Electronic Supplementary Material (ESI) for RSC Advances.

Supporting information

Hydrogen-bonded bent-core blue phase liquid crystal complexes containing various molar ratios of proton acceptors and donors

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Table S1 Phase transition temperatures[a,b] (°C) and enthalpies (KJ mol^{-1}) of H-bonded bent-core complexes containing H-accepters **T** (**$P_{III}C_5$**, **$P_{III}C_7$** and **$P_{III}C_9$**)
and various molar ratios of H-donor **$A_{II}F^*$**.

Complexes	Molar ratio (H-donor *V.S.* H-acceptor)	Phase transition temperatures (°C) [enthalpies (KJ mol^{-1})]	ΔT_{BPI} (°C)
$P_{III}C_5/A_{II}F^*$	55 : 45	Iso 76.4 [0.13] BPI 72.8[c] N* 43.3 [1.13] K	3.6
	60 : 40	Iso 77.9 [0.25] BPI 73.6[c] N* 46.2 [1.23] K	4.3
	65 :35	Iso 84.5 [0.28] BPI 76.1[c] N* 52.1 [1.34] K	8.4
	70 : 30	Iso 91.1 [0.08] BPI 80.3[c] N* 60.4 [0.96] K	10.8
	75 : 25	Iso 101.3 [0.18] BPI 94.8[c] N* 67.0 [1.17] K	6.5
	80 : 20	Iso 104.4 [0.96] N* 73.2 [1.52] K	
	85 : 15	Iso 114.2 [1.24] N* 82.1 [1.44] K	
	90 : 10	Iso 144.3 [0.96] N* 102.6 [1.11] K	
	95 : 5	Iso 77.4 [1.21] N* 43.3 [1.61] K	
$P_{III}C_7/A_{II}F^*$	55 : 45	Iso 95.5 [0.22] BPI 87.7[c] N* 59.4 [0.87] K	7.8
	60 : 40	Iso 100.5 [0.37] BPI 88.9[c] N* 59.5 [1.49] K	11.6
	65 :35	Iso 106.1 [0.42] BPI 97.3[c] N* 69.8 [0.90] K	8.8
	70 : 30	Iso 109.7 [0.27] BPI 102.2[c] N* 76.3 [1.16] K	7.5
	75 : 25	Iso 122.4 [0.88] N* 87.2 [1.20] K	
	80 : 20	Iso 128.9 [1.22] N* 88.8[1.37] K	
	85 : 15	Iso 136.7 [1.17] N* 89.5 [1.19] K	
	90 : 10	Iso 144.6 [0.95] N* 92.9 [1.04] K	
	95 : 5	Iso 146.5 [0.78] N* 95.7 [1.20] K	
$P_{III}C_9/A_{II}F^*$	55 : 45	Iso 95.3 [0.34] BPI 88.3[c] N* 60.7 [1.23] K	7
	60 : 40	Iso 101.9 [0.34] BPI 92.8[c] N* 60.3 [1.22] K	9.1
	65 :35	Iso 105.4 [0.11] BPI 96.8[c] N* 62.3 [1.00] K	8.6
	70 : 30	Iso 114.5 [0.25] BPI 102.5[c] N* 67.3 [1.60] K	12
	75 : 25	Iso 117.7 [0.18] BPI 106.8[c] N* 71.4 [0.87] K	10.9
	80 : 20	Iso 125.4 [0.23] BPI 114.7[c] N* 76.8 [0.85] K	10.7
	85 : 15	Iso 134.2 [1.25] N* 83.5 [1.55] K	
	90 : 10	Iso 136.9 [1.24] N* 95.2 [1.53] K	
	95 : 5	Iso 140.7 [1.09] N* 92..6 [1.21] K	
$A_{II}F^*/A_{II}F^*$	100 : 0	Iso 150.1 [1.15] N* 97.8 [1.44] K	

[a]Peak temperatures in the DSC profiles obtained during the first cooling at a rate of 0.5 °C min^{-1}. [b]Iso = isotropic phase; BPI = blue phase I; N* = chiral nematic phase; K = crystalline phase. [c]The transition to this phase was observed under the polarizing optical microscope (POM) and it was too weak to be recognized by the DSC.

Table S2 Phase transition temperatures[a,b] (°C) and enthalpies (KJ mol^{-1}) of covalent-bonded bent-core mixtures containing covalent-bonded bent-core molecule **$P_{III}C_9A_{II}F^*$** and various molar ratios of H-donor **$A_{II}F^*$**.

Mixtures	Molar ratio (H-donor *V.S.* H-acceptor)		Phase transition temperatures (°C) [enthalpies (KJ mol^{-1})]	ΔT_{BPIII} (°C)
	H-donor	Covalent-bonded bent-core molecule		
$P_{III}C_9A_{II}F^*/A_{II}F^*$	0	100	Iso 127.3 [3.01] K	
	18.2	81.8	Iso 84.1 [2.28] K	
	33.3	66.7	Iso 71.2 [2.28] K	
	46.2	53.8	Iso 86.4 [1.98] K	
	57.1	42.9	Iso 89.3 [1.93] K	
	66.7	33.3	Iso 110.2 [0.44] N* 84.2 [1.19] K	
	75	25	Iso 102.3 [0.51] BPIII 99.9[c] N* 83.7 [1.62] K	2.4
	82.4	17.6	Iso 108.6 [0.35] BPIII 107.5[c] N* 84.8 [1.36] K	1.1
	88.9	12.1	Iso 126.6 [0.30] N* 89.1 [1.11] K	
	94.7	5.3	Iso 140.7 [0.38] N* 100.3 [1.19] K	
	100	0	Iso 150.3 [0.40] N* 97.8 [1.55] K	

[a]Peak temperatures in the DSC profiles obtained during the first cooling at a rate of 0.5 °C min^{-1}. [b]Iso = isotropic phase; BPIII = blue phase III; N* = chiral nematic phase; K = crystalline phase. [c]The transition to this phase was observed under the polarizing optical microscope (POM) and it was too weak to be recognized by the DSC.

Table S3 Phase transition temperatures[a,b] (°C) and enthalpies (KJ mol^{-1}) of hybrid H-bonded ben-core complexes containing H-accepters **T** (**$P_{III}C_5$**, **$P_{III}C_7$** and **$P_{III}C_9$**) and hybrid H-donors **D** (**$A_{II}F^*$**+**$A_{II}F$** and **$A_{II}F^*$**+**A_{II}^***).

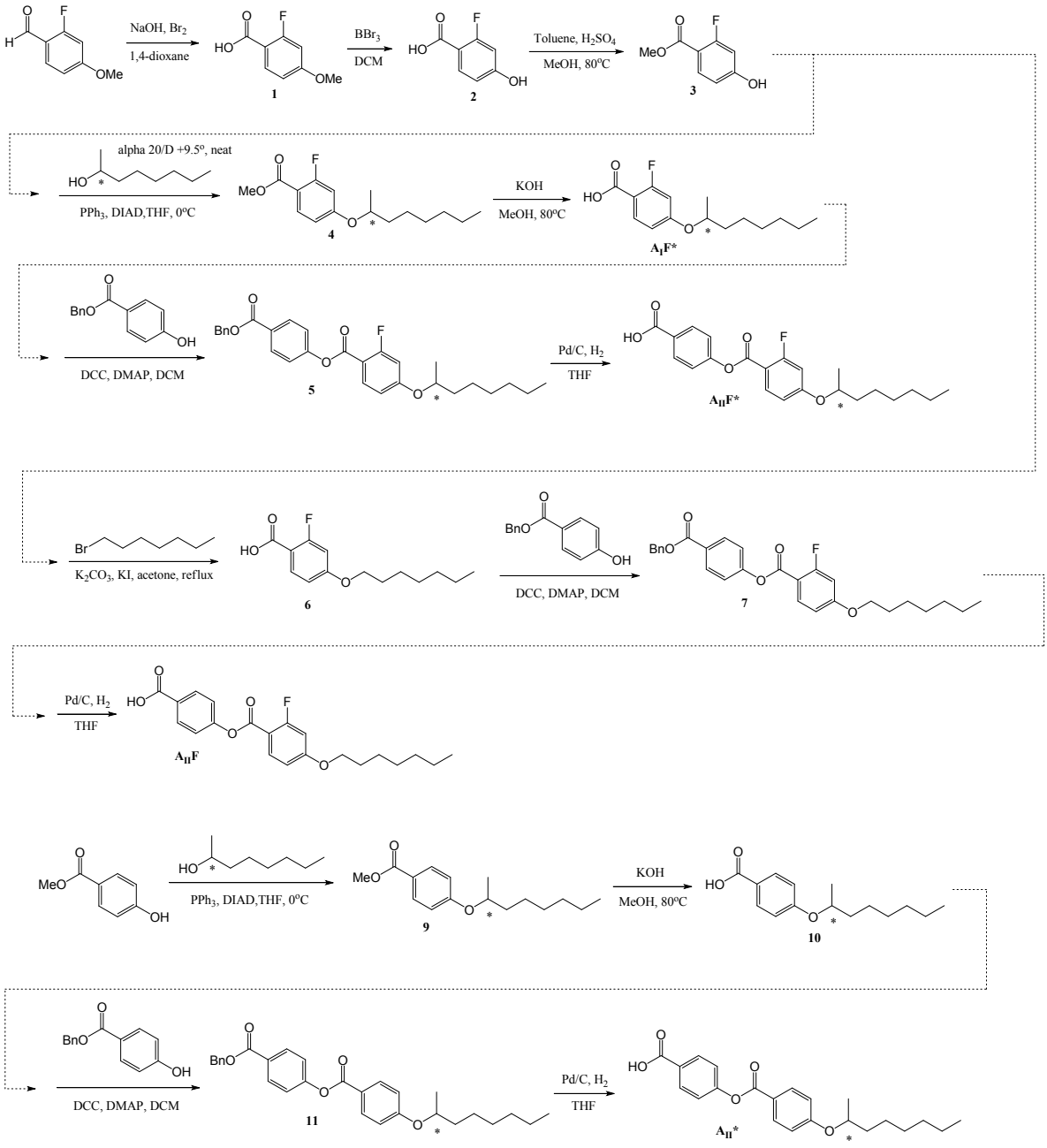
Complexes	Molar ratio (H-donor *V.S.* H-acceptor)				Phase transition temperatures (°C) [enthalpies (KJ mol^{-1})]	ΔT_{BP} (°C)
	H-accepter	H-donor				
	$P_{III}C_9$	**$A_{II}F^*$**	**$A_{II}F$**	**A_{II}^***		
$P_{III}C_9$/($A_{II}F^*$+$A_{II}F$)	30	70	-	-	Iso 114.5 [0.25] BPI 102.5[c] N* 67.3 [1.60] K	12
	30	63	7	-	Iso 115.8 [0.34] BPI 105.7[c] N* 71.7 [1.13] K	10.1
	30	56	14	-	Iso 120.6 [0.30] BPI 111.8[c] N* 76.3 [0.94] K	8.8
	30	49	21	-	Iso 123.5 [0.17] BPI 117.6[c] N* 80.6 [1.24] K	5.9
	30	42	28	-	Iso 124.9 [0.24] BPI 120.7[c] N* 88.3 [1.12] K	4.2
	30	35	35	-	Iso 126.7 [0.40] BPI 124.8[c] N* 92.9 [1.09] K	1.9
	30	28	42	-	Iso 127.1 [0.17] BPI 126.8[c] N* 97.2 [1.17] K	0.3
	30	21	49	-	Iso 131.9 [0.27] BPI 131.4[c] N* 104.1 [0.96] K	0.5
	30	14	56	-	Iso 134.4 [1.11] N* 110.2 [1.66] K	
	30	7	63	-	Iso 133.7 [0.85] N* 113.6 [1.60] K	
$P_{III}C_9$/($A_{II}F^*$+A_{II}^*)	30	63	-	7	Iso 114.2 [0.23] BPI 105.1[c] N* 68.2 [1.28] K	9.1
	30	56	-	14	Iso 113.5 [0.25] BPI 110.6[c] N* 72.4 [1.17] K	2.9
	30	49	-	21	Iso 113.1 [0.32] BPI 112.4[c] N* 75.9 [1.10] K	0.7
	30	42	-	28	Iso 111.8 [0.99] N* 77.4 [1.18] K	
	30	35	-	35	Iso 110.3 [1.26] N* 79.5 [1.17] K	
	30	28	-	42	Iso 110.7 [1.20] N* 80.6 [1.51] K	
	30	21	-	49	Iso 108.4 [1.19] N* 82.1 [1.65] K	
	30	14	-	56	Iso 108.0 [0.80] N* 84.6 [1.15] K	
	30	7	-	63	Iso106.4 [0.70] N* 85.9 [1.38] K	

