Supporting information

Lateral fluoro-substitution and chiral effects on supramolecular liquid crystals containing rod-like and H-bonded bent-core mesogens

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Table S1 Phase transition temperatures[a,b] (°C) and enthalpies (J g^{-1}) of supramolecular complexes $\mathbf{P_{III}}$*/$\mathbf{A_{II}}$* with various molar ratios of H-donor $\mathbf{A_{II}}$*

	H-donor $\mathbf{A_{II}}$* (mol%)	Phase transition temperatures (°C) [enthalpies (J g^{-1})]	ΔT_{BPI} (°C)	ΔT_{N*} (°C)	ΔT_{SmA} (°C)
$\mathbf{P_{III}}$*/$\mathbf{A_{II}}$*	50	Iso 151.2 [0.45] BP 137.5^{C} N* 106.6 [2.02] SmA 68.2 [0.99] K	13.7	33.8	38.4
$\mathbf{P_{III}}$*/$\mathbf{A_{II}}$*	55	Iso 152.2 [0.45] BP 138.7^{C} N* 103.8 [2.02] SmA 70.2 [0.99] K	13.5	34.9	33.6
$\mathbf{P_{III}}$*/$\mathbf{A_{II}}$*	60	Iso 149.9 [0.45] BP 142.5^{C} N* 105.6 [2.02] SmA 75.8 [0.99] K	7.4	36.9	29.8
$\mathbf{P_{III}}$*/$\mathbf{A_{II}}$*	65	Iso 145.8 [0.45] BP 142.6^{C} N* 98.7 [2.02] SmA 73.4 [0.99] K	3.2	43.9	25.3
$\mathbf{P_{III}}$*/$\mathbf{A_{II}}$*	70	Iso 146.9 [0.45] N* 99.8 [2.02] SmA 78.1 [0.99] K		47.1	21.7
$\mathbf{P_{III}}$*/$\mathbf{A_{II}}$*	75	Iso 151.4 [0.45] N* 99.9 [2.02] SmA 82.5 [0.99] K		51.5	17.4

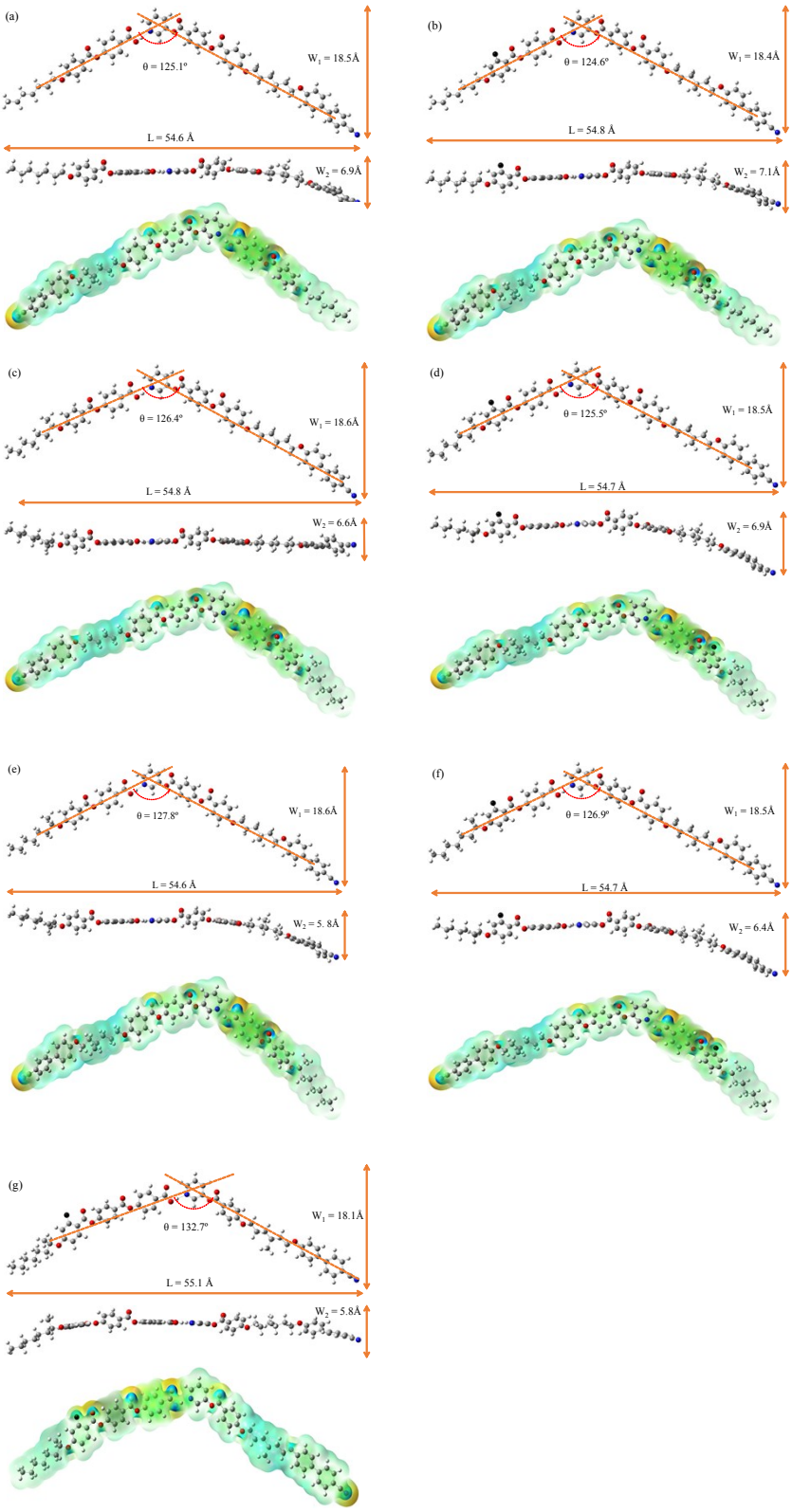


Fig. S1 Molecular models (top photos) and molecular electrostatic potentials mapped on the electron densities (bottom photos) of the lowest energy structures for supramolecular diads (a) $\mathbf{P_{III}}$*/$\mathbf{A_{II}}$, (b) $\mathbf{P_{III}}$*/$\mathbf{A_{II}}$**F**, (c) $\mathbf{P_{III}}$/$\mathbf{A_{II}}$*, (d) $\mathbf{P_{III}}$/$\mathbf{A_{II}}$**F***, (e) $\mathbf{P_{III}}$*/$\mathbf{A_{II}}$*, (f) $\mathbf{P_{III}}$*/$\mathbf{A_{II}}$**F*** and (g) $\mathbf{P_{II}}$*/$\mathbf{A_{III}}$**F***.

