Supporting Information

Tuning the Phase Transition and Fluorescence Quenching in 0D Organic-Inorganic Hybrid Materials by Precise Organic Cation Modification

Leqi Chen, [a] Zining Zhou, [a] Yawen Yang, [a] and Qiong Ye*[a]

Jiangsu Key Laboratory for Science and Applications of Molecular Ferroelectrics and School of Chemistry and Chemical Engineering, Southeast University, Nanjing 211189, People's Republic of China.

Corresponding authors: *yeqiong@seu.edu.cn

EXPERIMENTAL SECTION

Synthesis:

The preparation of ethyl-trimethyl-phosphonium bromide ([ETMP]Br) propyl-trimethyl-phosphonium bromide ([PTMP]Br), allyl-trimethyl-phosphonium bromide ([ATMP]Br) has been described elsewhere[1]. $(ETMP)_2MnBr_4$ was synthesized by the slow evaporation of an aqueous solution containing [ETMP]Br (2 mmol, 0.370 g) and $MnBr_2 \cdot 4H_2O$ (1 mmol, 0.286 g) stirred for 5 minutes. After the solution is completely clarified, it is evaporated in an oven set at 313 K. Three days later yellow-green crystals appeared in the breaker. $(PTMP)_2MnBr_4$ (2 mmol, 0.398 g) and $(ATMP)_2MnBr_4$ (2 mmol, 0.394 g) were offered by the similar method, just replacing [ETMP]Br with [PTMP]Br and [ATMP]Br.

Thermal analysis:

Differential scanning calorimetry (DSC) curves were recorded on a NETZSCH DSC 200F3 instrument at a standard scan rate of 20 $K \cdot min^{-1}$ under a nitrogen atmosphere. The sample masses used for the DSC analysis were as follows: 8.4 mg for compound 1, 13.9 mg for compound 2 and 6.1 mg for compound 3, respectively. Thermogravimetric analysis (TGA) curves were recorded on a NETZSCH TG209 F3 instrument with a heating rate of 20$K \cdot min^{-1}$ from 300K-1000K under nitrogen atmosphere.

Dielectric measurements.

The powder-pressed pellets of 1, 2 and 3 coated with silver conducting glue on both sides were used in dielectric measurements. The complex dielectric constant ($\varepsilon = \varepsilon' - I\,\varepsilon''$, where ε' is the real part, and ε'' is the imaginary part) was tested on a Tonghui TH2828A impedance analyzer over the frequency range from 500 Hz to 1 MHz with an AC voltage of 1 V.

Single-crystal X-ray diffraction

Single-crystal X-ray diffraction data of compound 1, 2 and 3 were performed on a Rigaku Saturn 924 diffractometer by using Cu Kα radiation (λ=1.54178 Å). The crystal structure was solved by direct methods and then refined by direct methods. Crystallographic data and structure refinement details are given in Table S1-S6.

Powder X-ray diffraction.

Powder X-ray diffraction (PXRD) analyses were performed using a Smart Lab X-ray diffractometer with Cu-Kα radiation (λ = 1.54056 Å). Measurements were taken in the range of 5-50° with a step size of 0.02° at 293K-383K. Simulated powder patterns were generated, and crystallographic files obtained using single crystal X-ray diffraction experiments were calculated using Mercury software.

Hirshfeld surfaces analysis.

Hirshfeld surfaces were calculated by using the CrystalExplorer program with inputting structure file in CIF format. In this work, all the Hirshfeld surfaces were generated using a standard (high) surface resolution. The intensity of molecular interaction is mapped onto the Hirshfeld surface by using the respective red-blue-white scheme: where the white or green regions exactly correspond to the distance of Van der Waals contact, the blue regions correspond to longer contacts, and the red regions represent closer contacts.

Photoluminescence Measurements.

The emission and excitation spectra were measured using an Edinburgh FLS1000 fluorescence spectrophotometer equipped with a xenon lamp as the excitation source, and time-resolved spectra were recorded through the Edinburgh spectrophotometer equipped with a microsecond pulsed hydrogen lamp. The temperature range of the multi-temperature fluorescence spectroscopies was 293 K-413 K. The PLQYs were characterized using an integrating sphere in the spectrofluorometer. The direct method was used for this determination. The photoluminescent quantum yield is obtained by measuring the luminescent intensity of the sample at the optimal excitation wavelength.