[a]Peak temperatures in the DSC profiles obtained during the first cooling at a rate of 0.5 °C min^{-1}. [b]Iso = isotropic phase; BPI = blue phase I;N* = chiral nematic phase; K = crystalline phase. [c]The transition to this phase was observed under the polarizing optical microscope and it was too weak to be recognized by the DSC.

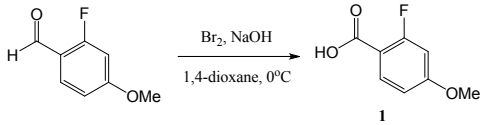
Additional details on the methods

Preparation of H-donors **D** (**A_IF***, **A_{II}F***, **A_{II}F** and **A_{II}***), H-accepters **T** (**$P_{IV}C_9$**, **$P_{III}C_5$**, **$P_{III}C_7$** and **$P_{III}C_9$**), and covalent-bonded bent-core molecules (**$P_{III}C_5A_{II}F$*** and **$P_{III}C_9A_{II}F$***):

Scheme S1. Synthesis of H-donors D (A_IF*, A_{II}F*, A_{II}F and A_{II}*).**

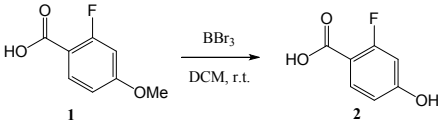


(i) Synthesis of 2-fluro-4-methoxybenzoic acid (1)



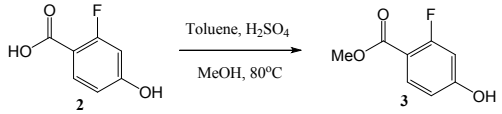
2-fluoro-4-methoxyacetophenone (5g, 29.8mmol) was dissolved in 1,4-dioxane. NaOH (3.57g, 89.3mmol) was dissolved in DI water, then bromine (4.75g, 29.8mmol) was slowly added into the aqueous solution. The above two solutions were mixed at 0°C under ice bath, and the mixing solution was reacted at room temperature for overnight. The mixture was extracted by DI water/DCM, then aqueous phase maintain acidity at pH=3 by HCl. The sample **1** was got by filtration and water washing, and the sample 1 was white solid (yield: 90%). ^{1}H NMR (300 MHz, $CDCl_3$) δ(ppm): 7.9(d, *J* = 8.7 Hz, 1H, Ar-H), 7.83-7.78 (d, *J* = 8.7 Hz, 1H, Ar-H), 7.02 (t, *J* = 9.0 Hz, 1H, Ar-H), 3.97 (s, 3H, -OCH_3).

(ii) Synthesis of 2-fluoro-4-hydroxybenzoic acid (2)



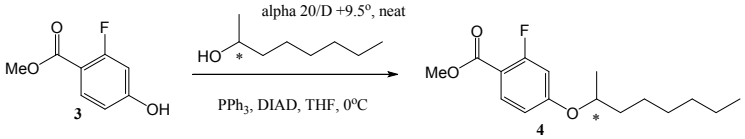
The sample **1** (4.9g, 28.8mmol) was dissolved in dry DCM (30ml), then BBr_3 (14.4g, 57.6mmol) was slowly added into DCM solution at -78°C. After uniformly mixed, the solution was reacted at room temperature for 16 hours. Then reaction was terminated by adding 2N NaOH into DCM solution. The mixture was extracted by DI water/ethyl acetate, then the organic phase was dried by $MgSO_4$ and concentrated by a rotary evaporator. The sample **2** was white solid (yield: 95%). ^{1}H NMR (300 MHz, $CDCl_3$) δ(ppm): 7.62-7.58 (m, 1H, Ar-H), 7.01 (t, *J* = 9.0Hz, 2H, Ar-H).

(iii) Synthesis of 2-fluoro-4-hydroxybenzoic acid (3)



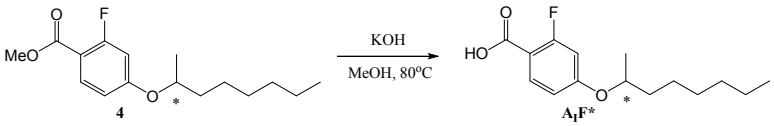
The sample **2** (5g, 32mmol) and H_2SO_4 (7ml) were dissolved in MeOH, then the solution was reacted at 90°C for 12 hours. The mixture was extracted by DI water/ethyl acetate, then the organic phase was dried by $MgSO_4$ and concentrated by a rotary evaporator. The residue was purified by column chromatography on silica (*n*-hexane/ethyl acetate = 3:1, v/v). The sample **3** was a white solid (yield: 80%). ^{1}H NMR (300 MHz, $CDCl_3$) δ(ppm): 7.76 (d, *J* = 8.7 Hz, 1H, Ar-H), 7.74 (d, *J* = 8.7 Hz 1H, Ar-H), 7.06 (d, *J* = 9.0 Hz 1H, Ar-H), 6.10 (s,1H, Ar-OH), 3.91 (s, 3H, -OCH_3).

(iv) Synthesis of methyl 4-((R)-octan-2-yloxy)-2-fluorobenzoate (4)



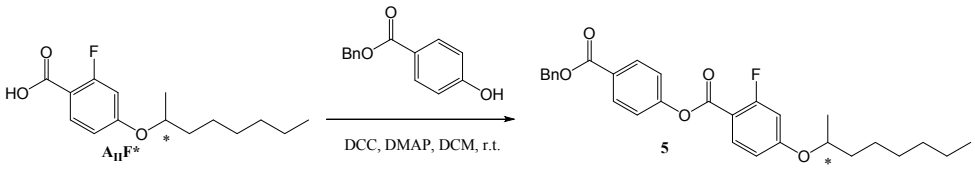
The sample **3** (5g, 29.4mmol) and PPh_3 (8.89g, 33.8mmol) were dissolved in dry DCM upon nitrogen system, then (S)-(+)-2-octanol ([α]20/D +9.5°, neat) (4.6g, 35.2mmol) and DIAD (8.9g, 44mmol) were added in the solution at 0°C under ice bath. The solution reacted at room temperature for more than 12 hours, then mixture was concentrated by a rotary evaporator. The residue was purified by column chromatography on silica (*n*-hexane/DCM = 5:1, v/v), and the sample **4** was a light yellow oil (yield: 85%). ^{1}H NMR (300 MHz, $CDCl_3$) δ(ppm): 7.92 (d, *J* = 9.0 Hz, 1H, Ar-H), 7.25 (d, *J* = 8.7Hz, 1H, Ar-H), 6.87 (d, *J* = 8.7 Hz, 1H, Ar-H), 4.30 (m,1H, -OCH-), 3.84 (s, 3H, -OCH_3), 1.71-1.57 (m, 2H, -CH_2-), 1.42-1.25 (m, 11H, -CH_2CH_3), 0.83 (t, *J* = 6.0 Hz, 3H, -CH_3).

(v) Synthesis of 4-((R)-octan-2-yloxy)-2-fluorobenzoic acid (A_IF*)



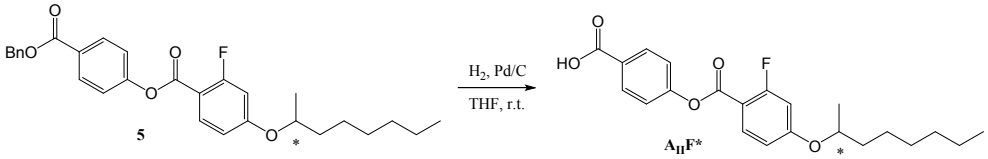
The sample **4** (10g, 35.5mmol) and KOH (5.95g, 106mmol) were dissolved in MeOH, then the solution was reacted at 90°C for 24 hours. The mixture was concentrated by a rotary evaporator, then HCl aqueous solution was added to until pH=3. The product **A_IF*** was a light yellow solid (yield: 89%). ^{1}H NMR (300 MHz, $CDCl_3$) δ(ppm): 7.96 (t, *J* = 8.7 Hz, 1H, Ar-H), 6.71 (d, *J* = 9.0 Hz, 1H, Ar-H), 6.50 (d, *J* = 9.0 Hz, 1H, Ar-H), 4.41 (m, 1H, -OCH-), 1.79-1.60 (m, 2H, -CH_2-), 1.47-1.26 (m, 11H, -CH_2CH_3), 0.88 (t, *J* = 6.6 Hz, 3H, -CH_3). Anal. Calcd for $C_{15}H_{21}FO_3$: C 67.14, H 7.89; Found: C 67.06, H 7.89.

(vi) Synthesis of (R)-4-((benzyloxy)carbonyl)phenyl-2-fluoro-4-(octan-2-yloxy)benzoate (5)



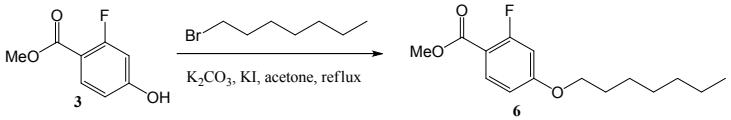
The product **A_IF*** (11.25 g, 42mmol), benzyl 4-hydroxybenzoate (8 g, 35mmol), DMAP (0.65 g, 5.3mmol) and DCC (14.5g, 70mmol) were dissolved in dry DCM upon nitrogen system, then the solution was reacted at room temperature for 16 hours. The mixture was extracted by DI water/DCM, then the organic phase was dried by $MgSO_4$ and concentrated by a rotary evaporator. The residue was purified by column chromatography on silica (*n*-hexane/DCM = 5:1, v/v), and the sample 5 was a light yellow solid (yield: 87%). ^{1}H NMR (300 MHz, $CDCl_3$) δ(ppm): 8.13 (d, *J* = 8.7 Hz, 2H, Ar-H), 8.02 (t, *J* = 9.0 Hz, 1H, Ar-H), 7.45-7.30 (m, 5H, Ar-H), 7.29-7.25 (m, 2H, Ar-H), 6.74 (dd, *J* = 8.7 Hz, 1H, Ar-H), 6.66 (dd, *J* = 8.7 Hz, 1H, Ar-H), 5.37 (s, 1H, -OCH_2Ph), 4.40 (m, 1H,-OCH-), 1.70-1.61 (m, 2H, -CH_2-), 1.41-1.26 (m,11H, -CH_2CH_3), 0.86 (t, *J* = 6.0 Hz, 3H, -CH_3).