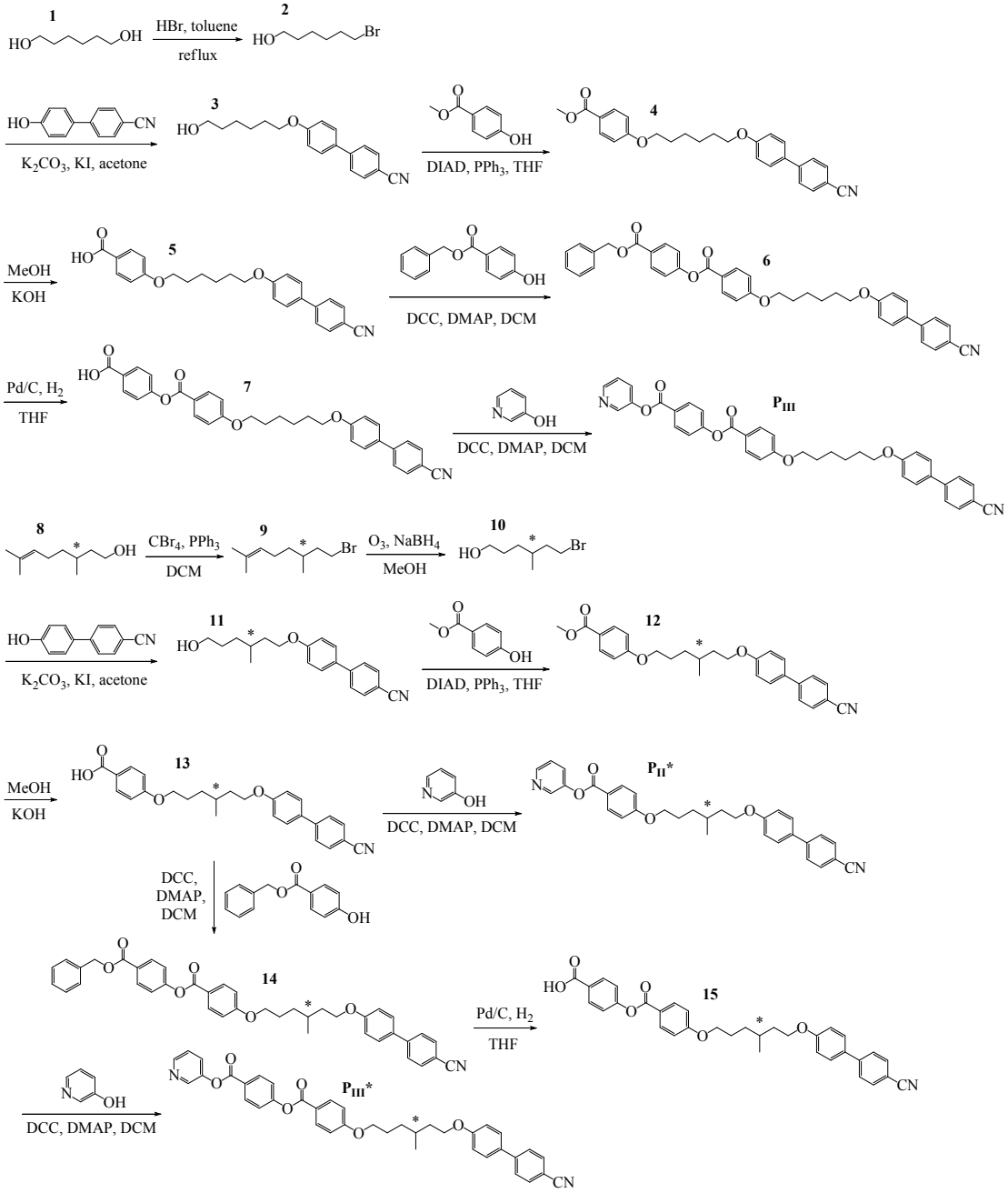
Table S2 XRD data of supramolecular diads **C**/**D**

	Theoretical molecular length (Å)	*d*-spacing (Å)	Mesophase	Measured temperature (°C) upon cooling
P_{III}*/A_{II}	54.6	61.2	SmA	69
P_{III}*/A_{II}F	54.8	60.9	SmA	67
P_{III}/A_{II}*	54.8	62.3	SmA	77
P_{III}/A_{II}F*	54.9	61.8	SmA	81
P_{III}*/A_{II}*	54.6	59.4	SmA	87
P_{III}*/A_{II}F*	54.7	58.7	SmA	74
P_{II}*/A_{III}F*	55.1	57.6	SmA	99

*Theoretical molecular lengths were calculated by molecular simulation; the *d*-spacing values were obtained by X-ray diffraction (XRD); the measured temperatures were controlled within the smectic A (SmA) phase observed by polarizing optical microscopy (POM).

Additional details of synthetic procedures

Synthesis of H-accepters **C** (i.e., $\mathbf{P_{III}}$, $\mathbf{P_{III}}$* and $\mathbf{P_{II}}$*) along with H-donors **D** (i.e., $\mathbf{A_{II}}$, $\mathbf{A_{II}F}$, $\mathbf{A_{II}}$*, $\mathbf{A_{II}F}$* and $\mathbf{A_{III}F}$*) are shown in Schemes S1 and S2, respectively.



Scheme S1 Synthesis of H-accepters **C** (i.e., $\mathbf{P_{III}}$, $\mathbf{P_{III}}$* and $\mathbf{P_{II}}$*).

(i) Synthesis of compound 2. Hexane-1,6-diol (compound **1**) (10g, 85mmole) was dissolved in 500ml toluene at reflux temperature. Then, HBr (7.2g, 89mmole) was slowly added in toluene solution, and reacted overnight. After reaction, the solution was concentrated using a rotary evaporator. The residue was purified by column chromatography on silica (*n*-hexane). The final product as a light yellow oil has the yield of 90%. ^{1}H NMR (300 MHz, $CDCl_3$) δ(ppm): 3.72 (t, J = 5.8 Hz, 2H, -OCH_2-), 3.51 (t, J = 6.1 Hz, 2H, -OCH_2-), 1.81-1.42 (m, 8H, -CH_2-).

