200      | -0.36843                      |

| Excited State 3 | 3.0361 eV 408.37 nm f=0.0000 |
|-----------------|-------------------------------|
| 186 -> 199      | -0.14067                      |
| 189 -> 200      | 0.25272                       |
| 190 -> 199      | 0.39355                       |
| 191 -> 200      | -0.12880                      |
| 193 -> 200      | -0.16941                      |
| 194 -> 199      | 0.20511                       |
| 197 -> 199      | -0.28683                      |
| 198 -> 200      | 0.24453                       |

| Excited State 4 | 3.0528 eV 406.13 nm f=0.0052 |
|-----------------|-------------------------------|
| 186 -> 200      | -0.11798                      |
| 188 -> 199      | 0.10113                       |
| 189 -> 199      | 0.13018                       |
| 193 -> 199      | 0.27832                       |
| 194 -> 200      | -0.24708                      |
| 195 -> 200      | -0.32992                      |
| 196 -> 199      | 0.37037                       |
| 197 -> 200      | -0.11955                      |
| 198 -> 199      | 0.15146                       |

| Excited State 5 | 3.0558 eV 405.73 nm f=0.0000 |
|-----------------|-------------------------------|
| 178 -> 199      | 0.10474                       |
| 186 -> 199      | 0.10732                       |
| 193 -> 200      | -0.26211                      |
| 194 -> 199      | 0.25214                       |
| 195 -> 199      | 0.39474                       |
| 196 -> 200      | -0.35159                      |

| Excited State 6 | 3.0688 eV 404.28 nm f=0.0039 |
|-----------------|-------------------------------|
| 173 -> 199      | 0.10446                       |
| 193 -> 199      | 0.42196                       |
| 194 -> 200      | -0.37796                      |
| 195 -> 200      | 0.24614                       |
| 196 -> 199      | -0.27597                      |

| Excited State 7 | 3.0692 eV 403.96 nm f=0.0000 |
|-----------------|-------------------------------|
| 193 -> 200      | -0.30326                      |
| 194 -> 199      | 0.34737                       |
| 195 -> 199      | -0.30601                      |
| 196 -> 200      | 0.27282                       |
| 197 -> 199      | 0.19298                       |
| 198 -> 200      | -0.17592                      |

| Excited State 8 | 3.0792 eV 402.65 nm f=0.0438 |
|-----------------|-------------------------------|
| 171 -> 199      | 0.11736                       |
| 172 -> 200      | 0.10764                       |
| 189 -> 199      | 0.16187                       |
| 195 -> 200      | 0.16713                       |
| 196 -> 199      | -0.18829                      |
| 197 -> 200      | -0.38989                      |
| 198 -> 199      | 0.43851                       |

| Excited State 9 | 3.1041 eV 399.42 nm f=0.0000 |
|-----------------|-------------------------------|
| 172 -> 199      | -0.10117                      |
| 185 -> 200      | 0.13271                       |
| 186 -> 199      | -0.13319                      |
| 187 -> 199      | -0.20677                      |
| 189 -> 200      | 0.18627                       |
| 190 -> 199      | 0.30966                       |
| 193 -> 200      | 0.10149                       |
| 194 -> 199      | 0.34400                       |
| 197 -> 199      | 0.30608                       |

| Excited State 10| 3.1338 eV 395.64 nm f=0.0331  |
|-----------------|-------------------------------|
| 183 -> 199      | -0.11551                      |
| 185 -> 199      | 0.22670                       |
| 186 -> 200      | -0.26596                      |
| 187 -> 200      | -0.17814                      |
| 188 -> 199      | 0.14908                       |
| 189 -> 199      | 0.41208                       |
| 190 -> 200      | 0.20010                       |
| 197 -> 200      | 0.17151                       |
| 198 -> 199      | -0.17550                      |
Figure S14. Kohm-Sham molecular orbitals (no. 189-200) of face-to-face trityl PF$_6$ dimer at 83 K (upper) and its energy diagram (lower). The calculation was conducted by CAM-B3LYP/6-311+G(d,p) level with tuned parameters ($\mu = 0.15$, $\alpha = 0.079$, $\beta = 0.921$).
Figure S15. Simulated UV-vis spectra of face-to-face trityl PF$_6$ dimers (a) 273 K, and (b) 83 K. Red bars in the spectra indicated a charge-transfer transition from PF$_6$ anion to trityl cation.
TD-DFT calculations of trityl PF$_6$ monomer in O-crystal.

