Electronic Supplementary Information (ESI)

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4. Structure Information

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1. General Information

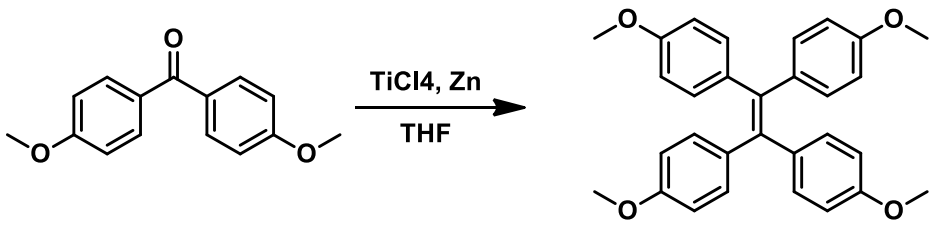
Materials Tetrahydrofuran was dried over and distilled from K–Na alloy under an atmosphere of dry argon. Zinc dust was purchased from Sinopharm Chemical Reagent Co.,

Ltd and activated by 1.5 M HCl aqueous. 4, 4'-DiMethoxybenzophenone and 4,4'-Dihydroxybenzophenone were purchased from Energy Chemical. $TiCl_4$, 1-Bromobutane, 1-Bromohexane and all other solvents were purchased from Sinopharm Chemical Reagent Co., Ltd. The water/tetrahydrofuran mixtures with different water fractions were prepared by slowly adding distilled water into the THF solution of the samples under ultrasonic at room temperature. The single crystals of TMPE in C_p-form polymorph were grown from a dilute mixture solution, which was prepared by dissolving 15 mg sample in 5 mL dichloromethane and then dropping methanol careful on the surface of dichloromethane. After the slow volatilization of good solvent (dichloromethane), single crystals were formed. The preparation method of C_c-form crystals was similar to that of C_p-form, whereas the solvents were changed to hexane/ dichloromethane mixture.

Characterization ^{1}H NMR spectra were recorded on a 300 MHz Varian Mercury in $CDCl_3$ solutions, using $CDCl_3$ as solvent and tetramethylsilane (TMS) as an internal standard (δ = 0.00 ppm). ^{13}C NMR spectra were recorded on a 400 MHz Varian Mercury, using $CDCl_3$ as a solvent and an internal standard (δ = 77.09 ppm). UV-Vis spectra were measured on a Shimadzu UV-2550. Photoluminescence spectra were performed on a Hitachi F-4600 fluorescence spectrophotometer. The FTIR spectra were recorded on a PerkinElmer-2 spectrometer in the region of 4000-400 cm^{-1} on KBr pellets. Fluorescence quantum yields were determined with a HamamatsuC11347 Quantaurus-QY absolute fluorescence quantum yield spectrometer. Fluorescence lifetimes were determined with a Hamamatsu C11367-11 Quantaurus-Tau time-resolved spectrometer. The powder X-ray diffraction patterns were recorded by Rigaku MiniFlex 600 with an X-ray source of Cu Kα (λ = 1.5418 Å) at 25 ^{o}C at 40 KV and 15 mA at a scan rate of 10 ^{o}(2θ) / min (scan range: 2 - 50^o). The single-crystal X-ray diffraction data of TMPE polymorphs crystals were collected in an Bruker Smart Apex CCD diffractometer. The diffraction data of THPE were collected in an Agilent Supernova CCD diffractometer. The ML spectra were collected from a spectrometer

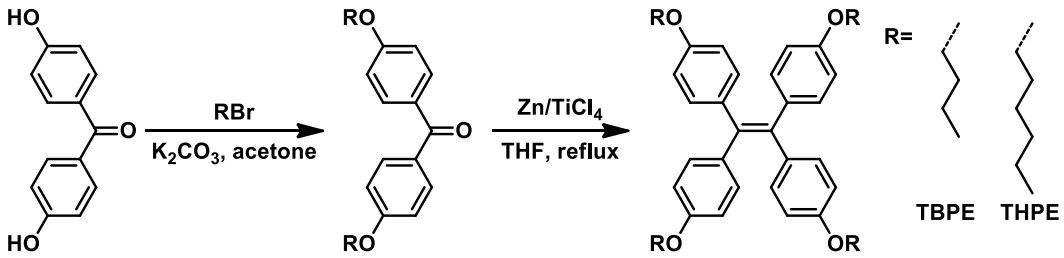
of Acton SP2750 with a liquid-nitrogen-cooled CCD (SPEC-10, Princeton) as a power detector. The images of crystal under visible light were taken by Leica M123 and Olympus IX71 research grade inverted microscope. The images of crystal under UV illumination were taken by Olympus IX71 research grade inverted microscope. The quantum chemistry calculations was performed at the B3LYP/6-31G (d, p) level of theory using the DFT method in the Gaussian 09 software.

2. Synthesis



Scheme S1. The synthetic route of TMPE.