(ii) Synthesis of compound 3. 4-Cyano-4'-hydroxybiphenyl (5g, 25.6mmole), K2CO3 (10.64g, 76.8mmole) and KI (3.25g,

12.8mmole) were dissolved in 250 ml acetone. Then, compound **2** (6g, 30.72mmole) was slowly added in acetone solution and reacted overnight at 60°C. After reaction, the solution was concentrated using a rotary evaporator. The residue was purified by column chromatography on silica (*n*-hexane). The final product as a white solid has the yield of 95%. ^{1}H NMR (300 MHz, $CDCl_3$) δ(ppm): 7.82 (t, *J* = 5.4 Hz, 4H, Ar-H), 7.61 (d, *J* = 8.3 Hz, 2H, Ar-H), 7.10 (d, *J* = 8.2 Hz, 2H, Ar-H), 4.12 (t, *J* = 6.2 Hz, 2H, -OCH_2), 3.63 (t, *J* = 5.8 Hz, 2H, -OCH_2), 1.82-1.41 (m, 8H, -CH_2).

(iii) Synthesis of compound 4. Compound **3** (5g, 16.9mmole) and PPh_3 (6.65g, 25.3mmol) were dissolved in dry THF. Then added methyl 4-hydroxybenzoate (3.15g, 20.3mmol) and DIAD (5.1g, 25.3mmol) in THF solution. After reaction, the solution was concentrated using a rotary evaporator. The residue was purified by column chromatography on silica (*n*-hexane/DCM = 5:1, v/v). The final product as a white solid has the yield of 80%. ^{1}H NMR (300 MHz, $CDCl_3$) δ(ppm): 7.83 (s, 4H, Ar-H), 7.62 (d, *J* = 8.7 Hz, 2H, Ar-H), 7.12 (d, *J* = 8.2 Hz, 2H, Ar-H), 7.03 (d, *J* = 7.9 Hz, 2H, Ar-H), 6.83 (d, *J* = 7.8 Hz, 2H, Ar-H), 4.06 (t, *J* = 6.5 Hz, 4H, -OCH2-), 3.84 (s, 3H, -OCH_2-), 1.76 (m, 4H, -CH_2-), 1.42 (d, *J* = 7.8 Hz, 4H, -CH_2-).

(iv) Synthesis of compound 5. Compound **4** (5g, 11.6mmol) and KOH (1.96g, 34.9mmol) were dissolved in MeOH solvent. The mixed solution was reacted for 24 hours at 90°C. After reaction, the solution was concentrated using a rotary evaporator, then added HCl aqueous solution until pH=3. The final product as a white solid (yield: 92%). ^{1}H NMR (300 MHz, $CDCl_3$) δ(ppm): 8.15 (d, *J* = 7.7 Hz, 2H, Ar-H), 7.83 (s, 4H, Ar-H), 7.67 (d, *J* = 7.5 Hz, 2H, Ar-H), 7.20 (d, *J* = 7.5 Hz, 2H, Ar-H), 7.02 (d, *J* = 7.6 Hz, 2H, Ar-H), 4.11 (t, *J* = 6.0 Hz, 4H, -OCH_2-), 1.71 (m, 4H, -CH_2-), 1.35 (d, *J* = 7.8 Hz, 4H, -CH_2-).

(v) Synthesis of compound 6. Compound **5** (5g, 12mmole), benzyl 4-hydroxybenzoate (3.3g, 14.4mmol) and DMAP (0.15 g, 1.2mmol) were dissolved in dry DCM upon nitrogen system, then added DCC (7.5g, 36mmol). The solution was reacted for 16 hours at room temperature (30°C). After reaction, the solution first through filtration followed by DCM washing. The solution was extracted with deionized water/DCM, then the organic phase of solution was obtained The organic phase was dried by $MgSO_4$ and concentrated using a rotary evaporator. The residue was purified by column chromatography on silica (*n*-hexane/DCM = 5:1, v/v). The final product as a white solid has the yield of yield: 85%. ^{1}H NMR (300 MHz, $CDCl_3$) δ(ppm): 8.15 (d, *J* = 7.9 Hz, 2H, Ar-H), 8.15 (d, *J* = 8.1 Hz, 2H, Ar-H), 8.09 (d, *J* = 7.8 Hz, 2H, Ar-H), 7.84 (s, 4H, Ar-H), 7.62 (d, *J* = 7.9 Hz, 2H, Ar-H), 7.45 (d, *J* = 7.6 Hz, 2H, Ar-H), 7.42-7.30 (m, 5H, Ar-H), 7.14 (d, *J* = 8.0 Hz, 2H, Ar-H), 7.05 (d, *J* = 7.8 Hz, 2H, Ar-H), 5.25 (s, 2H, -OCH_2Ph), 4.12 (t, *J* = 5.8 Hz, 4H, -OCH_2-), 1.72 (m, 5H, -CH_2-), 1.23 (m, 4H, -CH_2-).

(vi) Synthesis of compound 7. Compound **6** (5g, 8mmole) and 15% Pd/C (0.75g) were dissolved in dry THF. The mixed solution was reacted overnight at room temperature in hydrogen system. After reaction, the solution was first filtrated and followed by THF washing, then was concentrated using a rotary evaporator. The residue was recrystallization by *n*-hexane/DCM. The final product as a white solid has the yield of yield: 88%. ^{1}H NMR (300 MHz, $CDCl_3$) δ(ppm): 8.30 (d, *J* = 7.7 Hz, 2H, Ar-H), 8.15 (d, *J* = 8.2 Hz, 2H, Ar-H), 7.85 (s, 4H, Ar-H), 7.65 (d, *J* = 7.4 Hz, 2H, Ar-H), 7.54 (d, *J* = 7.9 Hz, 2H, Ar-H), 7.15 (d, *J* = 7.5 Hz, 2H, Ar-H), 7.02 (d, *J* = 8.2 Hz, 2H, Ar-H), 4.10 (t, *J* = 5.8 Hz, 4H, -OCH2-), 1.73 (m, 4H, -CH2-), 1.21 (m, 4H, -CH2-).

(vii) Synthesis of H-accepter P_{III}. Compound **7** (2g, 3.7mmole), pyridin-3-ol (0.415g, 4.48mmol) and DMAP (0.048g, 0.37mmol) were dissolved in dry DCM upon nitrogen system, then DCC (2.27g, 11.1mmol) was added. The solution was reacted for 16 hours at room temperature. After reaction, the solution first through filtration followed by DCM washing. The solution was extracted with deionized water/DCM, then the organic phase of solution was obtained The organic phase was dried by $MgSO_4$ and concentrated using a rotary evaporator. The residue was purified by column chromatography on silica (*n*-hexane/DCM = 5:3, v/v). The final product as a white solid has the yield of 60%. FTIR (KBr, ν_{max}/cm^{-1}): 2936, 2851 (-CH_2-), 2226 (C-N=C in pyridine), 1732 (O-C=O), 1605 (-CN), 1510, 1493, 1472 (C=C in Ar), 1201 (C-O-C).