Table S6. TD-DFT calculation results of tritylPF$_6$ in O-crystal at (a) 273 K, and (b) 83 K. A yellow highlighted transition indicated a major contribution for its transition.

The calculation was conducted by CAM-B3LYP/6-311+G(d,p) level with tuned parameters ($\mu = 0.15$, $\alpha = 0.079$, $\beta = 0.921$).

![Molecular orbital energy diagram](no. 93-100) of trityl PF$_6$ monomer at (a) 273 K, and (b) 83 K. The calculation was conducted by CAM-B3LYP/6-311+G(d,p) level with tuned parameters ($\mu = 0.15$, $\alpha = 0.079$, $\beta = 0.921$).
Figure S17. Kohm-Sham molecular orbitals (no. 93-100) of trityl PF$_6$ monomer at 273 K. The molecular orbitals at 83 K shows identical distributions with that at 273 K.

Figure S18. Simulated UV-vis spectra of face-to-face trityl PF$_6$ monomers (a) 273 K, and (b) 83 K. Red bars in the spectra indicated a charge-transfer transition from PF$_6$ anion to trityl cation.
TD-DFT calculations of trityl PF₆ (lateral dimer) in O-crystal.

Figure S19. The calculated structure of lateral dimer observed in O-crystal. (a) Side view. (b) Top view.

Table S7. TD-DFT calculation results of lateral dimer in O-crystal at 273 K. A yellow highlighted transition indicated a major contribution for its transition.

The calculation was conducted by CAM-B3LYP/6-311+G(d,p) level with tuned parameters ($\mu = 0.15$, $\alpha = 0.079$, $\beta = 0.921$).

