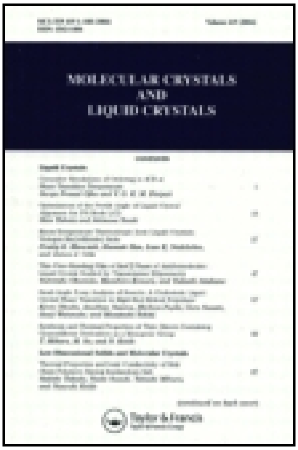

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Syntheses and Physical Properties of Ferrocene Derivatives (XI)

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Syntheses and Physical Properties of Ferrocene Derivatives (XI)

Crystal Structure of a Monosubstituted Ferrocene Derivative, ω-[4-(4-methoxyphenoxycarbonyl)-phenoxycarbonyl]ethyl 4-ferrocenylbenzoate

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The molecular and crystal structure of one of the monosubstituted ferrocene derivatives which has been discussed from a view point of liquid crystallinity, ω-[4-(4-methoxyphenoxycarbonyl)-phenoxycarbonyl]ethyl 4-ferrocenylbenzoate, was determined by the X-ray diffraction method. This compound had the $—C_2H_4—$ chain located between the phenylferrocenyl group and the mesogenic one. The $—C_2H_4—$ chain unit as a flexible spacer was an all-*trans* conformation. The molecule was slightly bent around the ester group to the ferrocenylbenzoate in order to form a rod-like structure. Two cyclopentadienyl rings in the ferrocenyl group exhibited an eclipsed conformation rather than a staggered one. In this crystal, the molecules constructed a layer structure just like the smectic one of the liquid crystals. The molecular and crystal structure was quite similar to those of other homologues showing liquid crystallinity in this series. This compound, however, did not exhibit a liquid crystalline phase.

Keywords: Crystal structure; ferrocene; ferrocene derivatives; metallomesogen; liquid crystal

INTRODUCTION

In recent years, metallomesogens, that is the liquid crystalline compounds containing transition metals, have been of great interest. The reason why the metallomesogen has attracted attention is that the metallomesogen is

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expected to show some interesting physical properties, for example electric, magnetic and chromatic properties, *etc.*

In our laboratory, two series of monosubstituted ferrocene derivatives were synthesized and studied in regard to liquid crystallinity by varying the spacer lengths using differential scanning calorimetry (DSC), polarizing optical microscopy (POM), wide-angle and/or small-angle X-ray diffraction (WAXD and/or SAXD), dielectric dispersion measurement apparatuses and so on. One is a series of [4-[ω-(cholesteryloxycarbonyl)alkoxycarbonyl]phenyl]ferrocene (abbreviated hereafter CAPF-*n*, where *n* is the number of carbon atoms in a flexible spacer), and 8 kinds of CAPF-*n* which exhibit liquid crystallinity, where $n=2$, 4, 6, 8, 9, 10, 11 and 15 [1–4]. The other is ω-[4-(4-methoxyphenoxycarbonyl)phenoxycarbonyl]alkyl only 4-ferrocenylbenzoate (abbreviated hereafter MPAF-*n*, where *n* is the number of carbon atoms in a methylene unit). The general structure of MPAF-*n* is shown in Figure 1. Only 4 kinds of MPAF-*n*, where $n=4$, 6, 10 and 11, showed liquid crystallinity, whereas 9 kinds of MPAF-*n*, where $n=1\sim7$, 10 and 11, were synthesized [5].

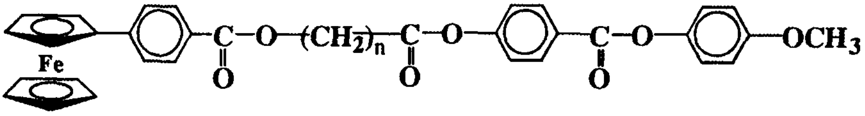

FIGURE 1 General structure of MPAF-*n*.