(viii) Synthesis of compound 9. (S)-(-)-β-Citronellol (sample **8**) (5g, 32mmole) and CBr_4 (11.5g, 35.2mmole) were dissolved in dry DCM at 0°C ice bath. Then, appropriate PPh_3 was slowly added in DCM solution. After reaction, the solution was concentrated using a rotary evaporator. The residue was purified by column chromatography on silica (*n*-hexane). The final product as a colorless liquid has the yield of 80%. ^{1}H NMR (300 MHz, $CDCl_3$) δ(ppm): 5.22 (t, *J* = 6.1 Hz, 1H, -CH), 3.43 (t, *J* = 5.9 Hz, 2H, -CH_2Br), 2.30-1.52 (m, 9H, -CH & –CH_2), 1.02 (t, *J* = 6.3 Hz, 3H, -CH_3).

(ix) Synthesis of compound 10. Compound **9** (5g, 22.93mmole) was dissolved in MeOH at -15°C upon O_3 system. After reaction (30min later), $NaBH_4$ (0.88g, 22.93mmole) was added in MeOH solution upon atmospheric system. After 2hr, ice and 3ml H_2SO_4 were added in MeOH solution. Then, the solution was extracted with deionized water/choloroform, then the organic phase of solution was obtained The organic phase was dried by $MgSO_4$ and concentrated using a rotary evaporator. The residue was purified by column chromatography on silica (*n*-hexane/EA = 10:1, v/v). The final product as a colorless liquid has the yield of 73%. ^{1}H NMR (300 MHz, $CDCl_3$) δ(ppm): 3.82 (t, *J* = 6.0 Hz, 2H, -OCH_2), 3.42 (t, *J* = 5.8 Hz, 2H, -OCH_2Br), 1.82-1.41 (m, 7H, -CH_2), 1.00(t, *J* = 6.1 Hz, 3H, -CH_3).

(x) Synthesis of compound 11. 4-Cyano-4'-hydroxybiphenyl (5g, 25.6mmole), K_2CO_3 (10.64g, 76.8mmole) and KI (3.25g, 12.8mmole) were dissolved in 250 ml acetone. Then, product **10** (6.42g, 76.8mmole) was slowly added in acetone solution and reacted overnight at 60°C. After reaction, the solution was concentrated using a rotary evaporator. The residue was purified by column chromatography on silica (*n*-hexane). The final product as a white solid has the yield of 95%. ^{1}H NMR (300 MHz, $CDCl_3$) δ(ppm): 7.82 (t, *J* = 5.7 Hz, 4H, Ar-H), 7.61 (d, *J* = 7.9 Hz, 2H, Ar-H), 7.05 (d, *J* = 8.7 Hz, 2H, Ar-H), 4.20 (t, *J* = 6.3 Hz, 2H, -OCH_2), 4.00 (t, *J* = 5.7 Hz, 2H, -OCH_2), 1.82-1.22 (m, 7H, -CH_2), 1.00 (t, *J* = 6.1 Hz, 3H, -CH_3).

(xi) Synthesis of product 12. Compound **11** (5g, 16.2mmole) and PPh_3 (6.39g, 24.3mmol) were dissolved in dry THF. Then added methyl 4-hydroxybenzoate (2.95g, 19mmol) and DIAD (4.9g, 24.3mmol) were added in THF solution. After reaction, the solution was concentrated using a rotary evaporator. The residue was purified by column chromatography on silica (*n*-hexane/DCM = 5:1, v/v). The final product as a light yellow oil has the yield of 80%. ^{1}H NMR (300 MHz, $CDCl_3$) δ(ppm): 7.88 (s, 4H, Ar-H), 7.68 (d, *J* = 8.1 Hz, 2H, Ar-H), 7.10 (d, *J* = 8.0 Hz, 2H, Ar-H), 7.05 (d, *J* = 7.9 Hz, 2H, Ar-H), 6.80 (d, *J* = 8.3 Hz, 2H, Ar-H), 4.05 (t, *J* = 6.3 Hz, 4H, -OCH_2-), 3.89 (s, 3H, -OCH_2-), 1.75-1.60 (m, 5H, -CH_2-), 1.21 (m, 2H, -CH_2-), 0.96 (d, *J* = 8.4 Hz, 3H, -CH_3).

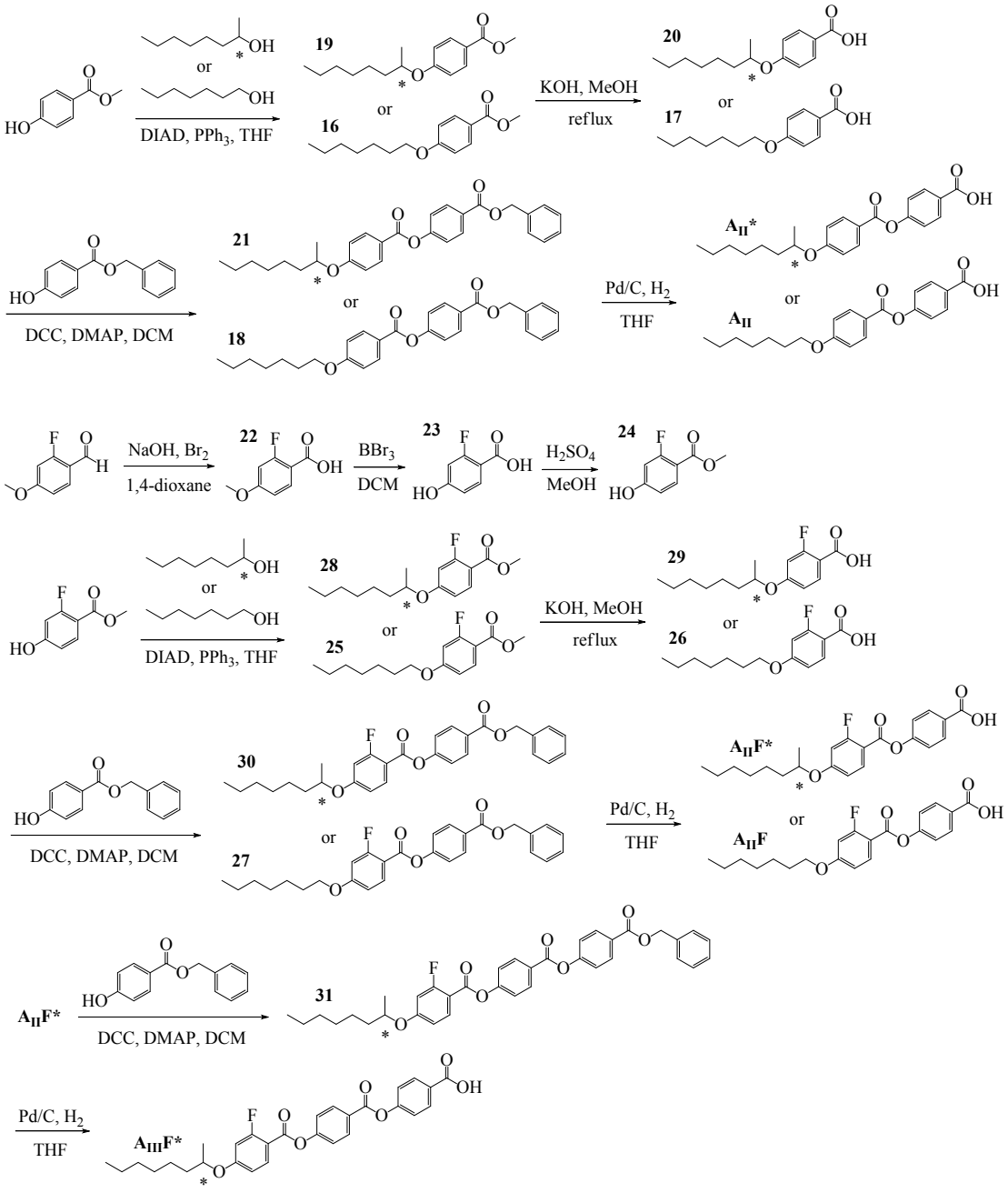
(xii) Synthesis of compound 13. Compound **12** (5g, 11.3mmol), KOH (1.9g, 33.9mmol) were dissolved in MeOH solvent. The mixed solution was reacted for 24 hours at 90°C. After reaction, the solution was concentrated using a rotary evaporator, then added HCl aqueous solution until pH=3. The final product as a white solid has the yield of 92%. ^{1}H NMR (300 MHz, $CDCl_3$) δ(ppm): 8.10 (d, *J* = 7.8 Hz, 2H, Ar-H), 7.85 (s, 4H, Ar-H), 7.70 (d, *J* = 8.3 Hz, 2H, Ar-H), 7.25 (d, *J* = 7.9 Hz, 2H, Ar-H), 7.03 (d, *J* = 8.2 Hz, 2H, Ar-H), 4.01 (t, *J* = 6.3 Hz, 4H, -OCH_2-), 1.71-1.65 (m, 5H, -CH_2-), 1.25 (m, 2H, -CH_2-), 1.03 (d, *J* = 8.1 Hz, 3H, -CH_3).