(vii) Synthesis of (R)-4-((2-fluoro-4-(octan-2-yloxy)benzoyl)oxy)benzoic acid ($A_{II}F^*$)



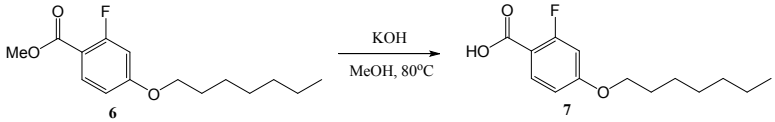
The sample **5** (10g, 20 mmol) and 15% Pd/C (1.5 g) were dissolved in dry THF, then the solution was reacted at room temperature for overnight upon hydrogen system. The mixture was filtrated by diatomaceous followed by THF cleaning and concentrated by a rotary evaporator. The residue was recrystallization by *n*-hexane/DCM, and the product $\mathbf{A_{II}F^*}$ was a white solid (yield: 95%). ^{1}H NMR (300 MHz, $CDCl_3$) δ(ppm): 8.16 (d, *J* = 8.7 Hz, 2H, Ar-H), 8.03 (t, *J* = 8.0 Hz, 1H, Ar-H), 7.32 (m, 2H, Ar-H), 6.74 (dd, *J* = 9.0 Hz, 1H, Ar-H), 6.68 (dd, *J* = 11.7 Hz, 1H, Ar-H), 4.42 (m, 1H, -OCH-), 1.71-1.60 (m, 2H, $-CH_2-$), 1.33-1.27 (m, 11H, $-CH_2CH_3$), 0.86 (t, *J* = 6.3 Hz, 3H, $-CH_3$). Anal. Calcd for $C_{22}H_{25}FO_5$: C 68. 03, H 6.49; Found: C 67.78, H 6.44.

(viii) Synthesis of methyl 2-fluoro-4-(heptyloxy)benzoate (6)



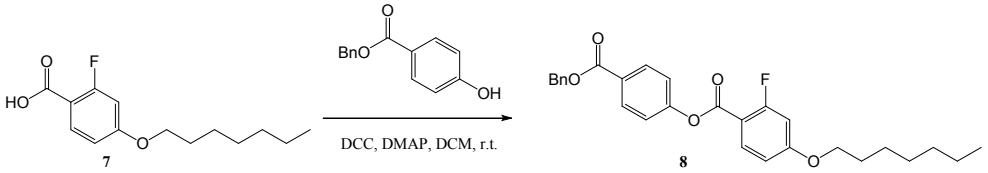
The sample **3** (11.05g, 65mmol), K_2CO_3 (27.2g, 197mmol), and KI (5.5g, 33mmol) were dissolved in acetone, then 1-bromoheptane (14g, 78mmol) was slowly added in the solution. The solution reacted at 60°C for overnight, then solution was concentrated by a rotary evaporator. The mixture was extracted by DI water/ EtOAc, then organic phase was dried by $MgSO_4$ and concentrated by a rotary evaporator. The residue was purified by column chromatography on silica (*n*-hexane/EtOAc = 5:1, v/v), and the sample **6** as a white solid (yield: 94%). ^{1}H NMR (300 MHz, $CDCl_3$) δ(ppm): 7.86 (d, *J* = 9.0 Hz, 1H, Ar-H), 6.69 (d, *J* = 8.7 Hz, 1H, Ar-H), 6.61 (d, *J* = 8.7 Hz, 1H, Ar-H), 3.97 (t, *J* = 6.3 Hz, 2H, $-OCH_2-$), 3.87 (s, 3H, $-OCH_3$), 1.77 (m, 2H, CH_2-), 1.45-1.20 (m, 8H, $-CH_2-$), 0.87 (t, *J* = 6.3 Hz, 3H, $-CH_3$).

(ix) Synthesis of 2-fluoro-4-(heptyloxy)benzoic acid (7)



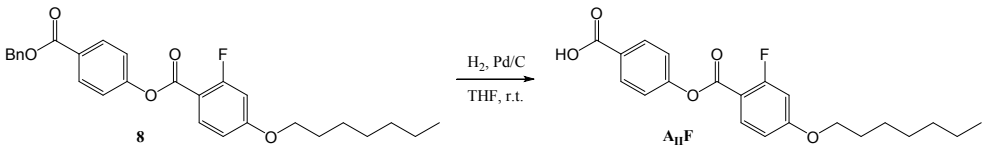
The sample **6** (9.66g, 36mmol) and KOH (6.06g, 108mmol) were dissolved in MeOH, then the solution was reacted at 90°C for 24 hours. The mixture was concentrated by a rotary evaporator, then HCl aqueous solution was added to until pH=3. The sample **7** was a light white solid (yield: 93%). ^{1}H NMR (300 MHz, $CDCl_3$) δ(ppm): 7.78 (d, *J* = 8.7 Hz, 1H, Ar-H), 6.86 (dd, *J* = 8.7 Hz, 1H, Ar-H), 6.80 (dd, *J* = 8.7 Hz, 1H, Ar-H), 4.03 (t, *J* = 6.7 Hz, 2H, $-OCH_2-$), 1.72 (m, 2H, $-CH_2-$), 1.38-1.27 (m, 8H, $-CH_2-$), 0.86 (t, *J* = 6.7 Hz, 3H, $-CH_3$). Anal. Calcd for $C_{14}H_{19}FO_3$: C 66.12, H,7.53; Found: C 64.88, H 7.50.

(x) Synthesis of 4-((benzyloxy)carbonyl)phenyl 2-fluoro-4-(heptyloxy)benzoate (8)



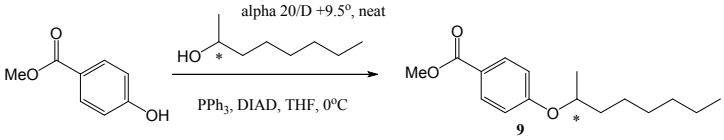
The sample **7** (10.68g, 42mmol), benzyl 4-hydroxybenzoate (8 g, 35mmol), DMAP (0.65 g, 5.3mmol) and DCC (14.5g, 70mmol) were dissolved in dry DCM upon nitrogen system, then the solution was reacted at room temperature for 16 hours. The mixture was extracted by DI water/DCM, then the organic phase was dried by $MgSO_4$ and concentrated by a rotary evaporator. The residue was purified by column chromatography on silica (*n*-hexane/DCM = 5:1, v/v), and the sample **8** was a white solid (yield: 87%). ^{1}H NMR (300 MHz, $CDCl_3$) δ(ppm): 8.11 (d, *J* = 8.7 Hz, 2H, Ar-H), 8.01 (t, *J* = 8.4 Hz, 1H, Ar-H), 7.44-7.34 (m, 4H, Ar-H), 7.32-7.22 (m, 2H, Ar-H), 6.74 (mdd, 1H, Ar-H), 6.70 (m, 2H, Ar-H), 5.35 (s, 2H, $-CH_2Ph$), 4.01 (t, *J* = 6.3 Hz, 2H, $-OCH_2-$), 1.77 (t, 2H, $-CH_2-$), 1.50-1.31 (m, 8H, $-CH_2-$), 1.02 (t, *J* = 6.3 Hz, 3H, $-CH_3$).

(xi) Synthesis of 4-((2-fluoro-4-(heptyloxy)benzoyl)oxy)benzoic acid ($A_{II}F$)



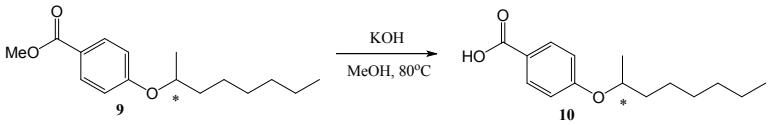
The sample **8** (10g, 21.5mmol) and 15% Pd/C (1.11 g) were dissolved in dry THF, then the solution was reacted at room temperature for overnight upon hydrogen system. The mixture was filtrated by diatomaceous followed by THF cleaning and concentrated by a rotary evaporator. The residue was recrystallization by *n*-hexane/DCM, and the product $\mathbf{A_{II}F}$ was a white solid (yield: 90%). ^{1}H NMR (300 MHz, $CDCl_3$) δ(ppm): 8.17 (d, *J* = 8.7 Hz, 2H, Ar-H), 8.14 (t, *J* = 8.7 Hz, 1H, Ar-H), 7.32 (d, *J* = 8.7 Hz, 2H, Ar-H), 6.77 (m, 1H, Ar-H), 6.68 (m, 1H, Ar-H), 4.00 (t, *J* = 6.6 Hz, 2H, $-OCH_2-$), 1.86 (t, 2H, $-CH_2-$), 1.47-1.27 (m, 8H, $-CH_2-$), 0.86 (t, *J* = 6.5 Hz, 3H, $-CH_3$). Anal. Calcd for $C_{21}H_{23}FO_5$: C 67.37, H 6.19; Found: C 67.25, H 6.39.

(xii) Synthesis of (R)-methyl 4-(octan-2-yloxy)benzoate (9)



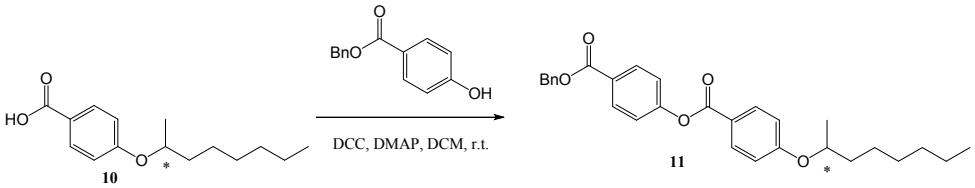
Benzyl 4-hydroxybenzoate (4.47g, 29.4mmol) and PPh_3 (8.89g, 33.8mmol) were dissolved in dry DCM upon nitrogen system, then (S)-(+)-2-octanol ([α]20/D +9.5°, neat) (4.6g, 35.2mmol) and DIAD (8.9g, 44mmol) were added in the solution at 0°C under ice bath. The solution reacted at room temperature for 12 hours, then mixture was concentrated by a rotary evaporator. The residue was purified by column chromatography on silica (*n*-hexane/DCM = 5:1, v/v), and the sample **9** was a white solid (yield: 74%). ^{1}H NMR (300 MHz, $CDCl_3$) δ(ppm): 7.10 (d, *J* = 8.7 Hz, 2H,Ar-H), 6.87 (d, *J* = 8.7 Hz, 2H, Ar-H), 4.42 (m,1H, -OCH), 3.88 (s, 3H, $-OCH_3$), 1.71-1.57 (m, 2H, $-CH_2$-), 1.42-1.25 (m, 11H, $-CH_2$), 0.88 (t, *J* = 6.0 Hz, 3H, $-CH_3$).