Into a 250 mL Schlenk flask, zinc dust (2.68 g, 41 mmol) in freshly distilled THF (30 mL) was cooled to 0 ℃ under N_2. $TiCl_4$ (2.2 mL, 20 mmol) was added dropwise to the cold mixture and stirred at 0 ℃ for 0.5 h. The suspension was warmed to 75 ℃ and then refluxed for 2 h. After cooling to 0 ℃, a solution of dissolved 4, 4'-DiMethoxybenzophenone (2.42g, 10 mmol) in freshly distilled THF (70 mL) was added to the suspension and refluxed overnight. After cooling to room temperature, 20 mL hydrochloric acid solution (6 M) was added. The mixture was extracted with CH_2Cl_2 for three times. The organic layers were combined and washed with brine twice, then dried over with Na_2SO_4, filtered, and concentrated, the crude product was purified on a silica gel column using CH_2Cl_2 / petroleum ether (v/v=1/2) as eluent. A withe solid was obtained (1.98 g, 87.6%). ^{1}H NMR (300 MHz , $CDCl_3$, δ): 6.93 (d, J = 8 Hz, 8H, Ar-H), 6.64 (d, J = 8 Hz, 8H, Ar-H), 3.75 (s, 12 H, CH_3). ^{13}C NMR (100 MHz, $CDCl_3$, δ): 157.7, 138.3, 136.8, 132.5, 111.9, 54.9. IR (KBr) υ (cm^{-1}): 2931 (w), 2835 (w), 1604 (w), 1509 (w), 1294 (w), 1244 (w), 1174 (w), 1033 (w), 830 (w). HRMS (ESI, m/z): $[M + H]^+$ calcd for $C_{30}H_{28}O_4$, 453.2054; found, 453.2060.



Scheme S2. The synthetic route of TBPE and THPE.

A mixture of 4,4'-dihydroxybenzophenone (2.14 g, 10 mmol), 1-bromoalkane (20 mmol), potassium carbonate (5.52 g, 40 mmol) and 150 mL of acetone were added into flask. The mixture were refluxed under nitrogen atmosphere until TLC exhibited complete conversion. After cooling to room temperature, the salt was removed by filtration. The filtrate were washed with 150 mL water in 3 times and extracted with CH_2Cl_2. The organic layers were dried over anhydrous Na_2SO_4 and filtered. The solvent of filtrate was removed with a rotary evaporator to give dialkoxyl benzophenone as white powder (9.8 mmol, 98%).

The self-McMurry coupling reaction of the dialkoxyl benzophenone were performed in the same condition as the preparation of TMPE.

TBPE: (white powder, 2.61 g, 84.1%). ^{1}H NMR (300 MHz ,$CDCl_3$, δ): 6.91 (d, *J* = 8 Hz, 8H, Ar-H), 6.62 (d, *J* = 8 Hz, 8 H, Ar-H), 3.88 (t, *J* = 6 Hz, 12 H, OCH_2), 1.72 (m, 8H, CH_2), 1.45 (m, 8H, CH_2), 0.96 (t, *J* = 7 Hz, 12H, CH_3). ^{13}C NMR (100 MHz, $CDCl_3$, δ): 157.3, 138.3, 136.8, 132.5, 113.5, 67.3, 31.4, 19.3, 13.9. IR (KBr) υ (cm^{-1}): 2958 (w), 2932 (w) , 2870 (w), 1605 (w), 1507 (w), 1246 (w), 1172 (w), 832 (w).

THPE: (white powder, 2.86 g, 78.4%). ^{1}H NMR (300 MHz , $CDCl_3$, δ): 6.91 (d, *J* = 8 Hz, 8H, Ar-H), 6.62 (d, *J* = 8 Hz, 8 H, Ar-H), 3.87 (t, *J* = 6 Hz, 8 H, OCH_2), 1.71 (m, 8H, CH_2), 1.43 (m, 8H, CH_2), 1.33 (m, 16H, CH_2), 0.89 (t, *J* = 6 Hz, 12H, CH_3). ^{13}C NMR (100 MHz, $CDCl_3$, δ): 157.3, 138.3, 136.8, 132.5, 113.5, 67.3, 31.4, 19.3, 13.9. IR (KBr) υ (cm^{-1}): 2927 (w), 2861 (w), 1605 (w), 1507 (w), 1242 (w), 1173 (w), 832 (w). HRMS (ESI, m/z): $[M + H]^+$ calcd for $C_{50}H_{68}O_4$, 732.5118; found, 732.5125.

3. Figures, Charts and Tables

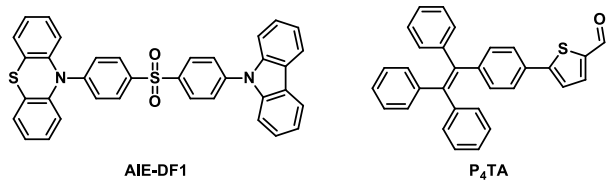


Chart S1. Molecular structures of the reported AIE ML compounds.

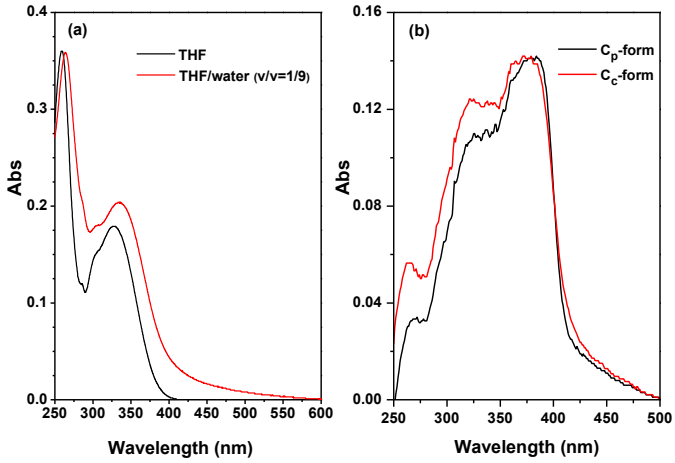


Figure S1. a) UV-Visible spectra of the dilute solution of TMPE in THF and in water /THF mixture (f_w =90%). Concentration: 10 μM. b) Solid state UV-visible spectra of TMPE in different polymorphs.