| Excited State | 1: 2.9678 eV 417.76 nm f=0.0287 |
|---------------|----------------------------------|
| 187 -> 199    | 0.13114                          |
| 191 -> 200    | 0.11134                          |
| 194 -> 200    | 0.15919                          |
| 195 -> 200    | 0.15988                          |
| 196 -> 200    | 0.54045                          |
| 198 -> 200    | 0.30516                          |
| Excited State | 2: 2.9762 eV 416.58 nm f=0.0123 |
| 181 -> 200    | -0.10807                         |
| 187 -> 199    | -0.14491                         |
| 196 -> 200    | -0.29121                         |
| 197 -> 200    | -0.14431                         |
| 198 -> 200    | -0.57732                         |
| Excited State | 3: 2.9812 eV 415.89 nm f=0.0554  |
| 182 -> 199    | -0.10646                         |
| 184 -> 199    | -0.21565                         |
| 186 -> 199    | 0.21723                          |
| 187 -> 199    | 0.56350                          |
| 196 -> 200    | -0.21998                         |
| Excited State | 4: 3.0052 eV 412.57 nm f=0.0083  |
| 180 -> 200    | -0.16618                         |
| 185 -> 200    | 0.10709                          |
| 194 -> 200    | -0.11677                         |
| 197 -> 200    | 0.63218                          |
| 198 -> 200    | 0.18611                          |
| Excited State | 5: 3.0366 eV 408.29 nm f=0.0502  |
| 193 -> 200    | -0.34970                         |
| 194 -> 200    | 0.21541                          |
| 195 -> 200    | 0.52010                          |
| 196 -> 200    | -0.19426                         |
| Excited State | 6: 3.0759 eV 403.08 nm f=0.0236  |
| 182 -> 199    | -0.21622                         |
| 184 -> 199    | 0.26621                          |
| 186 -> 199    | 0.30006                          |
| 189 -> 199    | 0.22306                          |
| 190 -> 199    | 0.12645                          |
| 192 -> 199    | 0.41459                          |
| Excited State | 7: 3.1088 eV 398.81 nm f=0.0284  |
| 189 -> 199    | 0.17473                          |
| 191 -> 200    | 0.28731                          |
| 193 -> 200    | 0.21576                          |
| 194 -> 200    | 0.50984                          |
| 195 -> 200    | -0.15806                         |
| 196 -> 200    | -0.10262                         |
| 197 -> 200    | 0.12157                          |
| 186 -> 199    | -0.11072                         |
| 188 -> 199    | 0.55802                          |
| 191 -> 199    | -0.11334                         |
| 192 -> 199    | -0.31958                         |
| 194 -> 200    | -0.11321                         |
| 186 -> 199    | 0.23993                          |
| 188 -> 199    | -0.23703                         |
| 190 -> 199    | 0.38067                          |
| 192 -> 199    | -0.35485                         |
| Excited State | 9: 3.1380 eV 395.10 nm f=0.0145  |
| 179 -> 199    | -0.10341                         |
| 182 -> 199    | -0.17409                         |
| 184 -> 199    | 0.13201                          |
| 186 -> 199    | 0.23993                          |
| 189 -> 199    | -0.23703                         |
| 190 -> 199    | 0.38067                          |
| 192 -> 199    | -0.35485                         |
| 173 -> 199    | 0.11735                          |
| 182 -> 199    | 0.19199                          |
| 184 -> 199    | -0.12596                         |
| 186 -> 199    | -0.26220                         |
| 190 -> 199    | 0.54155                          |
| 192 -> 199    | 0.20497                          |
**Figure S20.** Kohm-Sham molecular orbitals (no. 187-200) of lateral trityl PF$_6$ dimer at 273 K (upper) and its energy diagram (lower). The calculation was conducted by CAM-B3LYP/6-311+G(d,p) level with tuned parameters ($\mu = 0.15$, $\alpha = 0.079$, $\beta = 0.921$).
Table S8. TD-DFT calculation results of lateral dimer in O-crystal at 83 K. A yellow highlighted transition indicated a major contribution for its transition.

The calculation was conducted by CAM-B3LYP/6-311+G(d,p) level with tuned parameters ($\mu = 0.15$, $\alpha = 0.079$, $\beta = 0.921$).