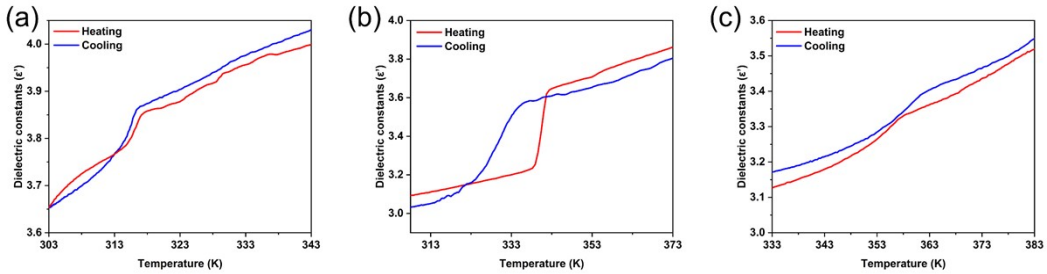

Figure S1. Temperature-dependent dielectric constant (ε') in a heating-cooling cycle of $(ETMP)_2MnBr_4$ (a), $(PTMP)_2MnBr_4$ (b), and $(ATMP)_2MnBr_4$ (c).

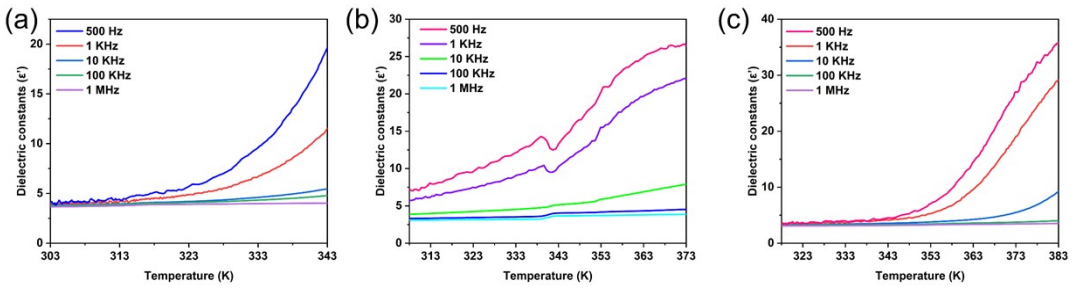

Figure S2. Variation of the dielectric constant with temperature for $(ETMP)_2MnBr_4$ (a), $(PTMP)_2MnBr_4$ (b), and $(ATMP)_2MnBr_4$ (c).

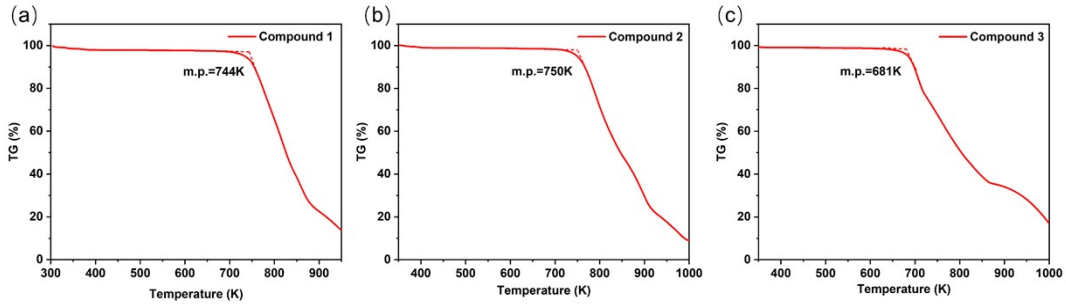

Figure S3. Thermogravimetric (TG) curve of $(ETMP)_2MnBr_4$ (a), $(PTMP)_2MnBr_4$ (b), and $(ATMP)_2MnBr_4$ (c).