(xiii) Synthesis of (R)-4-(octan-2-yloxy)benzoic acid (10)



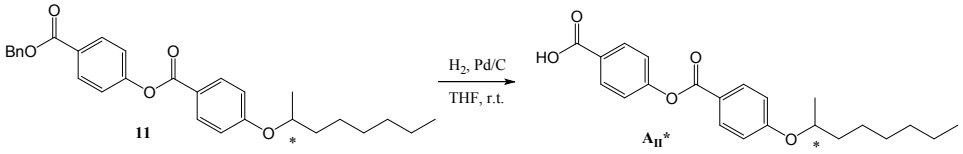
The sample **9** (9.51g, 36 mmol) and KOH (6.06g, 108mmol) were dissolved in MeOH, then the solution was reacted at 90°C for 24 hours. The mixture was concentrated by a rotary evaporator, then HCl aqueous solution was added to until pH=3. The sample **10** was a light white solid (yield: 94%). ^{1}H NMR (300 MHz, $CDCl_3$) δ(ppm): 8.06 (d, *J* = 8.4 Hz, 2H, Ar-H), 6.92 (d, *J* = 8.0 Hz, 2H, Ar-H), 4.05 (m, 1H, -OCH), 1.78-1.58 (m, 2H, $-CH_2$), 1.44-1.26 (m, 11H ,$-CH_2$), 0.90 (t, *J* = 6.0 Hz, 3H, $-CH_3$) Anal. Calcd for $C_{15}H_{22}O_3$: C 71.97, H 8.86; Found: C 71.34, H 8.87.

(xiv) Synthesis of (R)-benzyl 4-((4-(octan-2-yloxy)benzoyl)oxy)benzoate (11)



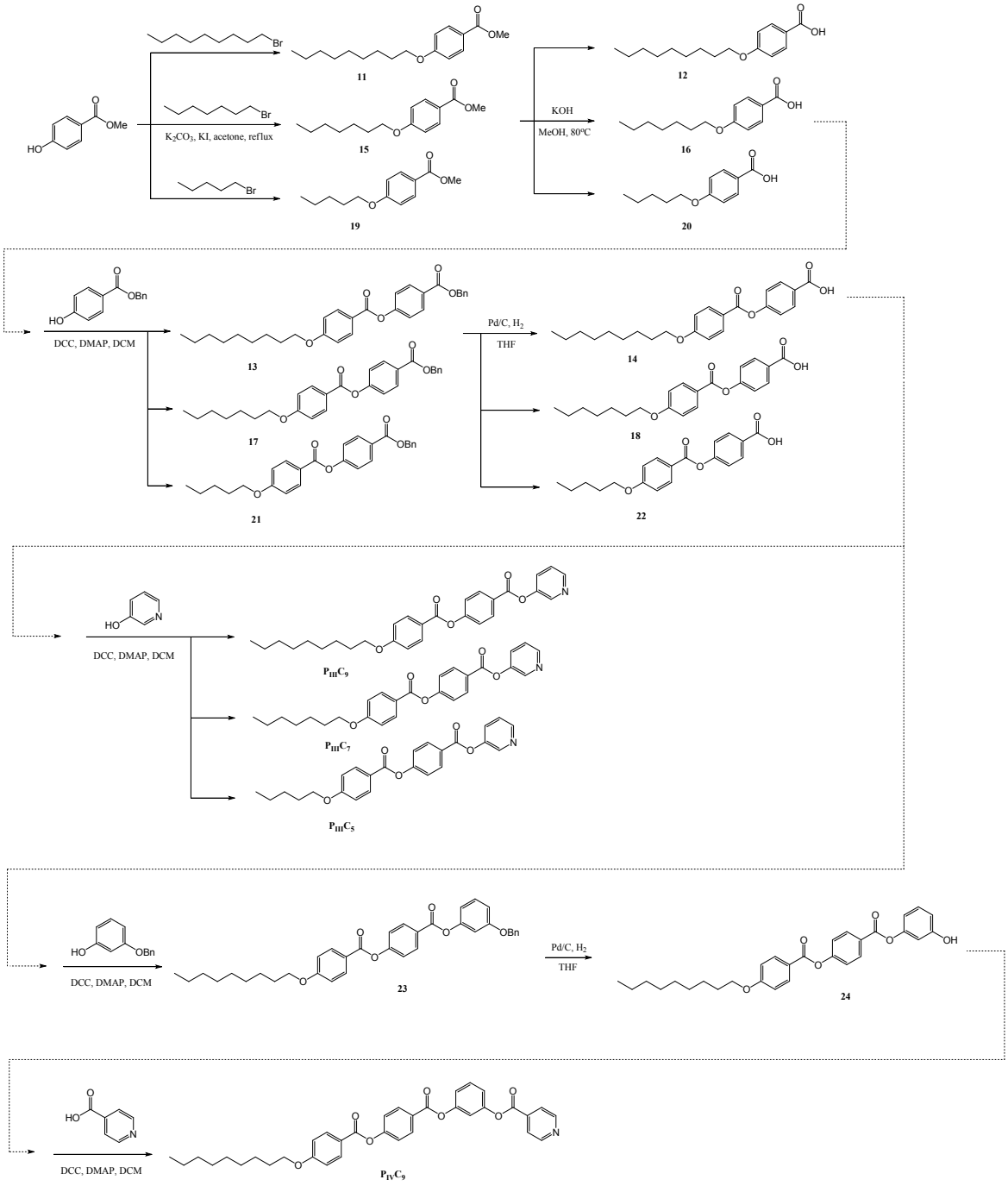
The sample **10** (10.51g, 42mmol), benzyl 4-hydroxybenzoate (8 g, 35mmol), DMAP (0.65 g, 5.3mmol) and DCC (14.5g, 70mmol) were dissolved in dry DCM upon nitrogen system, then the solution was reacted at room temperature for 16 hours. The mixture was extracted by DI water/DCM, then the organic phase was dried by $MgSO_4$ and concentrated by a rotary evaporator. The residue was purified by column chromatography on silica (*n*-hexane/DCM = 5:1, v/v), and the sample **11** was a white solid (yield: 87%). ^{1}H NMR (300 MHz, $CDCl_3$) δ(ppm): 8.14 (m, *J* = 8.7 Hz,4H, Ar-H), 7.44-7.32 (m, 5H, Ar-H), 7.27-7.25 (m, 3H, Ar-H), 6.94 (d, *J* = 8.7 Hz, 2H, Ar-H), 5.35 (s, 2H, $-OCH_2$-Ph), 4.45 (m, 1H, -OCH), 1.71-1.59 (m ,2H, $-CH_2$), 1.42-1.25 (m, 11H, $-CH_2$), 0.88 (t, *J* = 6.0 Hz, 3H, $-CH_3$).

(xv) Synthesis of (R)-4-((4-(octan-2-yloxy)benzoyl)oxy)benzoic acid (A_{II}*)

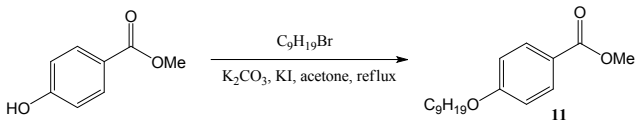


The sample **11** (7.4g, 20mmol) and 15% Pd/C (1.11 g) were dissolved in dry THF, then the solution was reacted at room temperature for overnight upon hydrogen system. The mixture was filtrated by diatomaceous followed by THF cleaning and concentrated by a rotary evaporator. The residue was recrystallization by *n*-hexane/DCM, and the product **A_{II}*** was a white solid (yield: 90%). ^{1}H NMR (300 MHz, $CDCl_3$) δ(ppm): 8.22-8.14 (m, 4H, Ar-H), 7.33 (d, *J* = 8.4 Hz, 2H, Ar-H), 6.98 (d, *J* = 8.4 Hz, 2H, Ar-H), 4.52 (m, 1H, -OCH), 1.79-1.60 (m, 2H, $-CH_2$), 1.39-1.32 (m, 11H, $-CH_2$), 0.91 (t, *J* = 5.7 Hz, 3H, $-CH_3$). Anal. Calcd for $C_{22}H_{26}O_5$: C 71.33, H, 7.07; Found: C 70.96, H 7.11.

Scheme 2. Synthesis of H-accepters T ($P_{IV}C_9$, $P_{III}C_5$, $P_{III}C_7$ and $P_{III}C_9$).

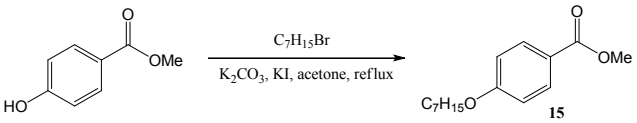


(i) Synthesis of methyl 4-(pentyloxy)benzoate (11)



The benzyl 4-hydroxybenzoate (10g, 65mmol), K_2CO_3 (27.2g, 197mmol), and KI (5.5g, 33mmol) were dissolved in acetone, then 1-bromononane (16.2g, 78mmol) was slowly added in the solution. The solution reacted at 60°C for overnight, then solution was concentrated by a rotary evaporator. The mixture was extracted by DI water/ EtOAc, then organic phase was dried by $MgSO_4$ and concentrated by a rotary evaporator. The residue was purified by column chromatography on silica (*n*-hexane/EtOAc = 5:1, v/v), and the sample **11** was a white solid (yield: 96%). ^{1}H NMR (300 MHz, $CDCl_3$) δ(ppm): 7.86 (d, *J* = 8.4 Hz, 2H, Ar-H), 6.88 (d, *J* = 8.4 Hz, 2H, Ar-H), 4.02 (t, *J* = 6.3 Hz, 2H, -OCH_2-), 3.88 (s, 3H, -OCH_3), 1.71-1.61 (m, 2H, -CH_2-), 1.71-1.29 (m, 6H, -CH_2-), 0.96 (t, *J* = 6.3 Hz, 3H, -CH_3).

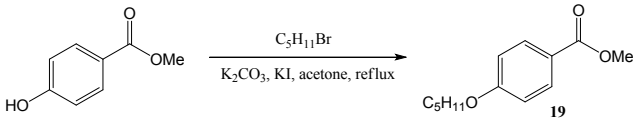
(ii) Synthesis of methyl 4-(heptyloxy)benzoate (15)



15

The benzyl 4-hydroxybenzoate (10g, 65mmol), K_2CO_3 (27.2g, 197mmol), and KI (5.5g, 33mmol) were dissolved in acetone, then 1-bromoheptane (14g, 78mmol) was slowly added in the solution. The solution reacted at 60°C for overnight, then solution was concentrated by a rotary evaporator. The mixture was extracted by DI water/ EtOAc, then organic phase was dried by $MgSO_4$ and concentrated by a rotary evaporator. The residue was purified by column chromatography on silica (*n*-hexane/EtOAc = 5:1, v/v), and the sample **15** was a white solid (yield: 95%). ^{1}H NMR (300 MHz, $CDCl_3$) δ(ppm): 7.97 (d, *J* = 8.4 Hz, 2H, Ar-H), 6.87 (d, *J* = 8.4 Hz, 2H, Ar-H), 4.02 (t, *J* = 6.3 Hz, 2H, -OCH_2-), 3.88 (s, 3H, -OCH_3), 1.71-1.61 (m, 2H, -CH_2-), 1.42-1.25 (m, 8H, -CH_2-), 0.88 (t, *J* = 6.3 Hz, 3H, -CH_3).