Recently, four papers describing the crystal structure of the monosubstituted liquid crystalline and related ferrocene derivatives have been published [6–9]. In 1993, the first one was reported by Loubser and her coworkers. The crystal structure of CAPF-6 was analyzed using a single crystal and the mechanism of the liquid crystalline phase transition was discussed [7]. Quite recently, the crystal structure of MPAF-3 [8] and MPAF-4 [9], which is one of the homologues of the title compounds, was analyzed by the present authors. The remarkable feature of MPAF-3 is that the molecular structure is a sharp, bent one. This fact suggests that MPAF-3 cannot easily show liquid crystallinity. On the other hand, the molecule structure of MPAF-4 is a slight, rod-like one. Therefore, MPAF-4 has the advantage of showing liquid crystallinity. In fact, MPAF-3 does not show liquid crystallinity, while MPAF-4 shows liquid crystallinity, as is already reported in our previous paper [5].

In this paper, we present the molecular and crystal structure of MPAF-2. The results will be discussed by comparing them with those of MPAF-3 and MPAF-4.

EXPERIMENTAL

The sample, MPAF-2, was synthesized in accordance with a method mentioned in our previous paper [5]. The compound obtained was confirmed to be MPAF-2 using ^{1}H-NMR (JEOL, JNMGX-400) spectra. The single crystal of the title compound was prepared by the slow evaporation method from a solution with a mixed solvent of benzene and methanol (1: 3). The single crystals obtained are orange in color and plate-like, having the approximate dimensions of 0.5 × 0.3 × 0.1 mm. The density of this crystal is measured by the flotation-method employed KI aqueous solution.

All measurements were made on a Rigaku AFC-5R diffractometer operated at 50 kV and 220 mA. The X-ray beam was monochromatized to Cu-Kα (λ = 1.54178 Å) with a graphite single crystal. The unit cell parameters were determined by a least-squares refinement of the setting angle of 25 reflections, with 2θ between 18.71 and 28.16°. The data were collected at a room temperature of 25±1°C, using the ω–2θ-scan technique to maximize the 2θ value of 120.2°.

4809 reflections were measured, of which 4572 were unique ($R_{\text{int}} = 0.031$). The intensity of three representative standard reflections was measured after every 150 reflections. Over the course of data collection, the standards decreased by −0.702%. As we judged this value is to be too small to have any bad effect on the data, a decay correction was not applied. The data were corrected for Lorentz and polarization effects and for the absorption effeet (ψ scan; minimum and maximum transmission factors were 0.5827 and 0.9996, respectively).

All calculations were performed using the teXsan crystallographic software package of the Molecular Structure Corporation [10]. The structure analysis was solved by direct methods employing the SIR92 program [11] and expanded using the Fourier technique. All non-hydrogen atoms were refined anisotropically, while the hydrogen atoms were introduced at their theoretical positions and allowed to ride with the carbon atoms to which they are attached. The final refinement was made by full-matrix least-squares based on 2784 observed reflections ($I > 3.0\sigma(I)$). The refinement was concluded with final reliability factors:

$$R = \Sigma(|F_0| - |F_C|)/\Sigma|F_0| = 0.049$$

$$R_W = (\Sigma W(|F_0| - |F_C|)^2/\Sigma W F_0^2)^{1/2} = 0.062$$

where the weighted scheme $W = 1/[\sigma^2(F_0) + 0.0000512F_0^2]$.

Final data may be obtained from the Cambridge Crystallographic Data Center, 12 Union Road, Cambridge, CB2 IEZ, UK.

RESULTS AND DISCUSSION

Data regarding collection and refinement are summarized in Table I. Fractional atomic coordinates and equivalent isotropic factors are given in Table II.

The molecular conformation with numbering each atom is presented in an ORTEP II [12] drawing in Figure 2. The representative bond lengths and bond angles are summarized in Table III. The defined least-squares planes and dihedral angles are given in Table IV.

1. Molecular Structure

It could be better to divide this molecular structure into two parts, that is ferrocenyl moiety and the mesogenic group in order to discuss it more exactly.