(xiii) Synthesis of H-accepter P_{II}*. Compound **13** (2g, 3.81mmole), pyridin-3-ol (0.43g, 4.6mmol) and DMAP (0.05g, 0.381mmol) were dissolved in dry DCM upon nitrogen system, then DCC (2.38g, 11.43mmol) was added. The solution was reacted for 16 hours at room temperature. After reaction, the solution first through filtration followed by DCM washing. The solution was extracted with deionized water/DCM, then the organic phase of solution was obtained The organic phase was dried by $MgSO_4$ and concentrated using a rotary evaporator. The residue was purified by column chromatography on silica (*n*-hexane/DCM = 5:3, v/v). The final product as a white solid has the yield of 60%. FTIR (KBr, ν_{max}/cm^{-1}): 3063, 3040 (-CH_3), 2930, 2861 (-CH_2-), 2226 (C-N=C in pyridine), 1733 (O-C=O), 1602 (-CN), 1514, 1493, 1471 (C=C in Ar), 1204 (C-O-C).

(xiv) Synthesis of compound 14. Compound **13** (5g, 11.6mmole), benzyl 4-hydroxybenzoate (3.2g, 14mmol) and DMAP (0.145 g, 1.16mmol) were dissolved in dry DCM upon nitrogen system, then added DCC (7.2g, 34.8mmol). The solution was reacted for 16 hours at room temperature (30°C). After reaction, the solution first through filtration followed by DCM washing. The solution was extracted with deionized water/DCM, then the organic phase of solution was obtained The organic phase was dried by $MgSO_4$ and concentrated using a rotary evaporator. The residue was purified by column chromatography on silica (*n*-hexane/DCM = 5:1, v/v). The final product as a white solid has the yield of 85%. ^{1}H NMR (300 MHz, $CDCl_3$) δ(ppm): 8.20 (d, *J* = 8.2 Hz, 2H, Ar-H), 8.10 (d, *J* = 7.8 Hz, 2H, Ar-H), 7.82 (s, 4H, Ar-H), 7.65 (d, *J* = 7.7 Hz, 2H, Ar-H), 7.50 (d, *J* = 7.9 Hz, 2H, Ar-H), 7.45-7.35 (m, 5H, Ar-H), 7.12 (d, *J* = 8.2 Hz, 2H, Ar-H), 7.01 (d, *J* = 8.1 Hz, 2H, Ar-H), 5.20 (s, 2H, -OCH_2Ph), 4.10 (t, *J* = 5.9 Hz, 4H, -OCH_2-), 1.70-1.55 (m, 5H, -CH_2-), 1.23 (m, 2H, -CH_2-), 1.00 (d, *J* = 7.6 Hz, 3H, -CH_3).

(xv) Synthesis of compound 15. Compound **14** (5g, 7.8mmole) and 15% Pd/C (0.75g) were dissolved in dry THF. The mixed solution was reacted overnight at room temperature in hydrogen system. After reaction, the solution first through filtration followed by THF washing, then concentrated using a rotary evaporator. The residue was recrystallization by *n*-hexane/DCM. The final product as a white solid has the yield of 88%. ^{1}H NMR (300 MHz, $CDCl_3$) δ(ppm): 8.30 (d, *J* = 7.8 Hz, 2H, Ar-H), 8.15 (d, *J* = 7.7 Hz, 2H, Ar-H), 7.85 (s, 4H, Ar-H), 7.70 (d, *J* = 8.0 Hz, 2H, Ar-H), 7.60 (d, *J* = 7.9 Hz, 2H, Ar-H), 7.14 (d, *J* = 8.0 Hz, 2H, Ar-H), 7.05 (d, *J* = 8.1 Hz, 2H, Ar-H), 4.07 (t, *J* = 6.5 Hz, 4H, -OCH_2-), 1.71-1.65 (m, 5H, -CH_2-), 1.21 (m, 2H, -CH_2-), 0.99 (d, *J* = 7.8 Hz, 3H, -CH_3).