| Excited State 1 | 2.9611 eV 418.71 nm $f=0.0911$ | Excited State 6 | 3.1452 eV 394.21 nm $f=0.0011$ |
|----------------|---------------------------------|----------------|---------------------------------|
| 185 -> 199     | -0.25830                        | 178 -> 200     | 0.12732                         |
| 186 -> 199     | 0.24392                         | 196 -> 200     | 0.35880                         |
| 187 -> 199     | 0.45201                         | 197 -> 200     | 0.44616                         |
| 188 -> 199     | 0.35410                         | 198 -> 200     | -0.35924                        |
| 189 -> 199     | -0.10270                        | 195 -> 200     | -0.10268                        |
| 195 -> 200     | -0.10268                        | 177 -> 200     | 0.17740                         |
| Excited State 2 | 3.0066 eV 412.38 nm $f=0.0537$  | 192 -> 200     | 0.19647                         |
| 192 -> 200     | -0.12974                        | 194 -> 200     | -0.16051                        |
| 193 -> 200     | -0.30104                        | 197 -> 200     | 0.40179                         |
| 194 -> 200     | 0.31588                         | 198 -> 200     | 0.46567                         |
| 195 -> 200     | 0.48082                         | 195 -> 200     | 0.16541                         |
| 196 -> 200     |                                | 191 -> 199     | -0.16596                        |
| Excited State 3 | 3.0741 eV 403.31 nm $f=0.0286$  | 184 -> 199     | 0.36215                         |
| 185 -> 199     | 0.12056                         | 185 -> 199     | 0.18805                         |
| 186 -> 199     | 0.15237                         | 186 -> 199     | -0.30551                        |
| 192 -> 200     | -0.30196                        | 187 -> 199     | -0.12257                        |
| 193 -> 200     | 0.24001                         | 188 -> 199     | 0.34976                         |
| 194 -> 200     | 0.40910                         | 189 -> 199     | -0.16272                        |
| 195 -> 200     | -0.21087                        | 181 -> 199     | 0.29319                         |
| 197 -> 200     | 0.11065                         | 184 -> 199     | -0.22291                        |
| 198 -> 200     | 0.22460                         | 184 -> 199     | -0.22291                        |
| Excited State 4 | 3.0957 eV 400.50 nm $f=0.0794$  | 185 -> 199     | 0.27181                         |
| 184 -> 199     | 0.36436                         | 185 -> 199     | 0.28598                         |
| 185 -> 199     | 0.28106                         | 188 -> 199     | -0.11128                        |
| 186 -> 199     | 0.38403                         | 192 -> 199     | -0.12617                        |
| 190 -> 199     | 0.10560                         | 193 -> 200     | -0.27395                        |
| 191 -> 199     | -0.17230                        | 194 -> 199     | 0.12711                         |
| 192 -> 200     | 0.12874                         | 195 -> 200     | -0.19978                        |
| 194 -> 200     | -0.13940                        | 180 -> 199     | -0.10611                        |
| 198 -> 200     | 0.22460                         | 184 -> 199     | -0.22291                        |
| Excited State 5 | 3.1382 eV 395.08 nm $f=0.0102$  | 181 -> 199     | 0.36787                         |
| 180 -> 200     | -0.11280                        | 189 -> 199     | -0.10444                        |
| 193 -> 200     | 0.12113                         | 190 -> 199     | -0.35444                        |
| 194 -> 200     | -0.14595                        | 191 -> 199     | 0.28381                         |
| 196 -> 200     | 0.55225                         | 192 -> 200     | -0.10131                        |
| 197 -> 200     | -0.26090                        | 193 -> 200     | 0.15842                         |
| 198 -> 200     | 0.21627                         | 195 -> 199     | 0.13414                         |
|                |                                 | 196 -> 200     | 0.13829                         |
Figure S21. Kohm-Sham molecular orbitals (no. 181-200) of lateral trityl PF₆ dimer at 83 K (upper) and its energy diagram (lower). The calculation was conducted by CAM-B3LYP/6-311+G(d,p) level with tuned parameters (μ = 0.15, α = 0.079, β = 0.921).
Figure S22. Simulated UV-vis spectra of lateral trityl PF$_6$ dimers (a) 273 K, and (b) 83 K. Red bars in the spectra indicated a charge-transfer transition from PF$_6$ anion to trityl cation.
Table S9. TD-DFT calculation results of trityl cation monomer and dimer without PF₆ anion in O-crystal at both 27 K and 83 K. The calculation was conducted by CAM-B3LYP/6-311+G(d,p) level with tuned parameters (μ = 0.15, α = 0.079, β = 0.921). Comparison with each conditions (temperature as well as monomer and dimer), no significant difference is observed, indicating that only the trityl-trityl interaction did not affect its optical properties.

### Trityl cation monomer at 273 K

| Excited State | Energy (eV) | Wavelength (nm) | f | 
|---------------|-------------|-----------------|---|
| 1: 62 -> 65   | 2.9646      | 418.22          | 63.79 |
| 1: 64 -> 65   | 0.35303     |                 |    |
| 2: 61 -> 65   | 3.0731      | 403.45          | 4.019 |
| 2: 62 -> 65   | 0.46770     |                 |    |
| 2: 63 -> 65   | 0.5915      |                 |    |