In ferrocenyl moiety, two cyclopentadienyl rings (planes 1 and 2) run parallel to each other with a dihedral angle of 2.72°. Also, the two cyclopentadienyl rings have an eclipsed conformation rather than a staggered one. Generally, this eclipsed conformation is found in other

TABLE I Summarized data regarding collection and refinement

Empirical formula	$C_{34}H_{28}O_7Fe$
Formula weight	604.44
Crystal system	monoclinic
Space group	$P2_1/a$
Lattice parameter	
a/Å	8.085(4)
b/Å	10.235(6)
c/Å	34.257(7)
β/°	92.57(3)
Volume/Å^3	2832(1)
Z value	4
D_{calc}/gcm^{-3}	1.417
D_{meas}/gcm^{-3}	1.453
Measured reflections	4809
Independent reflections	4572
Observed reflections ($I > 3.0\sigma(I)$)	2784
R	0.049
R_w	0.062
S	1.51

TABLE II Fractional atomic coordinates and equivalent isotropic temperature factors

Atom	*x*	*y*	*z*	B_{eq}
Fe(1)	0.6677(1)	-0.01815(7)	1.42879(2)	3.88(2)
O(1)	0.9328(5)	0.0415(4)	1.22089(10)	5.35(10)
O(2)	1.0947(6)	0.2003(5)	1.2467(1)	7.0(1)
O(3)	0.7237(5)	0.0260(4)	1.09224(10)	5.32(10)
O(4)	0.9344(7)	0.1601(5)	1.1039(1)	9.1(2)
O(5)	0.7164(5)	0.0579(4)	0.90933(9)	4.84(9)
O(6)	0.5466(5)	0.2263(4)	0.9196(1)	5.4(1)
O(7)	0.6633(6)	0.1093(4)	0.7486(1)	6.5(1)
C(1)	0.8616(7)	-0.0992(5)	1.4009(1)	4.1(1)
C(2)	0.7406(7)	-0.1959(5)	1.4093(2)	4.6(1)
C(3)	0.7200(8)	-0.2001(5)	1.4502(2)	5.1(1)
C(4)	0.8299(8)	-0.1067(6)	1.4677(1)	5.0(1)
C(5)	0.9142(7)	-0.0440(5)	1.4380(1)	4.4(1)
C(6)	0.570(1)	0.1159(7)	1.3912(2)	6.8(2)
C(7)	0.4496(10)	0.0271(7)	1.3997(2)	6.7(2)
C(8)	0.4283(8)	0.0281(7)	1.4389(2)	6.4(2)
C(9)	0.5356(10)	0.1203(7)	1.4563(2)	6.5(2)
C(10)	0.6253(9)	0.1759(6)	1.4266(3)	7.0(2)
C(11)	0.9111(7)	-0.0565(5)	1.362 1(1)	3.9(1)
C(12)	0.8647(8)	-0.1235(5)	1.3284(2)	5.1(1)
C(13)	0.8994(8)	-0.0760(6)	1.2922(2)	5.2(1)
C(14)	0.9821(7)	0.0397(6)	1.2887(1)	4.5(1)
C(15)	1.0386(9)	0.1041(6)	1.3220(2)	6.4(2)
C(16)	1.0033(9)	0.0555(6)	1.3585(2)	6.4(2)
C(17)	1.0132(8)	0.1043(6)	1.2506(2)	5.1(1)
C(18)	0.9460(8)	0.1036(6)	1.1832(2)	5.6(2)
C(19)	0.8453(7)	0.0222(6)	1.1550(2)	5.1(1)
C(20)	0.8426(7)	0.0795(6)	1.1146(2)	4.7(1)
C(21)	0.7108(7)	0.0613(5)	1.0525(1)	4.1(1)
C(22)	0.8000(7)	-0.0096(6)	1.0267(1)	4.6(1)
C(23)	0.7761(6)	0.0158(5)	0.9870(1)	4.2(1)
C(24)	0.6651(6)	0.1099(5)	0.9741(1)	3.4(1)
C(25)	0.5762(7)	0.1779(5)	1.0011(2)	4.4(1)
C(26)	0.5988(7)	0.1538(5)	1.0407(2)	4.7(1)
C(27)	0.6351(7)	0.1416(5)	0.9321(1)	3.9(1)
C(28)	0.6979(7)	0.0742(5)	0.8683(1)	4.2(1)
C(29)	0.6103(7)	-0.0190(6)	0.8478(1)	4.7(1)
C(30)	0.5952(7)	-0.0101(6)	0.8070(1)	4.9(1)
C(31)	0.6695(8)	0.0931(6)	0.7884(1)	4.7(1)
C(32)	0.7583(8)	0.1847(6)	0.8097(2)	5.3(1)
C(33)	0.7719(8)	0.1758(6)	0.8501(2)	5.2(1)
C(34)	0.5660(1)	0.0210(8)	0.7258(2)	8.0(2)

monosubstituted ferrocene derivatives [13], while a staggered one is widely observed in disubstituted ferrocene derivatives [14, 15] and ferrocene itself [16]. As was already reported in our previous paper, MPAF-3, which is one of the monosubstituted ferrocene derivatives, showed that the two cyclopentadienyl rings have staggered conformation. This is an exception. This may be regarded as its bent molecular structure. In MPAF-2, the