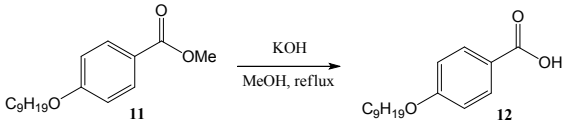
(iii) Synthesis of methyl 4-(nonyloxy)benzoate (19)



19

The benzyl 4-hydroxybenzoate (10g, 65mmol), K_2CO_3 (27.2g, 197mmol), and KI (5.5g, 33mmol) were dissolved in acetone, then 1-bromopentane (11.8g, 78mmol) was slowly added in the solution. The solution reacted at 60°C for overnight, then solution was concentrated by a rotary evaporator. The mixture was extracted by DI water/ EtOAc, then organic phase was dried by $MgSO_4$ and concentrated by a rotary evaporator. The residue was purified by column chromatography on silica (*n*-hexane/EtOAc = 5:1, v/v), and the sample **19** was a white solid (yield: 95%). ^{1}H NMR (300 MHz, $CDCl_3$) δ(ppm): 7.92 (d, *J* = 8.4 Hz, 2H, Ar-H), 6.88 (d, *J* = 8.4 Hz, 2H, Ar-H), 4.02 (m, 2H, -OCH_2-), 3.88 (s, 3H, -OCH_3), 1.71-1.61 (m, 2H, -CH_2-), 1.48-1.15 (m, 12H, -CH_2CH_3), 0.85 (t, *J* = 6.3 Hz, 3H, -CH_3).

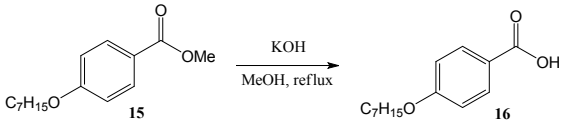
(iv) Synthesis of 4-(pentyloxy)benzoic acid (12)



11 **12**

The sample **11** (10g, 45mmol) and KOH (7.56g, 135mmol) were dissolved in MeOH, then the solution was reacted at 90°C for 24 hours. The mixture was concentrated by a rotary evaporator, then HCl aqueous solution was added to until pH=3. The sample **12** was a white solid (yield: 90%). ^{1}H NMR (300 MHz, $CDCl_3$) δ(ppm): 8.01 (d, *J* = 8.7 Hz, 2H, Ar-H), 6.98 (d, *J* = 8.7 Hz, 2H, Ar-H), 3.96 (t, *J* = 6.3 Hz, 2H, -OCH_2-), 1.70-1.61 (m, 2H, -CH_2-), 1.51-1.26 (m, 4H, -CH_2-), 0.86 (t, *J* = 6.3 Hz, 3H, -CH_3).

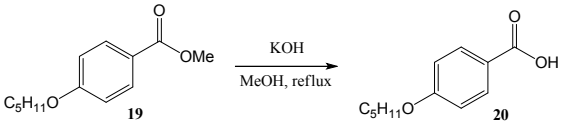
(v) Synthesis of 4-(heptyloxy)benzoic acid (16)



15 **16**

The sample **15** (10g, 40mmol) and KOH (7.56g, 135mmol) were dissolved in MeOH, then the solution was reacted at 90°C for 24 hours. The mixture was concentrated by a rotary evaporator, then HCl aqueous solution was added to until pH=3. The sample **16** was a white solid (yield: 90%). ^{1}H NMR (300 MHz, $CDCl_3$) δ(ppm): 8.04 (d, *J* = 8.7 Hz, 2H, Ar-H), 6.91 (d, *J* = 8.7 Hz, 2H, Ar-H), 4.02 (t, *J* = 6.3 Hz, 2H, -OCH_2-), 1.83-1.70 (m, 2H, -CH_2-), 1.46-1.25 (m, 8H, -CH_2-), 0.89 (t, *J* = 6.3 Hz, 3H, -CH_3). Anal. Calcd for $C_{14}H_{20}O_3$: C 71.57, H 8.70; Found: C 71.19, H 8.55.

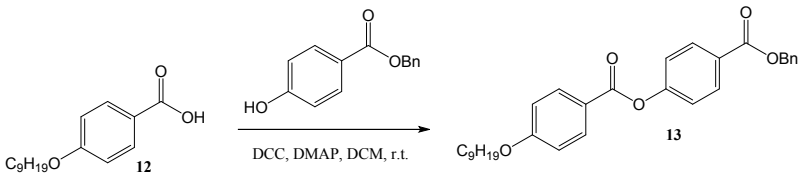
(vi) Synthesis of 4-(nonyloxy)benzoic acid (20)



19 **20**

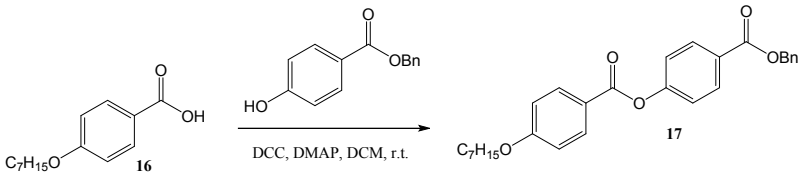
The sample **19** (10g, 36mmol) and KOH (7.56g, 135mmol) were dissolved in MeOH, then the solution was reacted at 90°C for 24 hours. The mixture was concentrated by a rotary evaporator, then HCl aqueous solution was added to until pH=3. The sample **20** was a white solid (yield: 92%). ^{1}H NMR (300 MHz, $CDCl_3$) δ(ppm): 8.12 (d, *J* = 8.7 Hz, 2H, Ar-H), 6.99 (d, *J* = 8.7 Hz, 2H, Ar-H), 4.07 (s, 2H, -OCH_2-), 1.80-1.71 (m, 2H, -CH_2-), 1.51-1.26 (m, 12H, -CH_2-), 0.86 (t, *J* = 6.6 Hz, 3H, -CH_3).

(vii) Synthesis of benzyl 4-((4-(pentyloxy)benzoyl)oxy)benzoate (13)



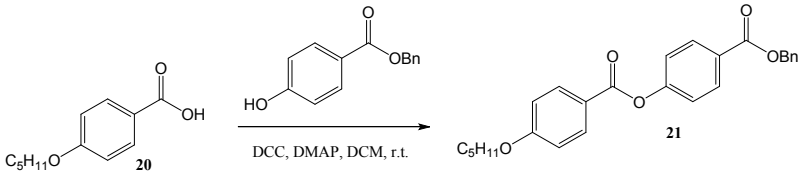
The sample **12** (10 g, 48mmol), benzyl 4-hydroxybenzoate (9.14g, 40mmol), DMAP (0.73g, 6mmol) and DCC (16.57g, 80mmol) were dissolved in dry DCM upon nitrogen system, then the solution was reacted at room temperature for 16 hours. The mixture was extracted by DI water/DCM, then the organic phase was dried by $MgSO_4$ and concentrated by a rotary evaporator. The residue was purified by column chromatography on silica (*n*-hexane/DCM = 5:1, v/v), and the sample **13** was a white solid (yield: 83%). ^{1}H NMR (300 MHz, $CDCl_3$) δ(ppm): 8.03 (m, 4H, Ar-H), 7.26 (d, *J* = 8.7 Hz, 2H, Ar-H), 7.19 (m, 5H, Ar-H), 6.94 (d, *J* = 9.0 Hz, 2H, Ar-H) , 5.36 (s, 2H, -OCH_2Ph), 3.94 (t, *J* = 6.3 Hz, 2H,-OCH-), 1.70-1.61 (m, 2H, -CH_2-), 1.33-1.29 (m, 4H, -CH_2-), 0.96 (t, *J* = 6.3 Hz, 3H, -CH_3).

(viii) Synthesis of benzyl 4-((4-(heptyloxy)benzoyl)oxy)benzoate (17)



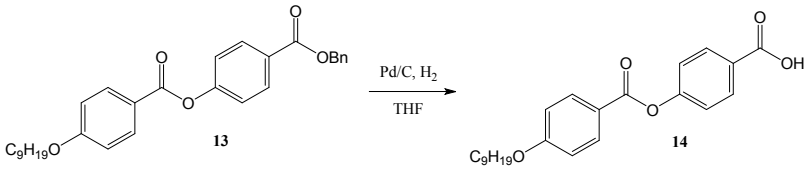
The sample **16** (10 g, 42 mmol), benzyl 4-hydroxybenzoate (9.14g, 40mmol), DMAP (0.73g, 6mmol) and DCC (16.57g, 80mmol) were dissolved in dry DCM upon nitrogen system, then the solution was reacted at room temperature for 16 hours. The mixture was extracted by DI water/DCM, then the organic phase was dried by $MgSO_4$ and concentrated by a rotary evaporator. The residue was purified by column chromatography on silica (*n*-hexane/DCM = 5:1, v/v), and the sample **17** was a white solid (yield: 87%). ^{1}H NMR (300 MHz, $CDCl_3$) δ(ppm): 8.05 (m, 4H, Ar-H), 7.45-7.30 (m, 5H, Ar-H), 7.29-7.25 (m, 2H, Ar-H), 6.94 (d, *J* = 9.0 Hz, 2H, Ar-H) , 5.36 (s, 2H, -OCH_2Ph), 4.10 (t, *J* = 6.3 Hz, 2H,-OCH-), 1.70-1.61 (m, 2H, -CH_2-), 1.41-1.25 (m, 8H, -CH_2-), 0.86 (t, *J* = 6.3 Hz, 3H, -CH_3).

(ix) Synthesis of benzyl 4-((4-(nonyloxy)benzoyl)oxy)benzoate (21)



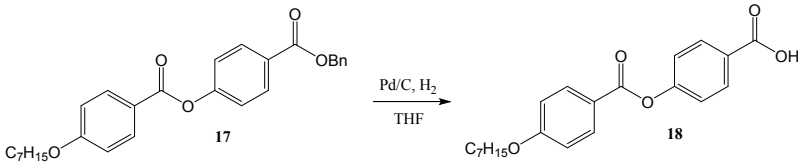
The sample **20** (10g, 37.8mmol), benzyl 4-hydroxybenzoate (9.14g, 40mmol), DMAP (0.73g, 6mmol) and DCC (16.57g, 80mmol) were dissolved in dry DCM upon nitrogen system, then the solution was reacted at room temperature for 16 hours. The mixture was extracted by DI water/DCM, then the organic phase was dried by $MgSO_4$ and concentrated by a rotary evaporator. The residue was purified by column chromatography on silica (*n*-hexane/DCM = 5:1, v/v), and the sample **21** was a white solid (yield: 82%). ^{1}H NMR (300 MHz, $CDCl_3$) δ(ppm): 8.15 (m, 4H, Ar-H), 7.45-7.31 (m, 5H, Ar-H), 7.32-7.25 (m, 2H, Ar-H), 6.97 (d, *J* = 8.4 Hz, 2H, Ar-H) , 5.37 (s, 2H, -OCH_2Ph), 4.10 (t, *J* = 6.3 Hz, 2H,-OCH-), 1.73-1.61 (m, 2H, -CH_2-), 1.50-1.25 (m, 12H, -CH_2-), 0.86 (t, *J* = 6.3 Hz, 3H, -CH_3).