### Trityl cation monomer at 83 K

| Excited State | Energy (eV) | Wavelength (nm) | f | 
|---------------|-------------|-----------------|---|
| 1: 62 -> 65   | 2.9477      | 420.62          | 63.78 |
| 1: 64 -> 65   | 0.38346     |                 |    |
| 2: 61 -> 65   | 3.0636      | 404.70          | 4.049 |
| 2: 62 -> 65   | 0.51192     |                 |    |
| 2: 63 -> 65   | 0.45935     |                 |    |

### Trityl cation dimer at 273 K

| Excited State | Energy (eV) | Wavelength (nm) | f | 
|---------------|-------------|-----------------|---|
| 1: 122->129   | 2.9115      | 425.84          | 6.000 |
| 1: 123->129   | 0.14209     |                 |    |
| 1: 124->130   | 0.17711     |                 |    |
| 1: 125->130   | -0.14251    |                 |    |
| 1: 126->130   | 0.17424     |                 |    |
| 1: 127->130   | -0.34020    |                 |    |
| 1: 128->129   | 0.51155     |                 |    |
| 2: 122->130   | 2.9513      | 420.10          | 6.0359 |
| 2: 123->130   | 0.16575     |                 |    |
| 2: 124->129   | 0.17547     |                 |    |
| 2: 125->129   | -0.27959    |                 |    |
| 2: 126->129   | 0.11956     |                 |    |
| 2: 127->129   | -0.14734    |                 |    |
| 2: 128->129   | 0.43217     |                 |    |
| 3: 121->130   | 3.0249      | 409.88          | 6.0000 |
| 3: 122->129   | 0.20854     |                 |    |
| 3: 123->129   | 0.21221     |                 |    |
| 3: 125->130   | -0.23477    |                 |    |
| 3: 126->129   | 0.45460     |                 |    |
| 3: 127->130   | 0.11714     |                 |    |
| 3: 128->129   | -0.15125    |                 |    |
| 4: 121->129   | 3.0748      | 403.23          | 6.0381 |
| 4: 122->130   | -0.30561    |                 |    |
| 4: 123->130   | -0.25798    |                 |    |
| 4: 124->129   | 0.25611     |                 |    |
| 4: 125->129   | 0.21423     |                 |    |
| 4: 126->130   | 0.37923     |                 |    |

### Trityl cation dimer at 83 K

| Excited State | Energy (eV) | Wavelength (nm) | f | 
|---------------|-------------|-----------------|---|
| 1: 122->129   | 2.8831      | 430.03          | 6.0000 |
| 1: 123->129   | 0.12562     |                 |    |
| 1: 124->130   | -0.14763    |                 |    |
| 1: 125->130   | -0.17098    |                 |    |
| 1: 126->130   | -0.17996    |                 |    |
| 1: 127->129   | 0.16941     |                 |    |
| 1: 128->129   | 0.51921     |                 |    |
| 2: 122->130   | 2.9257      | 423.78          | 6.0325 |
| 2: 123->130   | -0.14812    |                 |    |
| 2: 124->129   | 0.20431     |                 |    |
| 2: 125->129   | 0.29235     |                 |    |
| 2: 126->129   | 0.15858     |                 |    |
| 2: 127->129   | 0.41870     |                 |    |
| 2: 128->130   | -0.13231    |                 |    |
| 3: 121->130   | 3.0039      | 412.74          | 6.0000 |
| 3: 122->129   | 0.20062     |                 |    |
| 3: 123->129   | -0.21595    |                 |    |
| 3: 125->130   | -0.22829    |                 |    |
| 3: 126->130   | -0.28615    |                 |    |
| 3: 127->129   | 0.15304     |                 |    |
| 3: 128->129   | 0.46549     |                 |    |
| 4: 121->129   | 3.0633      | 404.74          | 6.0419 |
| 4: 122->130   | -0.31781    |                 |    |
| 4: 123->130   | 0.26822     |                 |    |
| 4: 124->129   | 0.25177     |                 |    |
| 4: 125->129   | -0.24683    |                 |    |
| 4: 126->130   | 0.35645     |                 |    |
| 4: 127->130   | -0.23857    |                 |    |
**Emission spectra of trityl cation in frozen state**

![Emission spectra](image)

**Figure S23.** Emission spectra of frozen state of trityl cation at different temperature (CHCl₃ with 2% TFA, 5.0 x 10⁻⁶ M).