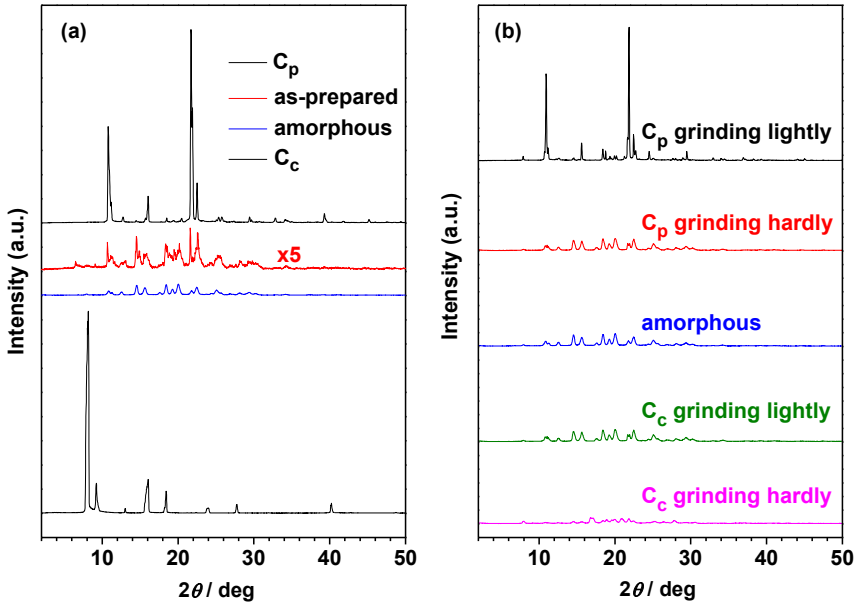


Figure S2. PXRD patterns of TMPE in different phases.

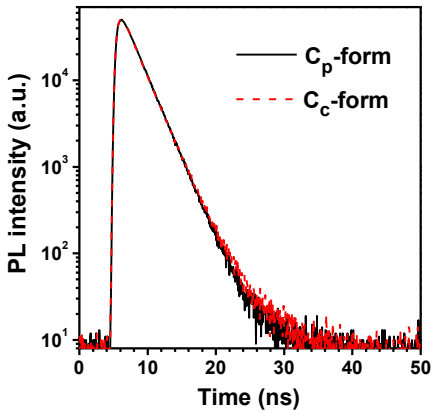


Figure S3. Emission decay of TMPE in different polymorphs.

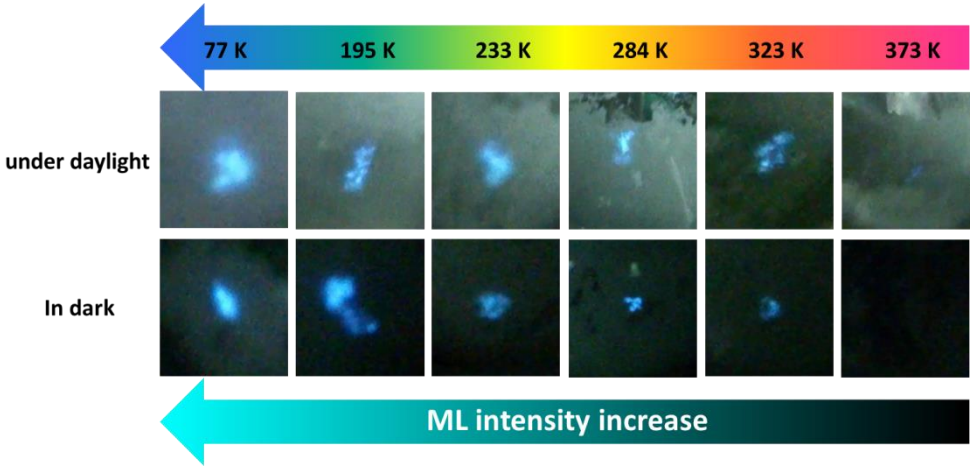


Figure S4. ML performances of the as-prepared TMPE powder after being treated with different temperature.

Table S1. Summarization of photophysical properties, single crystal information and ML activities of TMPE in different polymorphs.

Compound	λ_{max}^{abs} /nm	λ_{max}^{em} /nm	τ / ns	Φ_F	Crystal system	Space group	Symmetry	Polarity	ML activity
C_c-form	372	420	2.401	67.4 %	Monoclinic	*C2*	Centrosymmetry	Polar	Inactive
C_p-form	380	429	2.394	69.9 %	Monoclinic	*$P2_1(c)$*	Noncentrosymmetry	Nonpolar	Active