(x) Synthesis of 4-((4-(pentyloxy)benzoyl)oxy)benzoic acid (14)



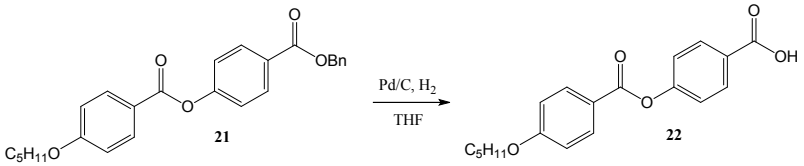
The sample **13** (10g, 20 mmol) and 15% Pd/C (1.5 g) were dissolved in dry THF, then the solution was reacted at room temperature for overnight upon hydrogen system. The mixture was filtrated by diatomaceous followed by THF cleaning and concentrated by a rotary evaporator. The residue was recrystallization by *n*-hexane/DCM, and the sample **14** was a white solid (yield: 95%). ^{1}H NMR (300 MHz, $CDCl_3$) δ(ppm): 8.20 (d, *J* = 8.4 Hz, 2H, Ar-H), 8.04 (d, *J* = 8.7 Hz, 2H, Ar-H), 7.35-7.15 (m, 2H, Ar-H), 6.90 (d, *J* = 8.7 Hz, 2H, Ar-H), 3.94 (t, *J* = 6.6 Hz, 2H,-OCH-), 1.70-1.61 (m, 2H, -CH_2-), 1.33-1.25 (m, 4H, -CH_2-), 0.86 (t, *J* = 6.6 Hz, 3H, -CH_3).

(xi) Synthesis of 4-(4-(heptyloxy)benzoyloxy)benzoic acid (18)



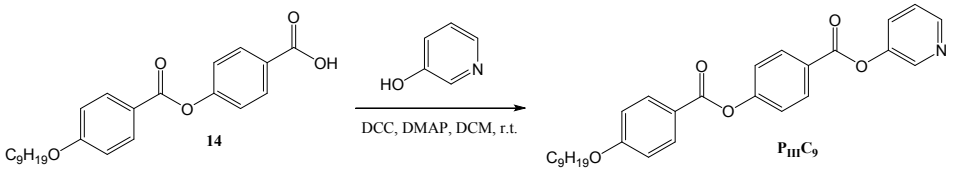
The sample **17** (10 g, 21mmol) and 15% Pd/C (1.5 g) were dissolved in dry THF, then the solution was reacted at room temperature for overnight upon hydrogen system. The mixture was filtrated by diatomaceous followed by THF cleaning and concentrated by a rotary evaporator. The residue was recrystallization by *n*-hexane/DCM, and the sample **18** was a white solid (yield: 95%). ^{1}H NMR (300 MHz, $CDCl_3$) δ(ppm): 8.14 (m, 4H, Ar-H), 7.32-7.25 (m, 2H, Ar-H), 6.94 (d, J = 8.7 Hz, 2H, Ar-H), 4.04 (t, J = 6.6 Hz, 2H,-OCH-), 1.81-1.76 (m, 2H, -CH_2-), 1.46-1.24 (m, 8H, -CH_2-), 0.88 (t, J = 6.6 Hz, 3H, -CH_3). Anal. Calcd for $C_{21}H_{24}O_5$: C 70.77, H 6.79; Found: C 70.61, H 6.94.

(xii) Synthesis of 4-((4-(nonyloxy)benzoyl)oxy)benzoic acid (22)



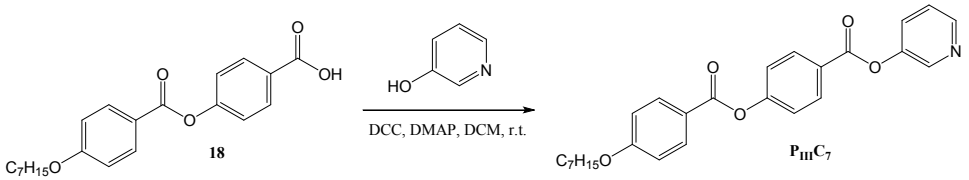
The sample **21** (10 g, 22mmol) and 15% Pd/C (1.5 g) were dissolved in dry THF, then the solution was reacted at room temperature for overnight upon hydrogen system. The mixture was filtrated by diatomaceous followed by THF cleaning and concentrated by a rotary evaporator. The residue was recrystallization by *n*-hexane/DCM, and the sample **22** was a white solid (yield: 96%). ^{1}H NMR (300 MHz, $CDCl_3$) δ(ppm): 8.05 (m, 4H, Ar-H), 7.39-7.15 (m, 2H, Ar-H), 6.90 (d, J = 8.7 Hz, 2H, Ar-H), 4.08 (t, J = 6.6 Hz, 2H, -OCH-), 1.70-1.61 (m, 2H, -CH_2-), 1.41-1.25 (m, 12H, -CH_2-), 0.85 (t, J = 6.6 Hz, 3H, -CH_3).

(xv) Synthesis of pyridin-3-yl 4-((4-(nonyloxy)benzoyl)oxy)benzoate ($P_{III}C_9$)



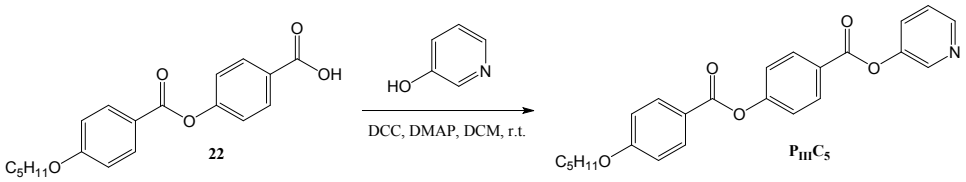
The sample **14** (4.58g, 11.9mmol), 3-Hydroxypyridine(1.13 g, 11.9mmol), DMAP (0.18g, 1.5mmol) and DCC (4.11g, 19.8mmol) were dissolved in dry DCM upon nitrogen system, then the solution was reacted at room temperature for 16 hours. The mixture was extracted by DI water/DCM, then the organic phase was dried by $MgSO_4$ and concentrated by a rotary evaporator. The residue was purified by column chromatography on silica (*n*-hexane/DCM = 5:1, v/v), and the product **$P_{III}C_5$** was a white solid (yield: 69%). ^{1}H NMR (300 MHz, $CDCl_3$) δ(ppm): 8.56 (m, 2H, Ar-H), 8.29 (d, J = 9.0 Hz, 2H, Ar-H), 8.15 (d, J = 9.0 Hz, 2H, Ar-H), 7.64 (m, 1H, Ar-H), 7.40-7.25 (m, 3H, Ar-H), 6.98 (d, J = 9.0 Hz, 2H, Ar-H), 4.05 (t, J = 6.5 Hz, 2H, -OCH_2-), 1.85-1.78 (m, 2H, -CH_2-), 1.548-1.22 (m, 12H, -CH_2-), 0.90 (t, J = 6.3 Hz, 3H, -CH_3). Anal. Calcd for $C_{28}H_{31}NO_5$: C 72.86, H 6.77, N 3.03, Found: C 72.85, H 6.86, N 3.22.

(xiv) Synthesis of pyridin-3-yl 4-((4-(heptyloxy)benzoyl)oxy)benzoate ($P_{III}C_7$)



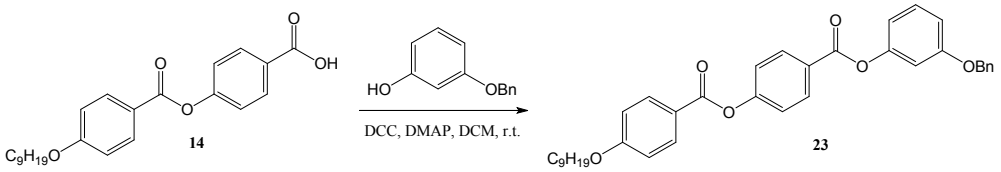
The sample **18** (4.24g, 11.9mmol), 3-Hydroxypyridine(1.13 g, 11.9mmol), DMAP (0.18g, 1.5mmol) and DCC (4.11g, 19.8mmol) were dissolved in dry DCM upon nitrogen system, then the solution was reacted at room temperature for 16 hours. The mixture was extracted by DI water/DCM, then the organic phase was dried by $MgSO_4$ and concentrated by a rotary evaporator. The residue was purified by column chromatography on silica (*n*-hexane/DCM = 5:1, v/v), and the product **$P_{III}C_5$** was a white solid (yield: 77%). ^{1}H NMR (300 MHz, $CDCl_3$) δ(ppm): 8.57 (m, 2H, Ar-H), 8.28 (d, J = 9.0 Hz, 2H, Ar-H), 8.16 (d, J = 9.0 Hz, 2H, Ar-H), 7.64 (m, 1H, Ar-H), 7.40-7.26 (m, 3H, Ar-H), 6.98 (d, J = 8.7 Hz, 2H, Ar-H), 4.06 (t, J = 6.6 Hz, 2H, -OCH_2-), 1.90-1.82 (m, 2H, -CH_2-), 1.48-1.33 (m, 8H, -CH_2-), 0.91 (t, J = 7.0 Hz, 3H, -CH_3). Anal. Calcd for $C_{26}H_{27}NO_5$: C 72.04, H 6.28, N 3.23, Found: C 71.96, H 6.46, N 3.52.

(xiii) Synthesis of pyridin-3-yl 4-((4-(pentyloxy)benzoyl)oxy)benzoate ($P_{III}C_5$)



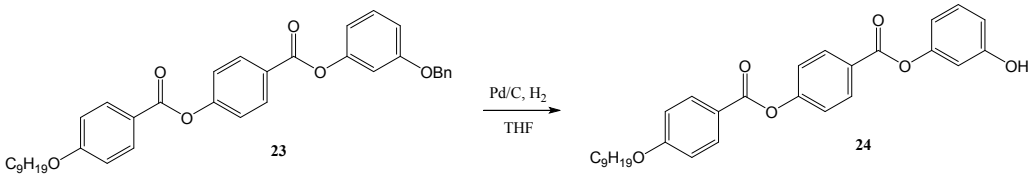
The sample **22** (3.9g, 11.9mmol), 3-Hydroxypyridine(1.13 g, 11.9mmol), DMAP (0.18g, 1.5mmol) and DCC (4.11g, 19.8mmol) were dissolved in dry DCM upon nitrogen system, then the solution was reacted at room temperature for 16 hours. The mixture was extracted by DI water/DCM, then the organic phase was dried by $MgSO_4$ and concentrated by a rotary evaporator. The residue was purified by column chromatography on silica (*n*-hexane/DCM = 5:1, v/v), and the product **$P_{III}C_5$** was a white solid (yield: 82%). ^{1}H NMR (300 MHz, $CDCl_3$) δ(ppm): 8.55 (m, 2H, Ar-H), 8.26 (d, *J* = 9.0 Hz, 2H, Ar-H), 8.15 (d, *J* = 9.0Hz, 2H, Ar-H), 7.62 (m, 1H, Ar-H), 7.40-7.26 (m, 3H, Ar-H), 6.96 (d, *J* = 9.0 Hz, 2H, Ar-H), 4.03 (t, *J* = 6.5 Hz, 2H, -OCH_2-), 1.77-1.68 (m, 2H, -CH_2-), 1.48-1.33 (m, 4H, -CH_2-), 0.93 (t, *J* = 7.1 Hz, 3H, -CH_3). Anal. Calcd for $C_{24}H_{23}NO_5$: C 71.10, H 5.72, N 3.45; Found: C 71.07, H 6.11, N 3.62.