(xvi) Synthesis of H-accepter P_{III}*. Compound **15** (2g, 3.1mmole), pyridin-3-ol (0.345g, 3.72mmol) and DMAP (0.04g, 0.31mmol) were dissolved in dry DCM upon nitrogen system, then DCC (1.9g, 9.3mmol) was added. The solution was reacted for 16 hours at room temperature. After reaction, the solution first through filtration followed by DCM washing. The solution was extracted with deionized water/DCM, then the organic phase of solution was obtained The organic phase was dried by $MgSO_4$ and concentrated using a rotary evaporator. The residue was purified by column chromatography on silica (*n*-hexane/DCM = 5:3, v/v). The final product as a white solid has the yield of 60%. FTIR (KBr, ν_{max}/cm^{-1}): 3075, 3042 (-CH_3), 2933, 2853 (-CH_2-), 2228 (C-N=C in pyridine), 1742 (O-C=O), 1603 (-CN), 1511, 1496, 1475 (C=C in Ar), 1211 (C-O-C).



Scheme S2 Synthesis of H-donors **D** (i.e., $\mathbf{A_{II}}$, $\mathbf{A_{II}F}$, $\mathbf{A_{II}}$*, $\mathbf{A_{II}F}$* and $\mathbf{A_{III}F}$*).

(i) Synthesis of compound 16. Benzyl 4-hydroxybenzoate (4.47g, 29.4mmol) and PPh_3 (8.89g, 33.8mmol) were dissolved in dry THF. Then added octanol (4.09g, 35.2mmol) and DIAD (8.9g, 44mmol) in THF solution. After reaction, the solution was concentrated using a rotary evaporator. The residue was purified by column chromatography on silica (*n*-hexane/DCM = 5:1, v/v). The final product as a white solid has the yield of 74%. ^{1}H NMR (300 MHz, $CDCl_3$) δ(ppm): 7.95 (d, J = 8.4 Hz, 2H, Ar-H), 6.87 (d, J = 8.4 Hz, 2H, Ar-H), 3.98 (t, J = 6.3 Hz, 2H, -OCH_2-), 3.86 (s, 3H, -CH_3), 1.77-1.24 (m, 10H, -CH_2-), 0.86 (t, J = 6.3 Hz, 3H, -CH_3).

(ii) Synthesis of compound 17. Compound **16** (9.01g, 36 mmol) and KOH (6.06g, 108mmol) were dissolved in MeOH solvent. The mixed solution was reacted for 24 hours at 90°C. After reaction, the solution was concentrated using a rotary

evaporator, then added HCl aqueous solution until pH=3. The final product as a light white solid has the yield of 94%. ^{1}H NMR (300 MHz, $CDCl_3$) δ(ppm): 7.85 (d, *J* = 8.4 Hz, 2H, Ar-H), 6.98 (d, *J* = 8.4 Hz, 2H, Ar-H), 4.01 (t, *J* = 6.4 Hz, 2H, -OCH_2-), 7.85 (d, *J* = 8.4 Hz, 2H, Ar-H), 1.74-1.66 (m, 10H, -CH_2-), 0.84 (t, *J* = 6.3 Hz, 3H, -CH_3),

(iii) Synthesis of compound 18. Compound **17** (9.92g, 42mmol), benzyl 4-hydroxybenzoate (8 g, 35mmol) and DMAP (0.65 g, 5.3mmol) were dissolved in dry DCM upon nitrogen system, then added DCC (14.5g, 70mmol). The solution was reacted for 16 hours at room temperature (30°C). After reaction, the solution first through filtration followed by DCM washing. The solution was extracted with deionized water/DCM, then the organic phase of solution was obtained The organic phase was dried by $MgSO_4$ and concentrated using a rotary evaporator. The residue was purified by column chromatography on silica (*n*-hexane/DCM = 5:1, v/v). The final product as a white solid (yield: 87%). ^{1}H NMR (300 MHz, $CDCl_3$) δ(ppm): 8.05 (m, 4H, Ar-H), 7.41 (m, 5H, Ar-H), 7.27 (m, 2H, Ar-H), 6.94 (d, *J* = 8.4 Hz, 2H, Ar-H), 5.36 (s, 2H, -OCH_2-), 4.10 (t, *J* = 6.3 Hz, 2H, -OCH_2-), 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).

(iv) Synthesis of H-donor A_{II}. Compound **18** (8.93g, 20mmol) and 15% Pd/C (1.11g) were dissolved in dry THF. The mixed solution was reacted overnight at room temperature in hydrogen system. After reaction, the solution first through filtration followed by THF washing, then concentrated using a rotary evaporator. The residue was recrystallization by *n*-hexane/DCM. The final product as a white solid (yield: 90%). ^{1}H NMR (300 MHz, $CDCl_3$) δ(ppm): 8.05 (m, 4H, Ar-H), 7.35 (d, *J* = 8.4 Hz, 2H, Ar-H), 6.90 (d, *J* = 8.4 Hz, 2H, Ar-H), 4.05 (t, *J* = 6.3 Hz, 2H, -OCH_2-), 1.70-1.61 (m, 2H, -CH_2-), 0.86 (t, *J* = 6.3 Hz, 3H, -CH_3).

(v) Synthesis of compound 19. Benzyl 4-hydroxybenzoate (4.47g, 29.4mmol) and PPh_3 (8.89g, 33.8mmol) were dissolved in dry THF. Then added (S)-2-octanol (4.6g, 35.2mmol) and DIAD (8.9g, 44mmol) in THF solution. After reaction, the solution was concentrated using a rotary evaporator. The residue was purified by column chromatography on silica (*n*-hexane/DCM = 5:1, v/v). The final product as a white solid has the yield of 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).

(vi) Synthesis of compound 20. Compound **19** (9.51g, 36 mmol) and KOH (6.06g, 108mmol) were dissolved in MeOH solvent. The mixed solution was reacted for 24 hours at 90°C. After reaction, the solution was concentrated using a rotary evaporator, then added HCl aqueous solution until pH=3. The final product as a light white solid has the yield of 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).

(vii) Synthesis of compound 21. Compound **20** (10.51g, 42mmol), benzyl 4-hydroxybenzoate (8 g, 35mmol) and DMAP (0.65 g, 5.3mmol) were dissolved in dry DCM upon nitrogen system, then added DCC (14.5g, 70mmol). The solution was reacted for 16 hours at room temperature (30°C). After reaction, the solution first through filtration followed by DCM washing. The solution was extracted with deionized water/DCM, then the organic phase of solution was obtained The organic phase was dried by $MgSO_4$ and concentrated using a rotary evaporator. The residue was purified by column chromatography on silica (*n*-hexane/DCM = 5:1, v/v). The final product as a white solid has the yield of 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).

(viii) Synthesis of H-donor A_{II}*. Compound **21** (7.4g, 20mmol) and 15% Pd/C (1.11g) were dissolved in dry THF. The mixed solution was reacted overnight at room temperature in hydrogen system. After reaction, the solution first through filtration followed by THF washing, then concentrated using a rotary evaporator. The residue was recrystallization by *n*-hexane/DCM. The

final product as a white solid has the yield of 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).