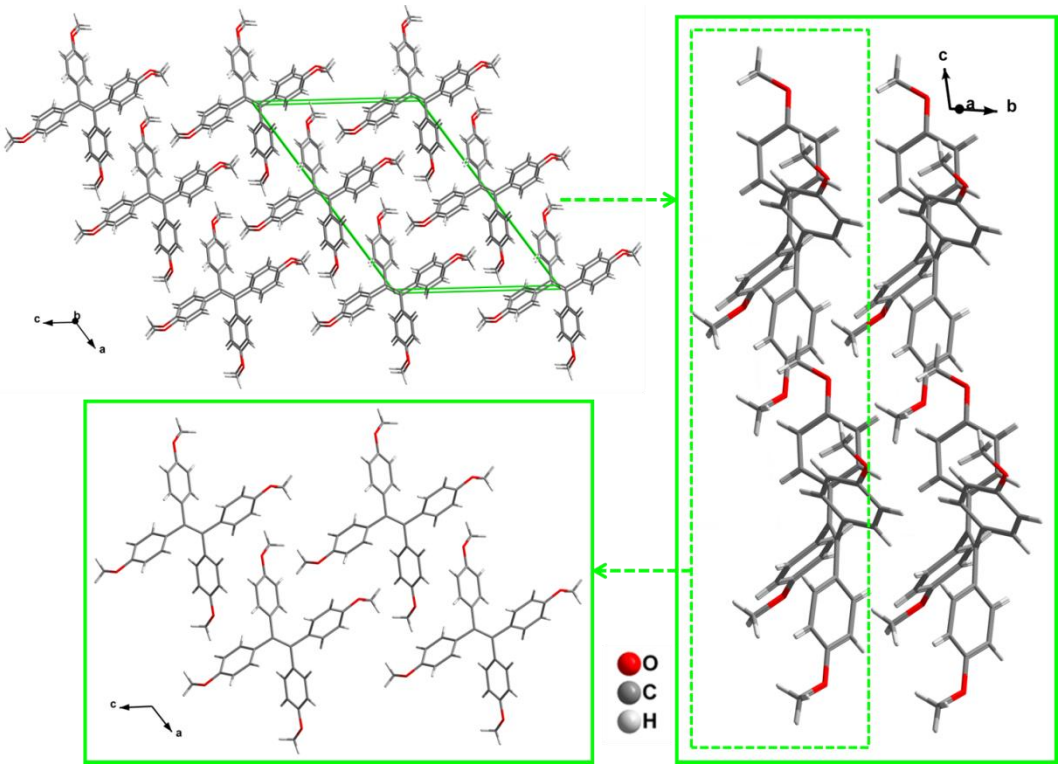


Figure S5. Stacking mode of the molecules in C_c-form crystal in different viewing directions.

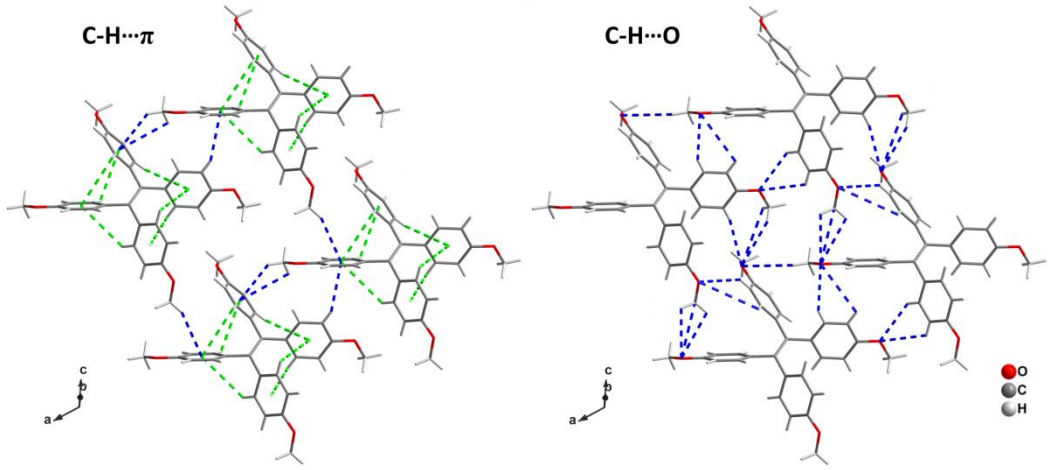


Figure S6. The C-H…π and C-H…O interactions in the C_c-form crystals. The intramolecular hydrogen bonds are displayed in green lines and intermolecular hydrogen bonds are displayed in blue lines. The figures below follow this rule too.

Table S2. Summarization of the C-H…π interactions in the C_c-form crystals.

Type of Interaction	Orientation of Interaction		d / Å [a]	A / °[b]
Intermolecular[e]	1	C-H…Ph[c]	2.8047(5)	131.349(179)
	2	C-H…Ph[c]	2.9936(7)	145.629(139)
	3	C-H…Ph[d]	3.0407(7)	145.188(113)
	4	C-H…Ph[c]	3.3624(9)	91.056(179)
Intramolecular[f]	5	C-H…Ph[d]	3.2877(6)	103.239(134)
	6	C-H…Ph[d]	3.5147(6)	96.304(125)
	7	C-H…Ph[d]	3.5388(7)	112.737(112)

[a] Distance of H…benzene ring. [b] Angel of C-H…benzene ring interaction. [c] C-H of CH_3 or CH_2 group. [d] C-H of benzene ring. [e] Intermolecular hydrogen bond interaction. [f] Intramolecular hydrogen bond interaction.

Table S3. Summarization of the C-H…O interactions in the C_c-form crystals.

Type of Interaction	No.	d / Å [a]	A / °[b]
C-H…O[c]	1	2.8328(21)	135.692(98)
	2	2.8533(20)	127.256(131)
	3	2.8598(22)	142.021(129)
	4	2.8928(18)	146.824(117)
	5	3.0365(15)	118.514(130)
	6	3.6160(16)	104.453(98)
	7	3.9642(16)	99.477(116)
C-H…O[d]	8	3.0517(20)	108.774(107)
	9	3.1498(23)	137.613(164)
	10	3.1871(21)	99.771(182)
	11	3.5603(17)	139.355(166)
	12	3.6812(22)	70.534(169)
	13	3.8125(24)	88.833(160)

[a] Distance of H…O. [b] Angel of C-H…O. [c] C-H of benzene ring. [d] C-H of CH_3 or CH_2 group.