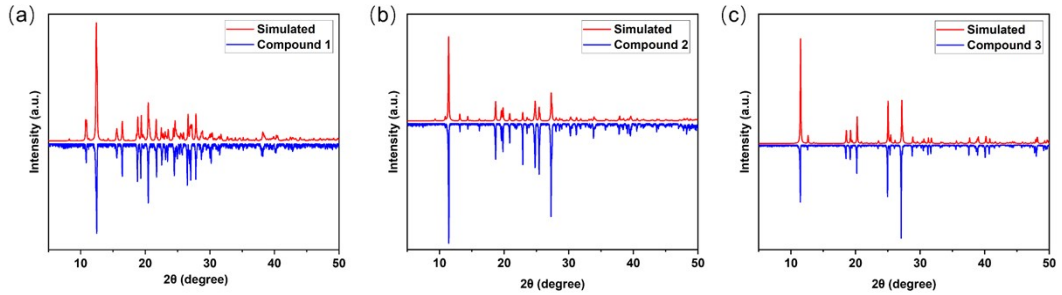

Figure S4. PXRD patterns of experiment and simulated for $(ETMP)_2MnBr_4$ (a), $(PTMP)_2MnBr_4$ (b), and $(ATMP)_2MnBr_4$ (c) single crystals, respectively.

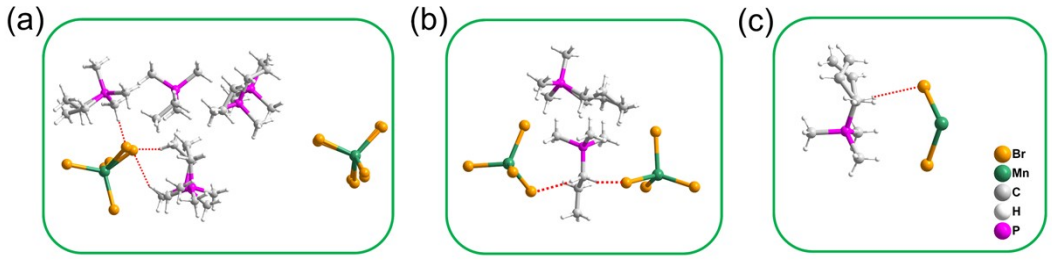

Figure S5. Asymmetric units of the $(ETMP)_2MnBr_4$ (a), $(PTMP)_2MnBr_4$ (b) and $(ATMP)_2MnBr_4$ (c). The red dot lines denote C-H···Br hydrogen bonds.

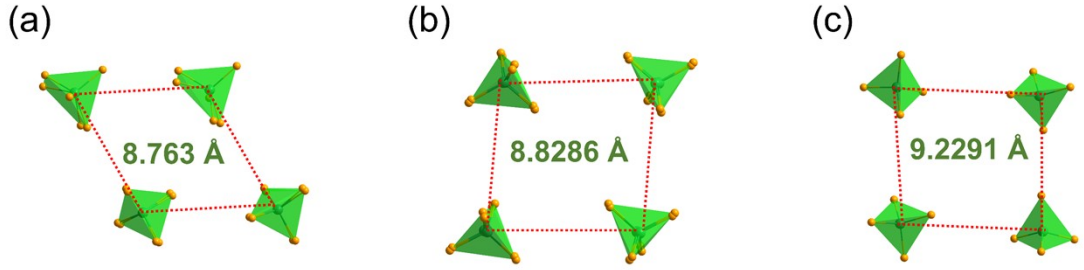

Figure S6. The shortest distance between adjacent $[MnBr_4]^{2-}$ units of the $(ETMP)_2MnBr_4$ (a), $(PTMP)_2MnBr_4$ (b) and $(ATMP)_2MnBr_4$ (c).

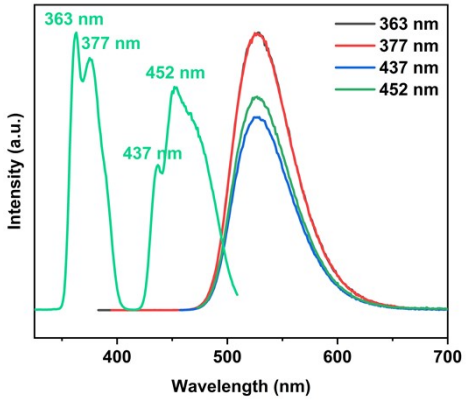

Figure S7. Excitation spectra and emission spectra at different excitation wavelengths of $(ETMP)_2MnBr_4$.

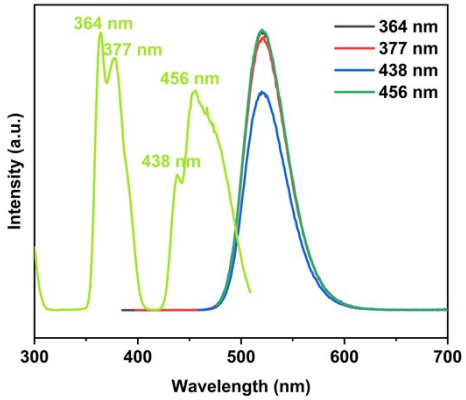

Figure S8. Excitation spectra and emission spectra at different excitation wavelengths of $(ATMP)_2MnBr_4$.