(ix) Synthesis of compound 22. 2-Fluoro-4-methoxyacetophenone (5g, 29.8mmol) was dissolved in 1,4-dioxane solvent. NaOH (3.57g, 89.3mmol) was dissolved in deionized water, then bromine (4.75g, 29.8mmol) was added in NaOH/water soultion. The NaOH and bromine solution were slowly added into 2-fluoro-4-methoxyacetophenone solution at 0°C in flask with round bottom. After mixing two solution, the mixed solution was reacted over night at room temperature. The solution was extracted with deionized water/DCM, then got the aqueous phase of solution. The aqueous phase can be maintain acidity at pH=3 by HCl solution, then filtration to give the product. The product was washed by deionized water, and the final product 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).

(x) Synthesis of compound 23. Compound **22** (4.9g, 28.8mmol) was dissolved in dry DCM solvent (30ml), then BBr_3 (14.4g, 57.6mmol) was slowly added at -78°C. The solution was reacted for 12 hours at room temperature, then the reaction was terminated by adding 2N NaOH in solution. The solution was extracted with deionized water/ethyl acetate, then the organic phase of solution was obtained The organic phase was dried by $MgSO_4$ and concentrated using a rotary evaporator. The final product was white solid has the yield of 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).

(xi) Synthesis of compound 24. Compound **23** (5g, 32mmol), H2SO4 (7ml), and MeOH (250ml) were mixed together in flask with round bottom, then the mixed solution was reacted for 12 hours at 90°C. The solution was extracted with deionized water/ethyl acetate, then the organic phase of solution was obtained The organic phase was dried by $MgSO_4$ and concentrated using a rotary evaporator. The residue was purified by column chromatography on silica (*n*-hexane/ethyl acetate = 3:1, v/v). The final product as a white solid has the yield of 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).

(xii) Synthesis of compound 25. Compound **24** (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. The solution was reacted overnight at 60°C. After reaction, the solution was concentrated using a rotary evaporator. The solution was extracted with deionized water/EtOAc, then the organic phase of solution was obtained The organic phase was dried by $MgSO_4$ and concentrated using a rotary evaporator. The residue was purified by column chromatography on silica (*n*-hexane/EtOAc = 5:1, v/v). The final product as a white solid has the yield of 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).

(xiii) Synthesis of compound 26. Compound **25** (9.66g, 36mmol) and KOH (6.06g, 108mmol) were dissolved in MeOH solvent. The mixed solution was reacted for 24 hours at 90°C. After reaction, the solution was concentrated using a rotary evaporator, then added HCl aqueous solution until pH=3. The final product as a light white solid has the yield of 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).

(xiv) Synthesis of compound 27. Compound **26** (10.68g, 42mmol), benzyl 4-hydroxybenzoate (8 g, 35mmol) and DMAP

(0.65 g, 5.3mmol) were dissolved in dry DCM upon nitrogen system, then DCC (14.5g, 70mmol) was added. The solution was reacted for 16 hours at room temperature. After reaction, the solution first through filtration followed by DCM washing. The solution was extracted with deionized water/DCM, then got the organic phase of solution. The organic phase was dried by $MgSO_4$ and concentrated using a rotary evaporator. The residue was purified by column chromatography on silica (*n*-hexane/DCM = 5:1, v/v). The final product as a white solid has the yield of 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).

(xv) Synthesis of H-donor A_{II}F. Compound **27** (10g, 21.5mmol) and 15% Pd/C (1.11g) were dissolved in dry THF. The mixed solution was reacted overnight at room temperature in hydrogen system. After reaction, the solution first through filtration followed by THF washing, then concentrated using a rotary evaporator. The residue was recrystallization by *n*-hexane/DCM. The final product as a white solid has the yield of 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).

(xvi) Synthesis of compound 28. Compound **24** (5g, 29.4mmol) and PPh_3 (8.89g, 33.8mmol) were mixed in flask with round bottom upon nitrogen system. The dry DCM was added into flask, then added (S)-2-octanol (4.6g, 35.2mmol) and DIAD (8.9g, 44mmol). After reaction, the solution was concentrated using a rotary evaporator. The residue was purified by column chromatography on silica (*n*-hexane/DCM = 5:1, v/v). The final product as a light yellow oil has the yield of 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).

(xvii) Synthesis of compound 29. Compound **28** (10g, 35.5mmol) and KOH (5.95g, 106mmol) were dissolved in MeOH solvent. The mixed solution was reacted for 24 hours at 90°C. After reaction, the solution was concentrated using a rotary evaporator, then added HCl aqueous solution until pH=3. The final product as a light yellow solid has the yield of 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).

(xviii) Synthesis of compound 30. Compound **29** (11.25 g, 42mmol), benzyl 4-hydroxybenzoate (8 g, 35mmol), and DMAP (0.65 g, 5.3mmol) were dissolved in dry DCM (250ml) in flask with round bottom upon nitrogen system, then DCC (14.5g, 70mmol) was added in solution. The solution was reacted for 16 hours at room temperature. After reaction, the solution first through filtration followed by DCM washing. The solution was extracted with deionized water/DCM, then the organic phase of solution was obtained The organic phase was dried by $MgSO_4$ and concentrated using a rotary evaporator. The residue was purified by column chromatography on silica (*n*-hexane/DCM = 5:1, v/v). The final product as a light yellow solid has the yield of 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).

(xix) Synthesis of H-donor A_{II}F*. Product **30** (10g, 20 mmol) and 15% Pd/C (1.5 g) were dissolved in dry THF. The mixed solution was reacted overnight at room temperature in hydrogen system. After reaction, the solution first through filtration followed by THF washing, then concentrated using a rotary evaporator. The residue was recrystallization by *n*-hexane/DCM. The final product as a white solid has the yield of 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, $-CH_3$).