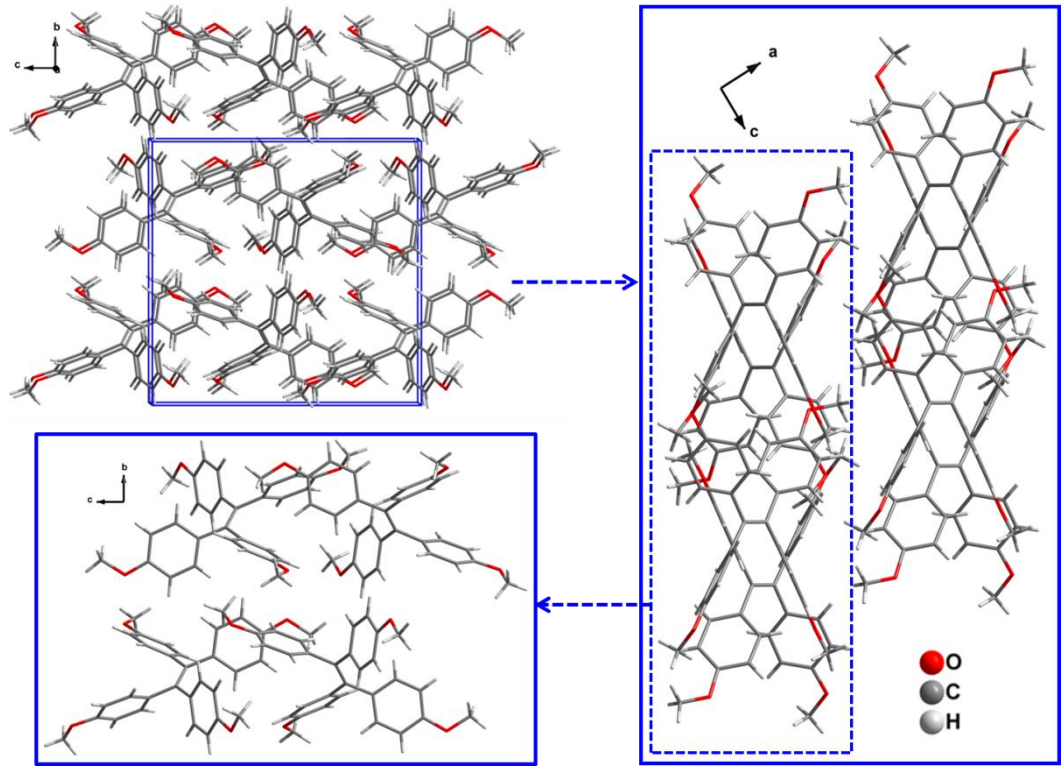


Figure S7. Stacking mode of the molecules in C_p-form crystal in different viewing directions.

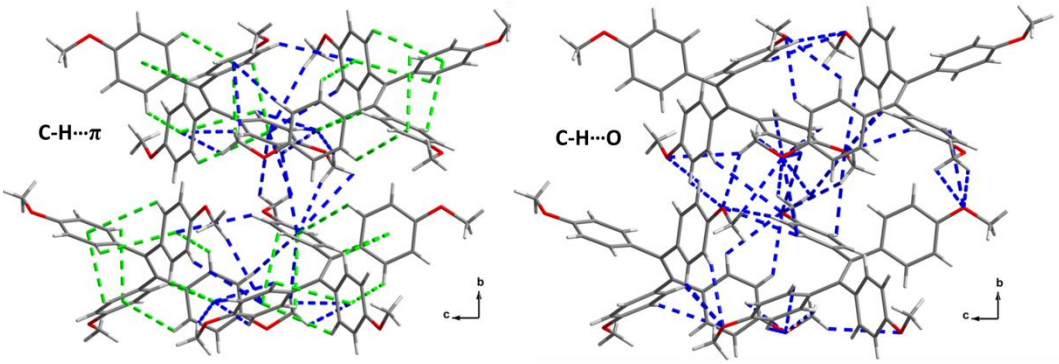


Figure S8. The C-H…π and C-H…O interactions in the C_p-form crystals.

Table S4. Summarization of the C-H…π interactions in the C_p-form crystals.

Type of Interaction	Orientation of Interaction		d / Å [a]	A / ° [b]
Intermolecular[e]	1	C-H…Ph[c]	2.6260(4)	158.672(134)
	2	C-H…Ph[d]	2.8230(4)	151.582(116)
	3	C-H…Ph[d]	2.8819(4)	106.349(112)
	4	C-H…Ph[c]	3.2708(5)	155.874(136)
	5	C-H…Ph[c]	3.3047(4)	156.163(119)
	6	C-H…Ph[c]	3.3261(4)	95.018(112)
	7	C-H…Ph[c]	3.4091(5)	166.004(188)
	8	C-H…Ph[d]	3.5184(4)	145.100(113)
	9	C-H…Ph[c]	3.5664(5)	103.202(185)
	10	C-H…Ph[d]	3.5779(6)	142.239(140)
	11	C-H…Ph[d]	3.7350(5)	138.677(122)
	12	C-H…Ph[d]	3.7367(4)	137.277(116)
	13	C-H…Ph[c]	3.7929(5)	89.203(183)
	14	C-H…Ph[c]	3.8260(5)	126.808(122)
	15	C-H…Ph[d]	3.8370(7)	107.990(119)
Intramolecular[f]	16	C-H…Ph[d]	3.3070(4)	107.290(116)
	17	C-H…Ph[d]	3.3147(6)	102.306(134)
	18	C-H…Ph[d]	3.4400(4)	103.481(117)
	19	C-H…Ph[d]	3.4884(6)	97.253(126)
	20	C-H…Ph[d]	3.5052(4)	113.189(112)
	21	C-H…Ph[d]	3.6627(6)	107.270(119)
	22	C-H…Ph[d]	3.6656(4)	107.923(123)