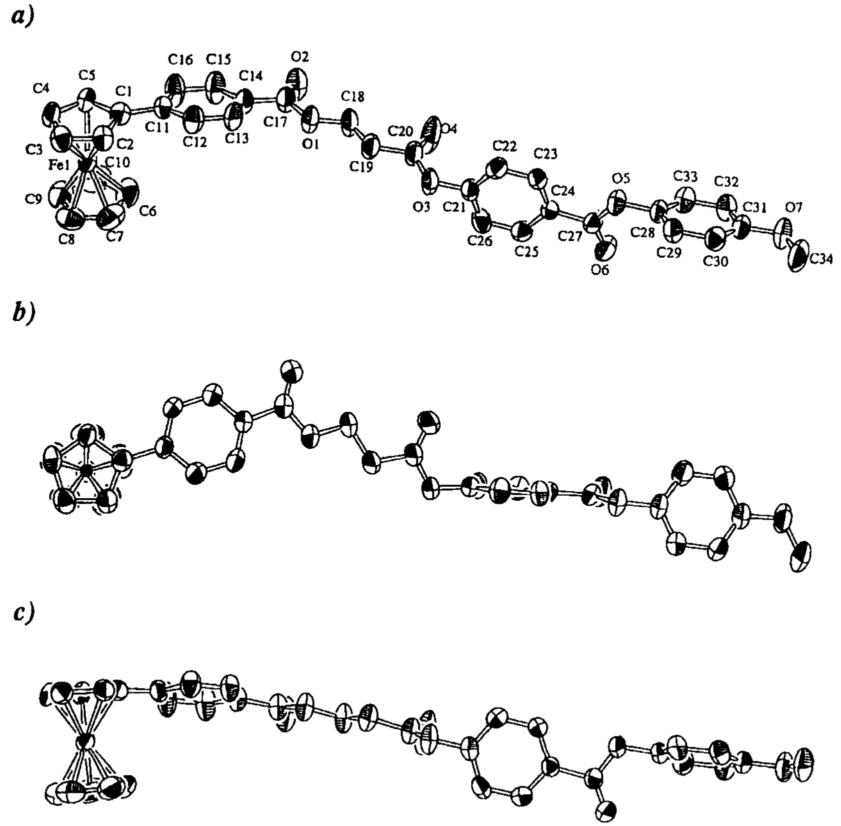

FIGURE 2 *ORTEP*II(Johnson, 1976) [12] view of the molecular structure, (a) showing the crystallographic numbering scheme, (b) over view onto the cyclopentadienyl rings, (c) side view onto the cyclopentadienyl rings. Thermal ellipsoids are drawn at 50% probability.

average values of Fe—C and C—C bond distances are 2.033 Å and 1.405 Å, respectively, and all C—C—C bond angles in the cyclopentadienyl rings are 108.0°. These values were in good agreement with those of ferrocene from the paper [16] within an experimental error. The dihedral angle of the substituted cyclopentadienyl ring (plane 1) and the adjacent phenyl ring (plane 3) is 13.22°, and that of the plane (plane 1) and the neighboring ester function (plane 6) is 164.62°. Therefore, it is considered that these planes (planes 1, 3 and 6) are approximately coplanar.