**Figure S24.** (a) Phosphorescence of Frozen state (CHCl₃ with 2% TFA at 77 K) of trityl cation with different concentrations (1.0 x 10⁻³ M and 5.0 x 10⁻⁶ M) to evaluate a dependence of the concentration. (b) Phosphorescent excitation spectra of frozen state (5.0 x 10⁻⁶ M) with different wavelength monitoring at 600 nm and 545 nm. (c) Phosphorescent excitation spectra of frozen state (1.0 x 10⁻³ M) with different wavelength monitoring at 600 nm and 545 nm.
Emission decay curves of trityl cation

Figure S25. Emission decay curves of trityl cation at 77 K. (a) Frozen state (CHCl₃ with 2% TFA). (b) Y-crystal. (c) O-crystal.

Figure S26. Emission decay curves of (a) Y-crystal, and (b) O-crystal at 293 K (excited with a nanosecond laser pulse at 450 nm). The monitoring wavelengths were set to 525 and 575 nm, respectively.
Figure S27. Long range emission decay curves (from ns to μs) of Y- and O-crystal at 77 K. (a) 0 to 1.5 μs, (b) 0 to over 400 μs (excited with a nanosecond laser pulse at 355 nm). Integration ratio of emission intensities between nanosecond region (< 240 ns) and microsecond region are 1.0 : 0.16 (for Y-crystal) and 1.0 : 0.10 (for O-crystal).
Evaluation of spin-orbit coupling between singlet and triplet states.

Figure S28. Spin-orbit coupling (SOC) calculation results of trityl cation monomers observed at 273 K and 83 K in O-crystal. (a) Calculated energy diagrams and its levels of (b) S\textsubscript{1-5} and (c) T\textsubscript{1-6}. (d) Calculated SOC values of S\textsubscript{0}/T\textsubscript{1} as well as S\textsubscript{1}/T\textsubscript{1-6}. However, the SOC values between S\textsubscript{1} and T\textsubscript{1-6} are quite small and thus only trityl cation scaffold seems not likely to exhibit the phosphorescence property. The calculation was conducted by CAM-B3LYP/6-31+G(d) level with tuned parameters ($\mu = 0.15$, $\alpha = 0.079$, $\beta = 0.921$).

Figure S29. SOC calculation results of trityl PF\textsubscript{6} ion pairs observed at 273 K in O-crystal. (a) Calculated energy diagrams and its levels of (b) S\textsubscript{1,8} and (c) T\textsubscript{1,9}. (d) Calculated SOC values of S\textsubscript{0}/T\textsubscript{1}, S\textsubscript{1}/T\textsubscript{6-8}, and S\textsubscript{2}/T\textsubscript{6-8} because the energy difference between S\textsubscript{1} and S\textsubscript{2} is quite small. Different from trityl cation itself, large SOCs between S\textsubscript{1,2} and T\textsubscript{6-8} could be observed. The calculation was conducted by CAM-B3LYP/6-31+G(d) level with tuned parameters ($\mu = 0.15$, $\alpha = 0.079$, $\beta = 0.921$).
Figure S30. SOC calculation results of trityl PF₆ ion pairs observed at 83 K in O-crystal. (a) Calculated energy diagrams and its levels of (b) S₁₋₈ and (c) T₁₋₉. (d) Calculated SOC values of Sₐ/Tₖ and Sₖ/Tₖ₋₈. Due to changing the energy levels from those at 273 K, the energy of S₁ is slightly off from those of T₆₋₈. The calculation was conducted by CAM-B3LYP/6-31+G(d) level with tuned parameters (μ = 0.15, α = 0.079, β = 0.921).