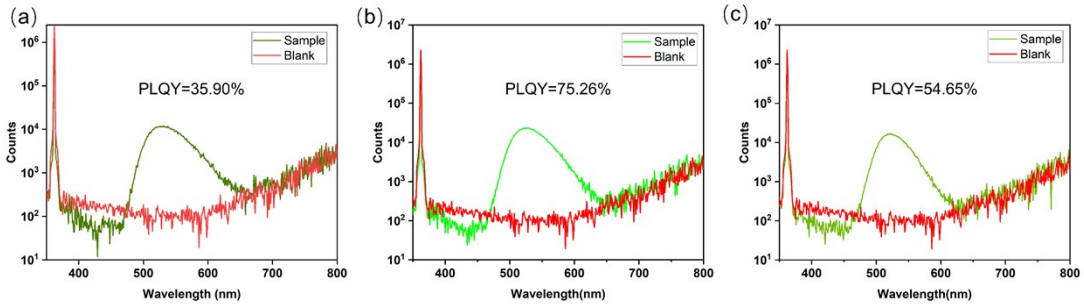

Figure S9. The PLQYs of $(ETMP)_2MnBr_4$ (a), $(PTMP)_2MnBr_4$ (b), and $(ATMP)_2MnBr_4$ (c).

Table S1. Crystal data and structure refinement for $(ETMP)_2MnBr_4$

Empirical formula	$C_{10}H_{28}Br_4MnP_2$
Formula weight	584.84
Temperature/K	100
Crystal system	monoclinic
Space group	$P2_1/c$
a/Å	18.5525(3)
b/Å	14.0694(2)
c/Å	18.3426(2)
α/°	90
β/°	117.916(2)
γ/°	90
Volume/Å^3	4230.69(12)
Z	8
F(000)	2264
Radiation	Cu Kα (λ = 1.54178)
R_{int}	0.0653
R_1	0.0432
wR_2	0.1064

Table S2. Crystal data and structure refinement for $(PTMP)_2MnBr_4$

Empirical formula	$C_{12}H_{32}Br_4MnP_2$
Formula weight	612.89
Temperature/K	275
Crystal system	Orthorhombic
Space group	*Ibca*
a/Å	19.0177(4)
b/Å	19.1067 (4)
c/Å	26.7409 (7)
α/°	90
β/°	90
γ/°	90
Volume/Å^3	9716.7 (4)
Z	16
F(000)	4784
Radiation	Cu Kα (λ = 1.54178)
R_{int}	0.094
R_1	0.0598
wR_2	0.1700

Table S3. Crystal data and structure refinement for $(ATMP)_2MnBr_4$

Empirical formula	$2(C_6H_{14}P)\cdot Br_4Mn$
Formula weight	608.86
Temperature/K	273
Crystal system	Tetragonal
Space group	$P4_12_12$
a/Å	9.2291 (1)
b/Å	9.2291(1)
c/Å	27.9955(5)

α/°	90
β/°	90
γ/°	90
Volume/Å^3	2384.55 (7)
Z	4
F(000)	1180
Radiation	Cu Kα (λ = 1.54178)
R_{int}	0.118
R_1	0.0453
wR_2	0.1362

Table S4. The bond lengths (Å) and angles (º) of $(ETMP)_2MnBr_4$ at 100K.