In the mesogenic group, the bond distances and angles in the phenylbenzoate are in agreement with those in other compounds having the same mesogenic group already reported [17, 18]. The dihedral angle of

TABLE III The list of bond lengths and bond angles

Atoms	*Bond distance/Å*	*Atoms*	*Bond distance/Å*
Fe(1)—C(1)	2.048(5)	C(6)—C(10)	1.414(10)
Fe(1)—C(2)	2.034(5)	C(7)—C(8)	1.363(9)
Fe(1)—C(3)	2.038(5)	C(8)—C(9)	1.397(9)
Fe(1)—C(4)	2.041(6)	C(9)—C(10)	1.395(10)
Fe(1)—C(5)	2.021(6)	C(11)—C(12)	1.379(7)
Fe(1)—C(6)	2.019(6)	C(11)—C(16)	1.376(7)
Fe(1)—C(7)	2.040(7)	C(12)—C(13)	1.374(7)
Fe(1)—C(8)	2.038(7)	C(13)—C(14)	1.368(7)
Fe(1)—C(9)	2.031(6)	C(14)—C(15)	1.376(7)
Fe(1)—C(10)	2.017(6)	C(14)—C(17)	1.497(7)
O(1)—C(17)	1.345(6)	C(15)—C(16)	1.387(8)
O(1)—C(18)	1.446(6)	C(18)—C(19)	1.490(8)
O(2)—C(17)	1.193(7)	C(19)—C(20)	1.503(7)
O(3)—C(20)	1.322(6)	C(21)—C(22)	1.372(7)
O(3)—C(21)	1.409(6)	C(21)—C(26)	1.358(7)
O(4)—C(20)	1.179(6)	C(22)—C(23)	1.391(7)
O(5)—C(27)	1.351(6)	C(23)—C(24)	1.376(7)
O(5)—C(28)	1.415(6)	C(24)—C(25)	1.385(7)
O(6)—C(27)	1.192(6)	C(24)—C(27)	1.482(6)
O(7)—C(31)	1.372(6)	C(25)—C(26)	1.383(7)
O(7)—C(34)	1.412(8)	C(28)—C(29)	1.364(7)
C(1)—C(2)	1.430(7)	C(28)—C(33)	1.367(7)
C(1)—C(5)	1.437(7)	C(29)—C(30)	1.399(7)
C(2)—C(3)	1.417(7)	C(30)—C(31)	1.384(8)
C(3)—C(4)	1.420(8)	C(31)—C(32)	1.372(8)
C(4)—C(5)	1.407(7)	C(32)—C(33)	1.385(8)
C(6)—C(7)	1.37(1)		
Atoms	*Bond angle/°*	*Atoms*	*Bond angle/°*
C(17)—O(1)—C(18)	114.3(4)	O(1)—C(18)—C(19)	105.8(5)
C(20)—O(3)—C(21)	118.4(4)	C(18)—O(19)—C(20)	111.3(5)
C(27)—O(5)—C(28)	117.7(4)	O(3)—C(20)—O(4)	124.0(5)
C(31)—O(7)—C(34)	117.9(5)	O(3)—C(20)—C(19)	110.6(5)
O(1)—C(17)—O(2)	124.1(5)	O(4)—C(20)—C(19)	125.3(6)
O(1)—C(17)—C(14)	110.7(5)	O(5)—C(27)—C(24)	111.0(4)
O(2)—C(17)—C(14)	125.2(5)	O(6)—C(27)—C(24)	125.3(5)

two phenyl rings (planes 4 and 5) is 77.32° and the C24−C27−O5−C28 torsion angle is equal to 178.9(4)°. The dihedral angle in liquid crystalline MPAF-4 was 69.41° [9]. This value may result in an appearance of liquid crystallinity. The disappearance of liquid crystallinity in the MPAF-2 may be the result of slight unfavorable steric interactions in the phenylbenzoate as a mesogen between neighboring molecules, because the dihedral angle in the mesogenic group of MPAF-2 is about 10% larger than that of liquid crystalline MPAF-4.

As a result, the molecular length (C3−C34) is estimated to be 25.06 Å long. This value is comparable to a model molecular length of 25.32 Å,

TABLE IV Dihedral angles between least-squares planes

Plane no.	*Least-squares planes*
Plane 1	substituted CP-ring
Plane 2	unsubstituted CP-ring
Plane 3	phenyl ring (C11∼C16)
Plane 4	phenyl ring (C21∼C26)
Plane 5	phenyl ring (C28∼C33)
Plane 6	C(17), O(1), O(2)
Plane 7	C(20), O(3), O(4)
Plane 8	C(27), O(5), O(6)
Planes	*Dihedral angle/°*
Plane 1 – Plane 2	2.72
Plane 1 – Plane 3	13.22
Plane 1 – Plane 6	164.62
Plane 4 – Plane 5	77.32
Plane 6 – Plane 7	15.27
Plane 6 – Plane 8	73.93
Plane 7 – Plane 8	86.97

calculated by molecular modeling software. The length of the mesogenic group (C20 – C31) is calculated as 11.20 Å long. The values of the C—C bond distance is 1.49 Å in the flexible spacer. Finally, the molecule is slightly bent at the C17 atom (Cl – C17 – C34).