(xvi) Synthesis of 4-((3-(benzyloxy)phenoxy)carbonyl)phenyl 4-(nonyloxy)benzoate (23)



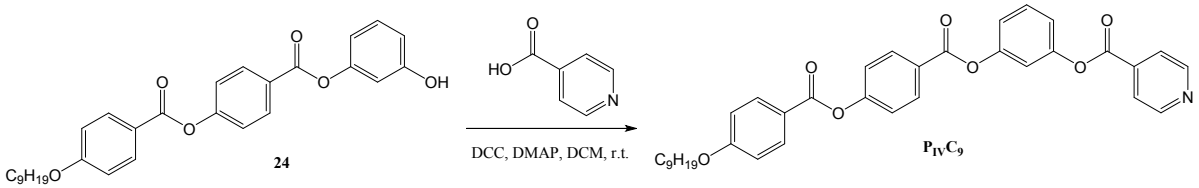
The sample **14** (7.68g, 20mmol), benzyl 3-hydroxybenzoate (5g, 25mmol), DMAP (0.385g, 3.15mmol) and DCC (8.654g, 41.67mmol) were dissolved in dry DCM upon nitrogen system, then the solution was reacted at room temperature for 16 hours. The mixture was extracted by DI water/DCM, then the organic phase was dried by $MgSO_4$ and concentrated by a rotary evaporator. The residue was purified by column chromatography on silica (*n*-hexane/DCM = 5:1, v/v), and the sample **23** was a white solid (yield: 84%). ^{1}H NMR (300 MHz, $CDCl_3$) δ(ppm): 8.21 (d, *J* = 8.4 Hz, 2H, Ar-H), 8.03 (d, *J* = 8.4 Hz, 2H, Ar-H), 7.30-7.22 (m, 8H, Ar-H), 6.83-6.66 (m, 5H, Ar-H), 5.12 (s, 2H, -OCH_2Ph), 3.94 (t, *J* = 6.3 Hz, 2H, -OCH_2-), 1.69 (m, 2H, -CH_2-), 1.43-1.26 (m, 12H, -CH_2-), 0.96 (t, *J* = 6.3 Hz, 3H, -CH_3).

(xvii) Synthesis of 4-((3-hydroxyphenoxy)carbonyl)phenyl 4-(nonyloxy)benzoate (24)

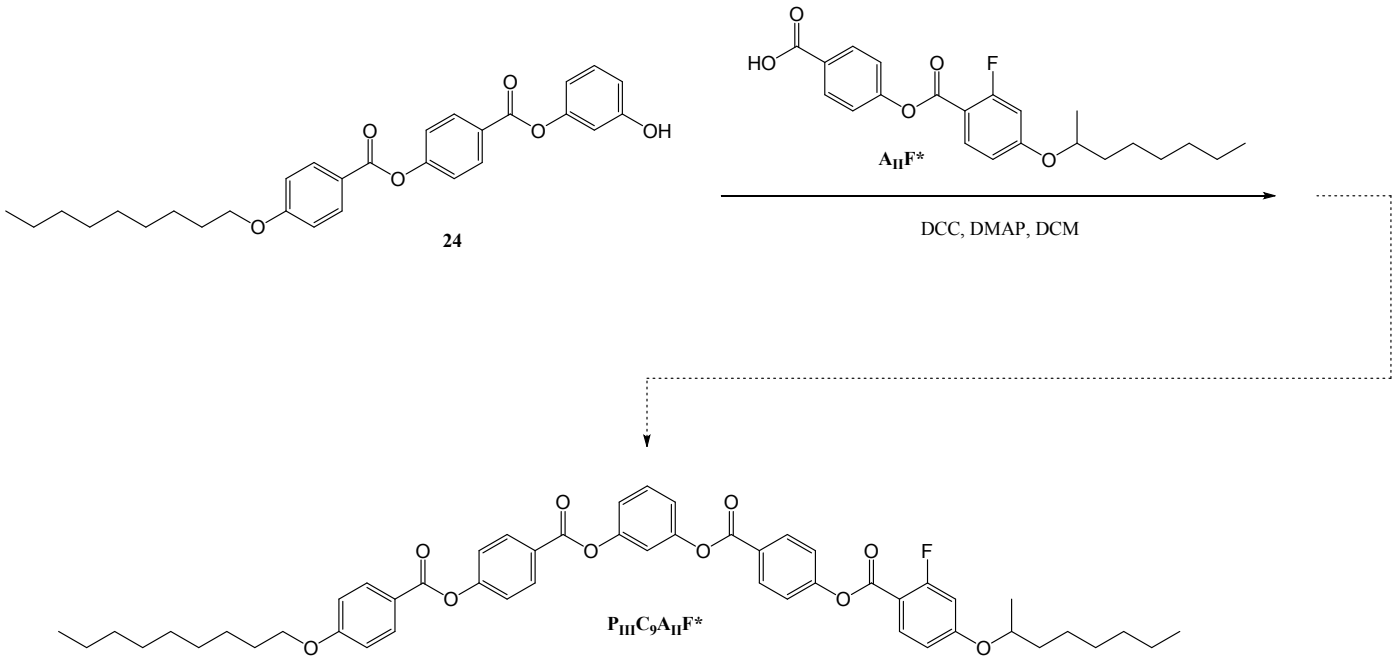


The sample **23** (10g, 17.7mmol) and 15% Pd/C (1.5 g) were dissolved in dry THF, then the solution was reacted at room temperature for overnight upon hydrogen system. The mixture was filtrated by diatomaceous followed by THF cleaning and concentrated by a rotary evaporator. The residue was recrystallization by *n*-hexane/DCM, and the sample **24** was a white solid (yield: 89%). ^{1}H NMR (300 MHz, $CDCl_3$) δ(ppm): 8.21 (d, *J* = 8.7 Hz, 2H, Ar-H), 8.03 (d, *J* = 8.7 Hz, 2H, Ar-H), 7.30-7.21 (m, 5H, Ar-H), 6.92-6.62 (m, 3H, Ar-H), 5.00 (s, 1H, -OCH_2Ph), 3.94 (t, *J* = 6.6 Hz, 2H, -OCH_2-), 1.69 (m, 2H, -CH_2-), 1.44-1.26 (m, 4H, -CH_2-), 0.96 (t, *J* = 6.6 Hz, 3H, -CH_3).

(xviii) Synthesis of 3-((4-((4-(nonyloxy)benzoyl)oxy)benzoyl)oxy)phenyl isonicotinate ($P_{IV}C_9$)



The sample **24** (5.67g, 11.9mmol), isonicotinic acid (1.46g, 11.9mmol), DMAP (0.18g, 1.5mmol) and DCC (4.11g, 19.8mmol) were dissolved in dry DCM upon nitrogen system, then the solution was reacted at room temperature for 16 hours. The mixture was extracted by DI water/DCM, then the organic phase was dried by $MgSO_4$ and concentrated by a rotary evaporator. The residue was purified by column chromatography on silica (*n*-hexane/DCM = 5:1, v/v), and the product **$P_{IV}C_9$** was a white solid (yield: 72%). ^{1}H NMR (300 MHz, $CDCl_3$) δ(ppm): 8.86 (m, 2H, Ar-H), 8.26 (d, *J* = 8.7 Hz, 2H, Ar-H), 8.13 (d, *J* = 9.0 Hz, 2H, Ar-H), 8.00 (d, *J* = 8.7 Hz, 2H, Ar-H), 7.64 (m, 1H, Ar-H), 7.37-7.34 (m, 2H, Ar-H), 7.24-7.19 (m, 3H, Ar-H), 6.97 (d, *J* = 9.3 Hz, 2H, Ar-H), 4.03 (t, *J* = 6.5 Hz, 2H, -OCH_2-), 1.42-1.20 (m, 14H, -CH_2-), 0.87 (t, *J* = 6.3 Hz, 3H, -CH_3). Anal. Calcd for $C_{35}H_{35}NO_7$: C 72.27, H 6.07, N 2.41, Found: C 71.64, H 6.32, N 2.56.



Scheme S3. Synthesis of covalent-bonded bent-core molecule $P_{III}C_9A_{II}F^*$.

Synthesis of (R)-4-((3-((4-((4-(nonyloxy)benzoyl)oxy)benzoyl)oxy)phenoxy)carbonyl)phenyl 2-fluoro-4-(octan-2-yloxy)benzoate ($P_{III}C_9A_{II}F^*$)
The sample **24** (5.67 g, 11.9 mmol), product $A_{II}F^*$ (4.62g, 11.9mmol), DMAP (0.18g, 1.5mmol) and DCC (4.11g, 19.8mmol) were dissolved in dry DCM, Then the solution reacted at room temperature for 16 hours upon nitrogen system. The mixture was extracted by deionized water/DCM, then organic phase was dried by $MgSO_4$ and concentrated by a rotary evaporator. The residue was purified by column chromatography on silica (*n*-hexane/DCM = 5:1, v/v), and the product $P_{III}C_9A_{II}F^*$ as a white solid (yield: 80%). ^{1}H NMR (300 MHz, $CDCl_3$) δ(ppm): 8.25 (d, *J* = 8.4 Hz, 4H, Ar-H), 8.13 (d, *J* = 8.7 Hz, 2H, Ar-H), 7.99 (t, *J* = 8.7 Hz, 1H, Ar-H), 7.46 (t, *J* = 8.4 Hz, 1H, Ar-H), 7.36 (d, *J* = 8.4 Hz, 4H, Ar-H), 7.18 (m, 3H, Ar-H), 7.13 (d, *J* = 8.7 Hz, 2H, Ar-H), 6.75-6.64 (m, 2H, Ar-H), 4.43 (m, 1H, -OCH-), 4.03 (t, *J* = 6.5 Hz, 2H, $-OCH_2-$), 1.49-1.23 (m, 26H, $-CH_2-$), 0.87 (m, 6H, $-CH_3$). Anal. Calcd for $C_{51}H_{55}FO_{10}$: C 72.32, H 6.55, Found: C 73.19, H 6.97.

Additional information

The additional information (phase transition temperatures °C) of H-bonded bent-core complexes **$P_{IV}C_9/A_IF^*$** was compared with the H-bonded bent-core complex **$P_{III}C_9/A_{II}F^*$** with different H-donors **A_IF^*** and **$A_{II}F^*$**, respectively.