	23	C-H…Ph[d]	3.6669(5)	107.106(128)

[a] Distance of H…benzene ring. [b] Angel of C-H…benzene ring interaction. [c] C-H of CH_3 or CH_2 group. [d] C-H of benzene ring. [e] Intermolecular hydrogen bond interaction. [f] Intramolecular hydrogen bond interaction.

Table S5. Summarization of the C-H…O interactions in the C_p-form crystals.

Type of Interaction	No.	d / Å [a]	A / ° [b]
C-H…O[c]	1	2.8537(21)	134.598(122)
	2	2.8760(16)	146.886(149)
	3	2.9033(17)	141.612(148)
	4	2.9401(16)	142.299(118)
	5	3.0974(15)	113.652(126)
	6	3.1027(15)	112.651(146)
	7	3.1617(21)	121.088(123)
	8	3.4612(16)	116.616(119)
	9	3.5387(16)	115.612(117)
	10	3.5511(16)	115.764(112)
	11	3.5771(17)	114.001(124)
	12	3.7294(17)	94.623(121)
	13	3.7449(21)	137.430(126)
	14	3.8135(17)	113.957(130)
	15	3.8239(16)	105.510(104)
	16	3.8770(21)	68.557(119)
	17	3.9155(17)	78.464(127)
C-H…O[d]	18	2.6946(18)	147.291(143)
	19	2.9946(16)	65.908(178)
	20	3.0928(15)	130.511(191)
	21	3.2517(16)	140.581(216)
	22	3.3152(17)	118.631(120)
	23	3.6822(16)	92.961(176)
	24	3.7444(21)	126.653(135)

[a] Distance of H…O. [b] Angel of C-H…O. [c] C-H of benzene ring. [d] C-H of CH_3 or CH_2 group.

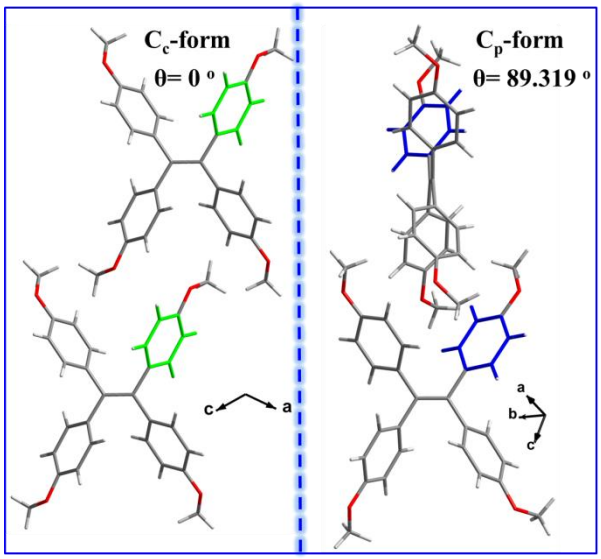


Figure S9. The torsion angles between the ethylenic bonds in the crystal of C_c-form and C_p-form.

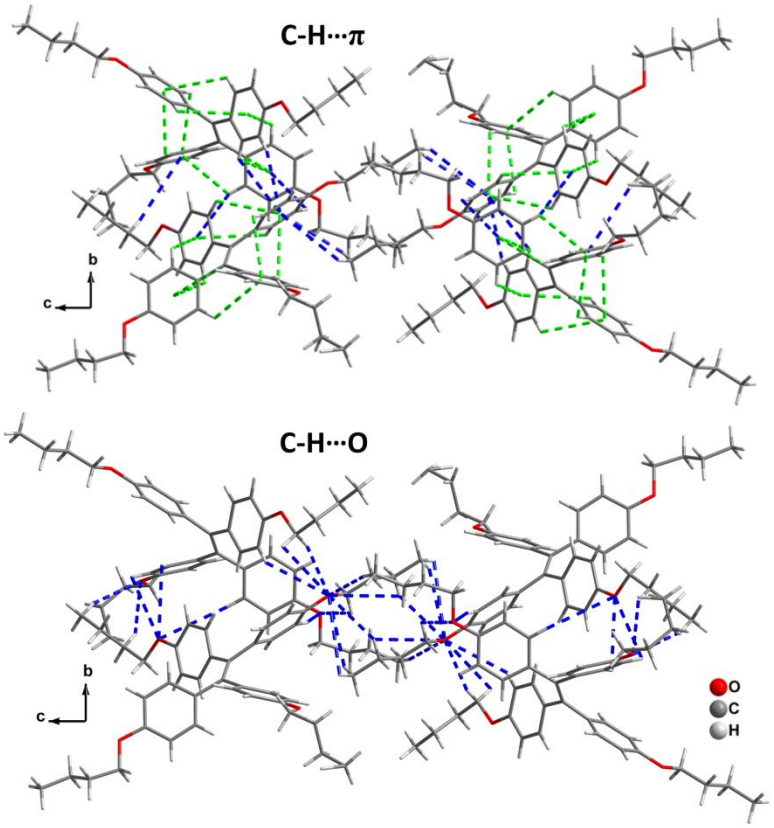


Figure S10. The C-H…π and C-H…O interactions in the TBPE crystal.