| Sₐ energy | Tₖ energy     | Sₐ / Tₖ | SOC / cm⁻¹ |
|------------|---------------|---------|------------|
| S₁ 3.019 eV (411 nm) | T₁ 2.319 eV (533 nm) | S₀ / T₁ 2.62 |
| S₂ 3.115 eV (398 nm) | T₂ 2.414 eV (514 nm) | S₁ / T₅ 4.24 |
| S₃ 3.124 eV (397 nm) | T₃ 2.590 eV (479 nm) | S₆ / T₆ 9.59 |
| S₄ 3.142 eV (395 nm) | T₄ 2.619 eV (473 nm) | S₇ / T₇ 7.41 |
| S₅ 3.214 eV (386 nm) | T₅ 2.771 eV (447 nm) | S₈ / T₈ 12.3 |
| S₆ 3.337 eV (372 nm) | T₆ 3.119 eV (398 nm) |          |
| S₇ 3.365 eV (369 nm) | T₇ 3.124 eV (397 nm) |          |
| S₈ 3.479 eV (356 nm) | T₈ 3.133 eV (396 nm) |          |
|          | T₉ 3.280 eV (375 nm) |          |

Figure S31. SOC calculation results of trityl PF₆ ion pairs observed at 170 K in Y-crystal. (a) Calculated energy diagrams and its levels of (b) S₁₋₈ and (c) T₁₋₉. (d) Calculated SOC values of S₀/T₁ as well as S₁/T₁₋₈. The calculation was conducted by CAM-B3LYP/6-31+G(d) level with tuned parameters (μ = 0.15, α = 0.079, β = 0.921).

| Sₐ energy | Tₖ energy     | Sₐ / Tₖ | SOC / cm⁻¹ |
|------------|---------------|---------|------------|
| S₁ 3.019 eV (411 nm) | T₁ 2.319 eV (533 nm) | S₀ / T₁ 2.89 |
| S₂ 3.115 eV (398 nm) | T₂ 2.414 eV (514 nm) | S₁ / T₅ 0.96 |
| S₃ 3.124 eV (397 nm) | T₃ 2.590 eV (479 nm) | S₆ / T₆ 4.11 |
| S₄ 3.142 eV (395 nm) | T₄ 2.619 eV (473 nm) | S₇ / T₇ 1.46 |
| S₅ 3.214 eV (386 nm) | T₅ 2.771 eV (447 nm) | S₈ / T₈ 1.99 |
| S₆ 3.337 eV (372 nm) | T₆ 3.119 eV (398 nm) | S₁ / T₅ 1.67 |
| S₇ 3.365 eV (369 nm) | T₇ 3.124 eV (397 nm) | S₆ / T₆ 15.3 |
| S₈ 3.479 eV (356 nm) | T₈ 3.133 eV (396 nm) | S₇ / T₇ 4.56 |
|          | T₉ 3.280 eV (375 nm) | S₈ / T₈ 10.3 |
Figure S32. SOC calculation results of trityl PF₆ face-to-face dimer observed at 273 K in O-crystal. (a) Calculated energy diagrams and its levels of (b) S₁₁–₁₄ and (c) T₁₁–₁₈. (d) Calculated SOC values of S₀/T₁. (e) Calculated SOC values between S₁ and T₁₁–₁₈. The calculation was conducted by CAM-B3LYP/6-31+G(d) level with tuned parameters (μ = 0.15, α = 0.079, β = 0.921).

Figure S33. SOC calculation results of trityl PF₆ face-to-face dimer observed at 83 K in O-crystal. (a) Calculated energy diagrams and its levels of (b) S₁₁–₁₄ and (c) T₁₁–₁₈. (d) Calculated SOC values of S₀/T₁. (e) Calculated SOC values between S₁ and T₁₁–₁₈. The calculation was conducted by CAM-B3LYP/6-31+G(d) level with tuned parameters (μ = 0.15, α = 0.079, β = 0.921).