2. Crystal Structure

The crystal structure placed onto the projections of *a*-*c* plane and *b*-*c* plane are shown in Figures 3 and 4, respectively. This crystal structure is exceedingly similar to that of MPAF-4. The phenylbenzoate introduced as the mesogenic group in the molecule is packed anti-parallel along the long crystallographic *c*-axis and the molecules are arranged in pairs in a head-to-head manner.

This molecular arrangement allows highly compact packing in the crystal structure, which is the most effective occupation of the space. As is

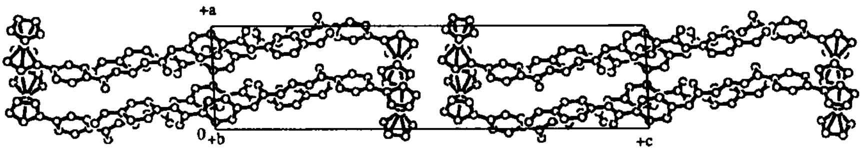

FIGURE 3 Crystal Structure of MPAF-2, the projection of *a*-*c* plane.

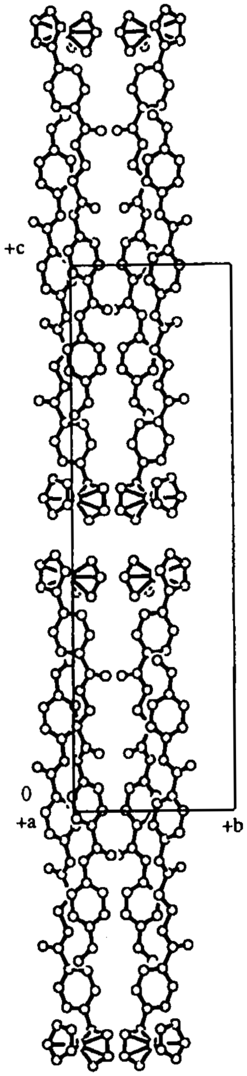

FIGURE 4 Crystal structure of MPAF-2, the projection of *b*-*c* plane.

mentioned above, the molecule is slightly bent around the ester group located at the nearest neighbor of the ferrocenylbenzoate section. This slight bend of the molecular structure also contributes effectively to the highly compact packing of the molecules in the crystal. As a result, the layer structure was formed and the present structure is somewhat similar to that of a smectic one, as is easily understood from Figures 3 and 4.

It may be interesting to think of a relation between a space group of the MPAF-*n* crystals and the appearance of liquid crystallinity. We already reported on the crystal structures of MPAF-3 [8] and MPAF-4 [9]. The structure analyses of MPAF-6 [19], 7 [19], and 11 [20] are now in progress not yet completed but the space group of these compounds is already decided. From the results obtained, all compounds show liquid crystallinity, that is MPAF-4, 6 and 11 have $P2_1/a$ as the space group, while the compounds which indicate no liquid crystallinity, that is MPAF-3 and 7, have other space groups, $C2/c$ for MPAF-3 and P-1 for MPAF-7. Therefore, it may be considered that the characteristic space group $P2_1/a$ is suitable for undergoing the liquid crystalline phase transition. In addition to this, the molecular shape of MPAF-2 is rod-like one which is vastly different from that of MPAF-3. Considering these facts, it is expected that the MPAF-2 will show liquid crystallinity. In our previous work, many different kinds of measuring methods under many different conditions were carried out in order to find out the liquid crystalline phase in MPAF-2 many times in our laboratory. But no liquid crystalline phase transition was observed in MPAF-2 [5]. Accordingly, we attempted sufficient purification of MPAF-2, measurements of the DSC and observations of the POM again in this work. However, we could not observe liquid crystallinity after all. It is difficult to understand why the liquid crystalline phase is not observed in MPAF-2. Probably, the large dihedral angle existing in the mesogenic group may disturb the appearance of liquid crystallinity due to its steric hindrance.

Acknowledgement

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