Atom–Atom	Length [Å]	Atom–Atom–Atom	Angle [°]
Br1—Mn1	2.4920 (11)	Br1—Mn1—Br2	111.01 (4)
Br2—Mn1	2.4938 (11)	Br1—Mn1—Br4	103.09 (9)
Mn1—Br3	2.474 (2)	Br1—Mn1—Br3A	105.71 (12)
Mn1—Br4	2.5752 (18)	Br2—Mn1—Br4	110.44 (5)
Mn1—Br3A	2.612 (4)	Br2—Mn1—Br3A	103.40 (14)
Mn1—Br4A	2.394 (2)	Br3—Mn1—Br1	111.16 (8)
Mn2—Br5	2.499 (3)	Br3—Mn1—Br2	109.30 (8)
Mn2—Br6	2.496 (3)	Br3—Mn1—Br4	111.74 (7)
Mn2—Br7	2.503 (3)	Br4A—Mn1—Br1	119.67 (15)
Mn2—Br8	2.508 (3)	Br4A—Mn1—Br2	107.05 (6)
Mn2—Br5A	2.503 (4)	Br4A—Mn1—Br3A	108.81 (12)
Mn2—Br6A	2.505 (4)	Br5—Mn2—Br7	106.71 (17)
Mn2—Br7A	2.499 (4)	Br5—Mn2—Br8	110.56 (15)
Mn2—Br8A	2.490 (4)	Br6—Mn2—Br5	110.33 (15)
C1—P1	1.765 (6)	Br6—Mn2—Br7	109.60 (15)
C2—P1	1.762 (7)	Br6—Mn2—Br8	111.46 (17)
C3—P1	1.783 (6)	Br7—Mn2—Br8	108.04 (13)
C11—P3	1.781 (5)	Br5A—Mn2—Br6A	110.4 (2)
C12—P3	1.782 (5)	Br7A—Mn2—Br5A	106.8 (2)
C13—P3	1.788 (6)	Br7A—Mn2—Br6A	109.8 (2)
C14—C15	1.534 (7)	Br8A—Mn2—Br5A	110.81 (19)
C14—P3	1.787 (5)	Br8A—Mn2—Br6A	110.24 (19)
P1—C4	1.807 (7)	Br8A—Mn2—Br7A	108.73 (19)
P1—C4A	1.811 (10)	C1—P1—C3	109.6 (4)
C4—C5	1.517 (11)	C1—P1—C4	115.2 (4)
C6—P2	1.783 (9)	C1—P1—C4A	98.7 (5)
C7—P2	1.789 (8)	C2—P1—C1	109.1 (4)
C8—P2	1.773 (8)	C2—P1—C3	108.6 (4)
C9—C10	1.527 (12)	C2—P1—C4	102.3 (4)
C9—P2	1.769 (9)	C2—P1—C4A	126.9 (7)
C16—P4	1.793 (8)	C3—P1—C4	111.7 (4)
C17—P4	1.788 (8)	C3—P1—C4A	103.0 (7)
C18—P4	1.799 (8)	C5—C4—P1	111.3 (6)
C19—C20	1.550 (13)	C11—P3—C12	109.8 (3)
C19—P4	1.778 (7)	C11—P3—C13	109.7 (3)
C6A—P2A	1.779 (12)	C11—P3—C14	109.0 (3)

C7A—P2A	1.791 (11)	C12—P3—C13	107.7 (3)
C8A—P2A	1.777 (12)	C12—P3—C14	110.1 (2)
C9A—C10A	1.524 (15)	C14—P3—C13	110.6 (3)
C9A—P2A	1.767 (12)	C10—C9—P2	115.5 (7)
C16A—P4A	1.806 (12)	C15—C14—P3	113.3 (4)
C17A—P4A	1.784 (11)	C6—P2—C7	108.7 (4)
C18A—P4A	1.800 (12)	C8—P2—C6	108.8 (5)
C19A—C20A	1.548 (16)	C8—P2—C7	110.4 (5)
C19A—P4A	1.770 (11)	C9—P2—C6	109.5 (4)
C4A—C5A	1.516 (13)	C9—P2—C7	110.6 (5)
		C9—P2—C8	108.9 (4)
		C20—C19—P4	109.9 (6)
		C16—P4—C18	108.5 (4)
		C17—P4—C16	109.5 (4)
		C17—P4—C18	108.9 (4)
		C19—P4—C16	109.3 (4)
		C19—P4—C17	110.2 (4)
		C19—P4—C18	110.4 (4)
		C10A—C9A—P2A	116.2 (10)
		C6A—P2A—C7A	108.7 (7)
		C8A—P2A—C6A	108.9 (8)
		C8A—P2A—C7A	110.0 (8)
		C9A—P2A—C6A	110.1 (7)
		C9A—P2A—C7A	110.6 (8)
		C9A—P2A—C8A	108.6 (7)
		C20A—C19A—P4A	110.3 (10)
		C17A—P4A—C16A	109.1 (7)
		C17A—P4A—C18A	109.0 (7)
		C18A—P4A—C16A	107.7 (7)
		C19A—P4A—C16A	109.3 (7)
		C19A—P4A—C17A	110.7 (7)
		C19A—P4A—C18A	111.0 (7)
		C5A—C4A—P1	111.2 (8)

Table S5. The bond lengths (Å) and angles (º) of $(PTMP)_2MnBr_4$ at 275K.