Table S6. Summarization of the C-H…π interactions in the TBPE crystals.

Type of Interaction	Orientation of Interaction		d / Å [a]	A / ° [b]
Intermolecular[e]	1	C-H…Ph[d]	3.1049(3)	147.256(80)
	2	C-H…Ph[c]	3.6336(3)	120.026(97)
	3	C-H…Ph[d]	3.6514(2)	112.666(77)
	4	C-H…Ph[d]	3.6728(2)	122.238(77)
	5	C-H…Ph[c]	3.7937(3)	141.807(80)
	6	C-H…Ph[d]	3.8173(2)	114.691(74)
	7	C-H…Ph[c]	3.8547(3)	104.649(97)
Intramolecular[f]	8	C-H…Ph[d]	3.1871(3)	110.074(16)
	9	C-H…Ph[d]	3.2423(3)	108.037(74)
	10	C-H…Ph[d]	3.3086(3)	105.465(74)
	11	C-H…Ph[d]	3.3276(3)	105.597(77)
	12	C-H…Ph[d]	3.3996(3)	115.563(77)
	13	C-H…Ph[d]	3.4321(2)	113.883(76)
	14	C-H…Ph[d]	3.4371(3)	114.418(77)
	15	C-H…Ph[d]	3.5057(2)	111.334(79)

[a] Distance of H…benzene ring. [b] Angel of C-H…benzene ring interaction. [c] C-H of CH_3 or CH_2 group. [d] C-H of benzene ring. [e] Intermolecular hydrogen bond interaction. [f] Intramolecular hydrogen bond interaction.

Table S7. Summarization of the C-H…O interactions in the TBPE crystals.

Type of Interaction	No.	d / Å [a]	A / ° [b]
C-H…O[c]	1	2.7775(9)	160.312(78)
	2	3.3643(1)	137.041(80)
	3	3.5099(9)	88.394(74)
	4	3.6067(1)	163.925(79)
	5	3.6357(9)	85.291(79)
C-H…O[d]	6	2.7138(9)	152.048(79)
	7	2.9210(9)	161.191(99)
	8	2.9916(1)	167.939(92)
	9	3.141(1)	136.196(86)
	10	3.159(1)	151.568(83)
	11	3.5067(9)	112.097(10)
	12	3.6152(9)	100.846(79)
	13	3.7468(9)	74.908(77)
	14	3.9558(9)	84.354(10)
	15	3.9902(9)	68.746(79)

[a] Distance of H…O. [b] Angel of C-H…O. [c] C-H of benzene ring. [d] C-H of CH_3 or CH_2 group.

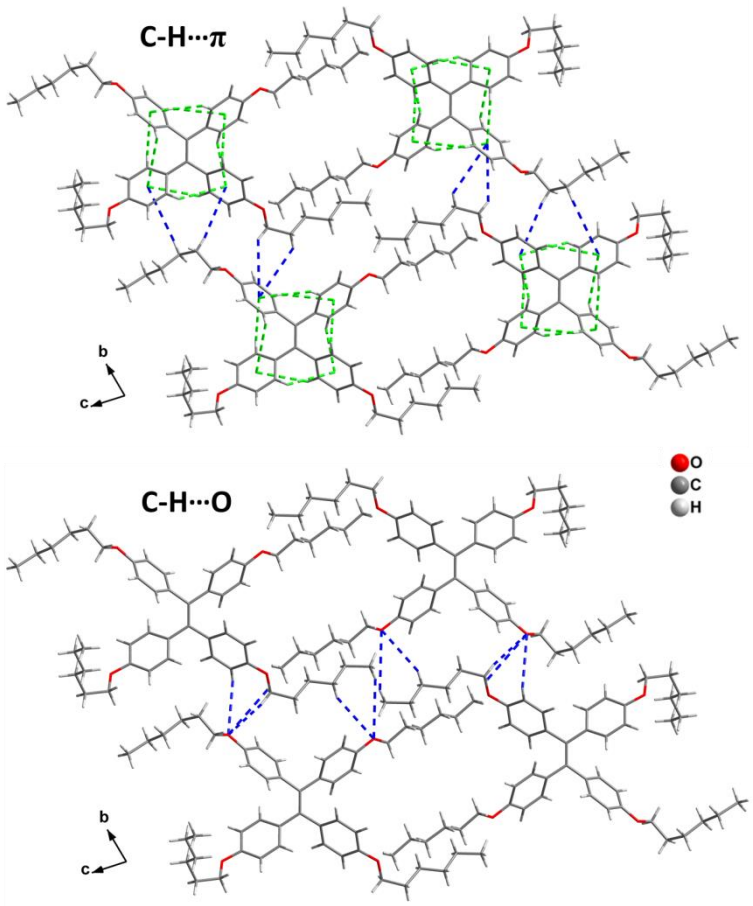


Figure S11. The C-H…π and C-H…O interactions in the THPE crystal.

Table S8. Summarization of the C-H…π interactions in the THPE crystals.