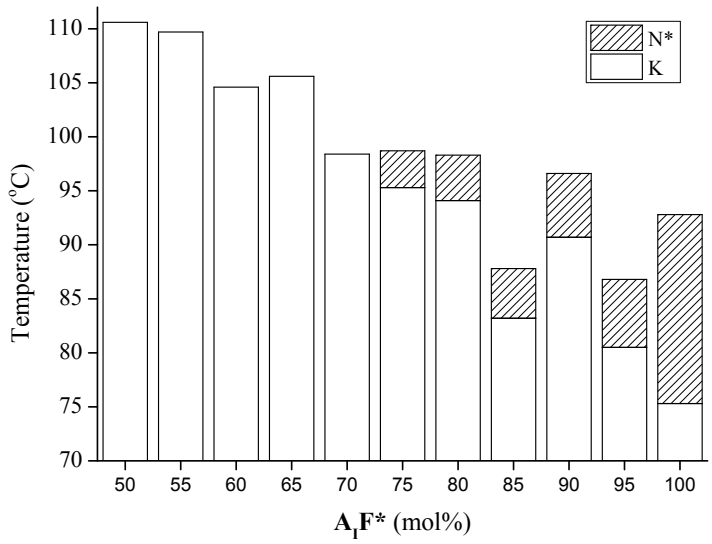


Fig. S1 Binary phase diagram of H-bonded bent-core complexes **$P_{IV}C_9/A_IF^*$** with various molar ratios of H-donor **A_IF^***.
(N*: chiral nematic phase; K: crystalline phase.)

The additional information (phase transition temperatures °C) of H-bonded bent-core complexes **$P_{III}C_9/A_{II}^*$** was compared with the H-bonded bent-core complex **$P_{III}C_9/A_{II}F^*$** with different H-donors **A_{II}^*** and **$A_{II}F^*$**, respectively.

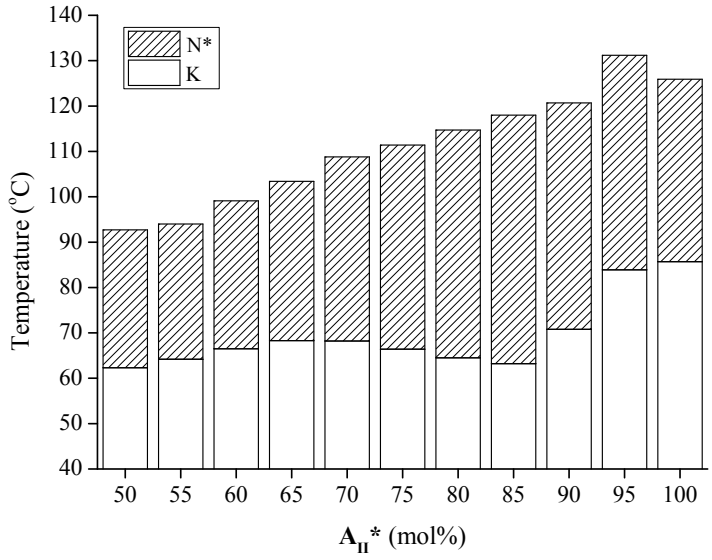


Fig. S2 Binary phase diagram of H-bonded bent-core complexes **$P_{III}C_9/A_{II}^*$** with various molar ratios of H-donor **A_{II}^***.
(N*: chiral nematic phase; K: crystalline phase.)

Identification of molecular structure

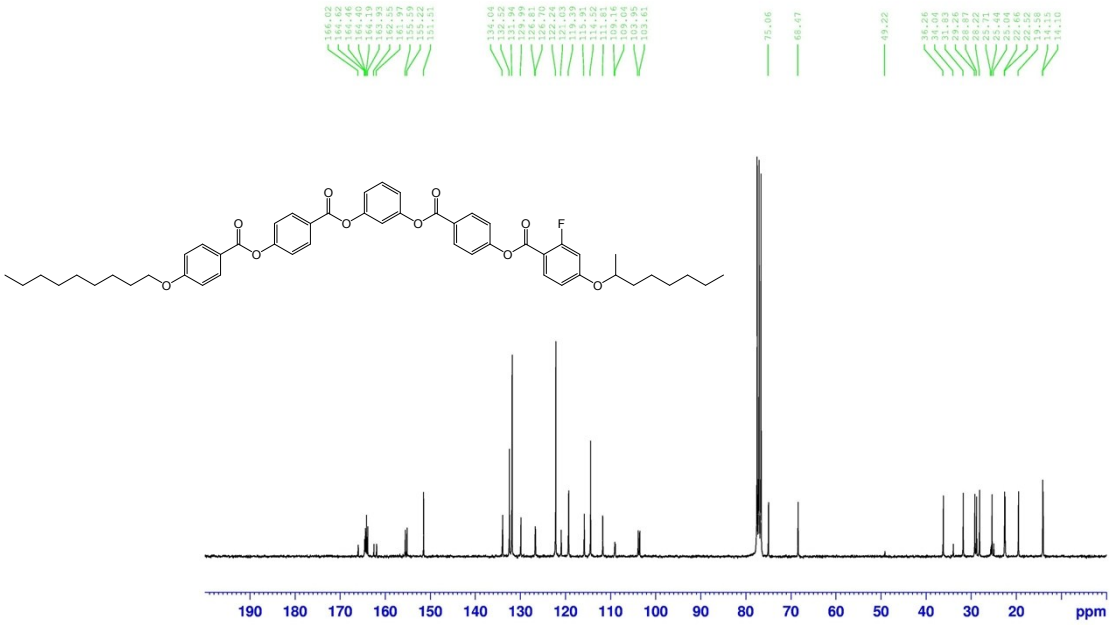


Fig. S3 ^{13}C NMR spectrum of $\mathbf{P_{III}C_9A_{II}F^*}$.

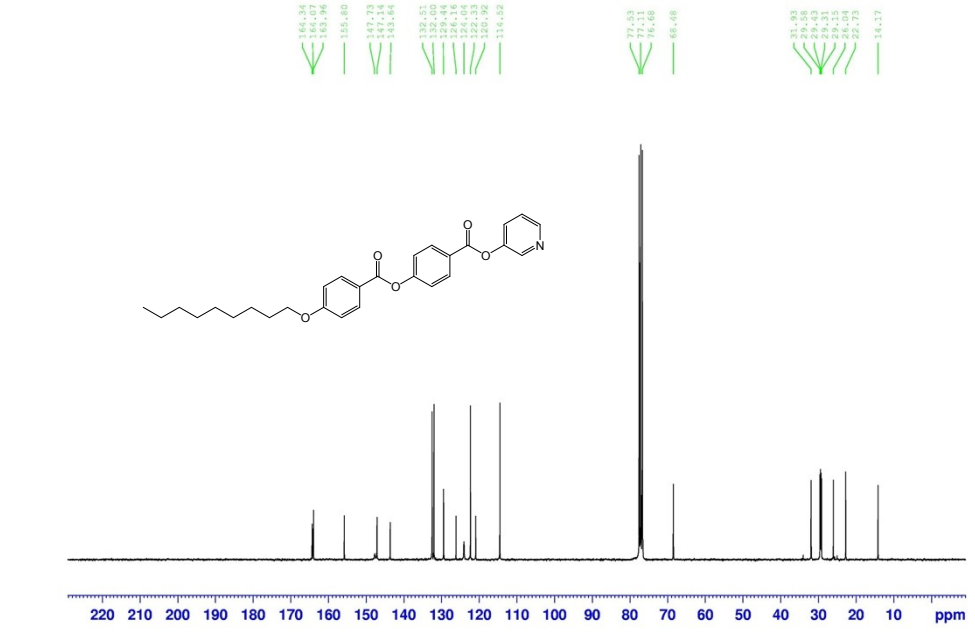


Fig. S4 ^{13}C NMR spectrum of $\mathbf{P_{III}C9}$.

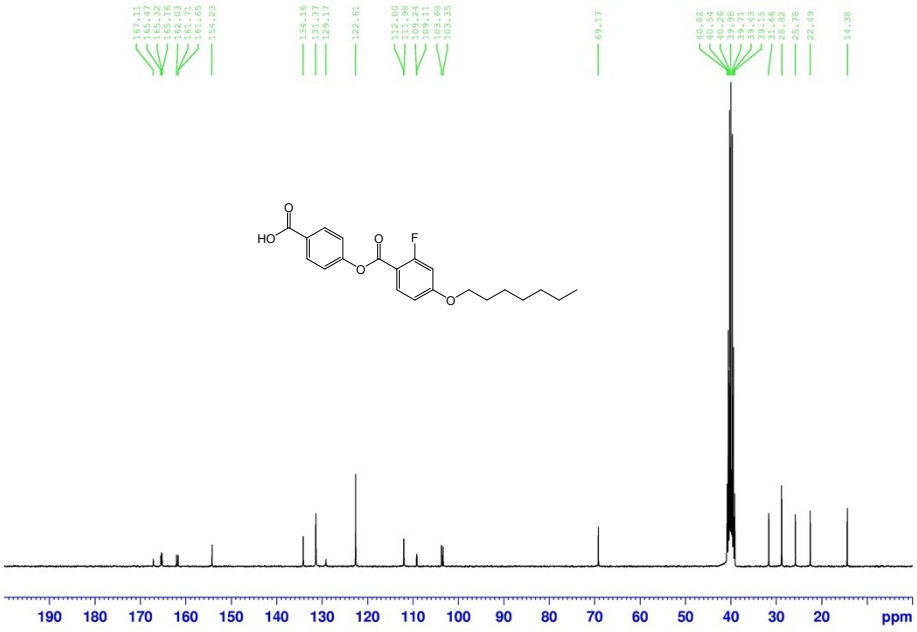


Fig. S5 ^{13}C NMR spectrum of $\mathbf{A_{II}F}$.

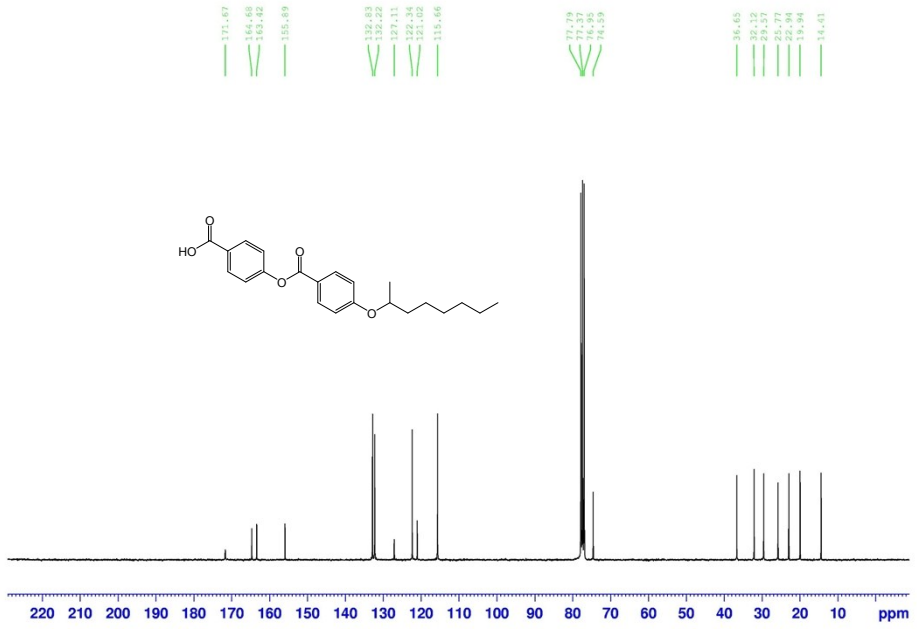


Fig. S6 ^{13}C NMR spectrum of $\mathbf{A_{II}}$*.