Atom–Atom	Length [Å]	Atom–Atom–Atom	Angle [°]
Br1—Mn1	2.401 (19)	Br1—Mn1—Br2	102.0 (8)
Br2—Mn1	2.574 (13)	Br1—Mn1—Br4	117.3 (6)
Mn1—Br4	2.423 (12)	Br1—Mn1—Br3	108.21 (14)
Mn1—Br3	2.567 (18)	Br4—Mn1—Br2	111.51 (8)
Br6—Mn2	2.52 (2)	Br4—Mn1—Br3	114.4 (8)
Mn2—Br7	2.49 (2)	Br3—Mn1—Br2	101.6 (5)
Mn2—Br5	2.45 (2)	Br7—Mn2—Br6	107.5 (11)
Mn2—Br8	2.47 (2)	Br5—Mn2—Br6	112.2 (7)
C1—P1	1.774 (6)	Br5—Mn2—Br7	113.54 (14)
C2—P1	1.768 (6)	Br5—Mn2—Br8	105.7 (11)
C3—P1	1.799 (7)	Br8—Mn2—Br6	109.78 (11)
C4—C5	1.500 (9)	Br8—Mn2—Br7	108.0 (7)
C4—P1	1.774 (6)	C5—C4—P1	113.4 (5)

C5—C6	1.493 (10)	C6—C5—C4	113.9 (7)
C7—P2	1.768 (7)	C1—P1—C3	107.1 (3)
C8—P2	1.753 (6)	C2—P1—C1	109.9 (3)
C9—P2	1.759 (6)	C2—P1—C3	108.6 (4)
P2—C10	1.829 (9)	C7—P2—C10	112.1 (6)
P2—C10A	1.830 (10)	C7—P2—C10A	113.7 (6)
C10—C11	1.459 (13)	C8—P2—C7	109.1 (3)
C11—C12	1.643 (15)	C8—P2—C9	110.5 (4)
C10A—C11A	1.467 (14)	C8—P2—C10	118.1 (6)
C11A—C12A	1.646 (15)	C8—P2—C10A	93.0 (5)
		C9—P2—C7	109.6 (3)
		C9—P2—C10	96.7 (5)
		C9—P2—C10A	119.5 (6)
		C11—C10—P2	111.8 (8)
		C10—C11—C12	102.3 (9)
		C11A—C10A—P2	110.2 (8)
		C10A—C11A—C12A	101.9 (10)

Table S6. The bond lengths (Å) and angles (º) of $(ATMP)_2MnBr_4$ at 273K.

Atom–Atom	**Length [Å]**	**Atom–Atom–Atom**	**Angle [°]**
Br1—Mn1	2.4918 (10)	Br1—Mn1—Br1^{i}	110.87 (7)
Br2—Mn1	2.4814 (11)	Br2^{i}—Mn1—Br1^{i}	107.61 (3)
C1—P1	1.781 (8)	Br2^{i}—Mn1—Br1	109.96 (3)
C2—P1	1.788 (8)	Br2—Mn1—Br1^{i}	109.96 (3)
C3—P1	1.774 (8)	Br2—Mn1—Br1	107.61 (3)
C4—C5	1.504 (10)	Br2—Mn1—Br2^{i}	110.85 (7)
C4—P1	1.794 (8)	C5—C4—P1	111.6 (9)
C4—C5A	1.509 (13)	C5A—C4—P1	111.9 (10)
C5—C6	1.330 (17)	C6—C5—C4	121.0 (13)
C5A—C6A	1.328 (18)	C1—P1—C2	109.9 (6)
		C1—P1—C4	109.2 (4)
		C2—P1—C4	109.6 (5)
		C3—P1—C1	109.5 (4)
		C3—P1—C2	109.0 (4)
		C3—P1—C4	109.7 (4)
		C6A—C5A—C4	121.3 (14)

Symmetry code: (i) *y*, *x*, −*z*+1.

Reference:

1. L. Zhou, P.-P. Shi, X. Zheng, F.-J. Geng, Q. Ye and D.-W. Fu, Molecular design of high-temperature organic dielectric switches, *Chemical Communications*, 2018, **54**, 13111-13114