Type of Interaction	Orientation of Interaction		d / Å [a]	A / ° [b]
Intermolecular[e]	1	C-H…Ph[c]	3.5401(2)	168.805(172)
	2	C-H…Ph[c]	3.6570(2)	135.058(174)
	3	C-H…Ph[c]	3.7947(2)	128.193(185)
	4	C-H…Ph[c]	3.8732(1)	150.395(165)
Intramolecular[f]	5	C-H…Ph[d]	3.0397(2)	121.068(162)
	6	C-H…Ph[d]	3.2309(2)	123.656(160)
	7	C-H…Ph[d]	3.3497(1)	106.222(163)
	8	C-H…Ph[d]	3.4047(2)	111.1679162)
	9	C-H…Ph[d]	3.4324(1)	103.595(164)
	10	C-H…Ph[d]	3.4407(2)	109.975(160)
	11	C-H…Ph[d]	3.5490(2)	104.277(158)
	12	C-H…Ph[d]	3.6199(1)	109.732(161)

[a] Distance of H…benzene ring. [b] Angel of C-H…benzene ring interaction. [c] C-H of CH_3 or CH_2 group. [d] C-H of benzene ring. [e] Intermolecular hydrogen bond interaction. [f] Intramolecular hydrogen bond interaction.

Table S9. Summarization of the C-H…O interactions in the THPE crystals.

Type of Interaction	No.	d / Å [a]	A / ° [b]
C-H…O[c]	1	3.5165(1)	124.964(174)
C-H…O[d]	2	2.7866(1)	160.866(187)
	3	3.4459(2)	152.743(254)
	4	3.7255(1)	138.40(39)
	5	3.9161(1)	71.045(192)

[a] Distance of H…O. [b] Angel of C-H…O. [c] C-H of benzene ring. [d] C-H of CH_3 or CH_2 group.

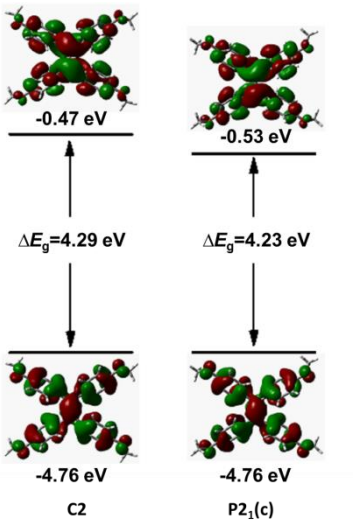


Figure S12. HOMO (lower images) and LUMO (upper images) of the conformations of TMPE in polymorphs C_c-form and C_p-form calculated at the B3LYP/6-31G (d, p) level.

4. Structure Information

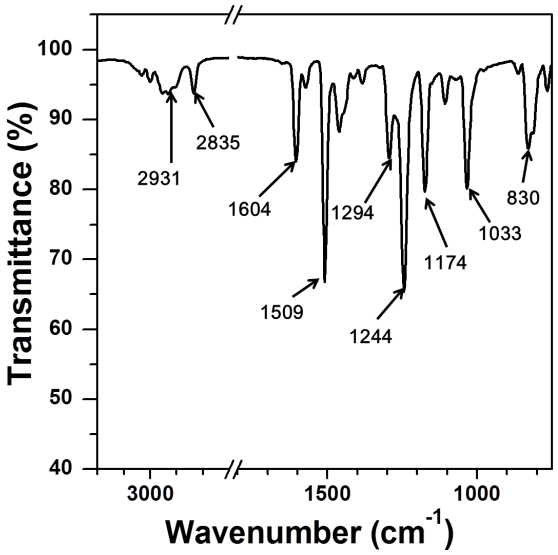


Figure S13. FT-IR spectra of TMPE

Table S10. Summary of crystal data and intensity collection parameters of polymorph crystal TMPE and THPE.

Polymorph	TMPE (C_c-form)	TMPE (C_p-form)	THPE
Empirical formula	C15H14O2	C30H28O4	C50H68O4
Formula weight	226.26	452.52	733.04
Crystal system	monoclinic	monoclinic	triclinic
Temp. / K	296(2)	296(2)	100
Space group	C2	$P2_1(c)$	P - 1
M(Mo Kα) / Å	0.71073	0.71073	0.71073
a / Å	19.510(5)	9.6656(15)	9.1934(4)
b / Å	5.6197(14)	15.743(3)	13.5122(5)
c / Å	13.730(4)	16.075(3)	18.2252(9)
α / º	90	90	76.830(4)
β / º	125.417(3)	91.961(3)	75.995(4)
γ / º	90	90	86.625(3)
volume / Å	1226.8(5)	2444.6(7)	2138.90(16)
Z	2	4	2
Dcalcd., g cm^{-3}	1.225	1.230	1.138
F(000)	480	960	800
Crystal size / mm	0.10 x 0.10 x 0.10	0.10 x 0.10 x 0.10	0.10 x 0.10 x 0.10
θ range /º	1.82 - 30.00	1.81 - 26.99	1.82 - 26.33
No. of collected reflns.	6316	19962	23659
No. of unique reflns.	3435	5335	8502
R(int)	0.1173	0.0329	0.0265
Data / restraints / parameters	3435/1/157	5335/0/311	8502/0/491
R1, wR_2 [obs I> 2σ (I)]	0.0580, 0.1498	0.0508, 0.1426	0.0880, 0.2673
R1, wR_2 (all data)	0.0643, 0.1593	0.0763, 0.1662	0.0957, 0.2758
Residual peak / hole e.$Å^{-3}$	0.263 / -0.248	0.599 / -0.288	1.08 / -0.84
Goodness-of-fit on F2	1.051	1.021	1.075