(xx) Synthesis of compound 31. Compound **$A_{II}F^*$** (6g, 15.4mmol), benzyl 4-hydroxybenzoate (2.9g, 12.8mmol), and DMAP (0.16 g, 1.3mmol) were dissolved in dry DCM (250ml) in flask with round bottom upon nitrogen system, then DCC (7.9g, 38.4mmol) was added in solution. The solution was reacted for 16 hours at room temperature. After reaction, the solution first through filtration followed by DCM washing. The solution was extracted with deionized water/DCM, then the organic phase of solution was obtained The organic phase was dried by $MgSO_4$ and concentrated using a rotary evaporator. The residue was purified by column chromatography on silica (*n*-hexane/DCM = 5:1, v/v). The final product as a light yellow solid has the yield of 85%. ^{1}H NMR (300 MHz, $CDCl_3$) δ(ppm): 8.25 (d, *J* = 7.2 Hz, 2H, Ar-H), 8.10 (d, *J* = 8.0 Hz, 2H, Ar-H), 8.00 (d, *J* = 7.8 Hz, 1H, Ar-H), 7.50 (d, *J* = 7.6 Hz, 2H, Ar-H), 7.42 (d, *J* = 7.6 Hz, 2H, Ar-H), 7.40-7.32 (m, 5H, Ar-H), 7.25 (d, *J* = 6.8 Hz, 1H, Ar-H), 7.00 (d, *J* = 8.0 Hz, 1H, Ar-H), 5.28 (s, 2H, $-CH_2Ph$), 3.86 (m, 1H, $-OCH_2-$), 1.67 (d, *J* = 7.8 Hz, 2H, $-CH_2-$), 1.40 (d, *J* = 8.1 Hz, 3H, $-CH_3$), 1.31-1.25 (m, 8H, $-CH_2-$), 0.85 (t, *J* = 8.6 Hz, 2H, $-CH_3$).

(xxi) Synthesis of H-donor $A_{III}F^*$. Compound **31** (5g, 8.35mmol) and 15% Pd/C (1.5 g) were dissolved in dry THF. The mixed solution was reacted overnight at room temperature in hydrogen system. After reaction, the solution first through filtration followed by THF washing, then concentrated using a rotary evaporator. The residue was recrystallization by *n*-hexane/DCM. The final product as a white solid has the yield of 92%. ^{1}H NMR (300 MHz, $CDCl_3$) δ(ppm): 8.30 (d, *J* = 8.4 Hz, 2H, Ar-H), 8.20 (d, *J* = 8.6 Hz, 2H, Ar-H), 8.02 (d, *J* = 8.4 Hz, 1H, Ar-H), 7.40 (d, *J* = 8.6 Hz, 2H, Ar-H), 7.30 (d, *J* = 8.5 Hz, 2H, Ar-H), 6.75 (d, *J* = 8.2 Hz, 1H, Ar-H), 4.40 (m, 1H, $-OCH_2-$), 1.60 (m, 2H, $-CH_2-$), 1.30-1.25 (m, 8H, $-CH_2-$), 0.89 (t, *J* = 8.7 Hz, 3H, $-CH_3$).

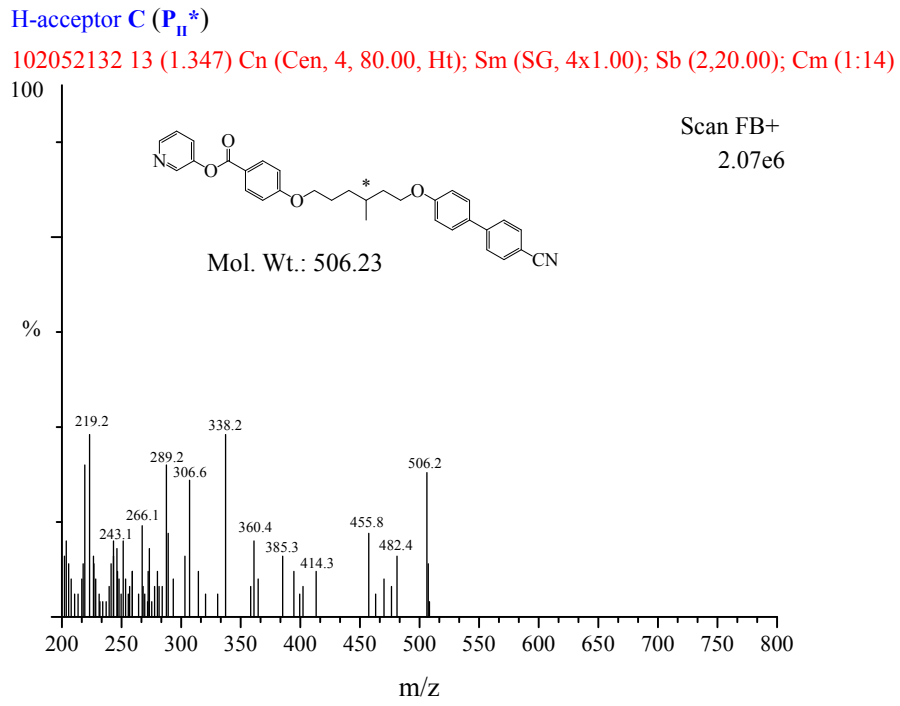


Fig. S2 Mass spectrum of H-acceptor $\mathbf{P_{II}}$*.

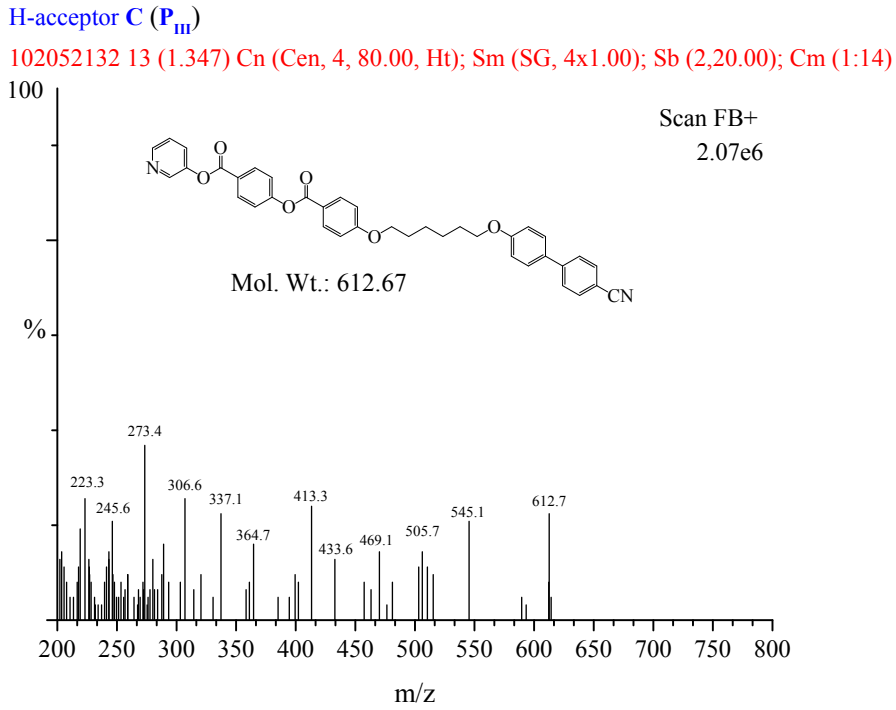


Fig. S3 Mass spectrum of H-acceptor $\mathbf{P_{III}}$.

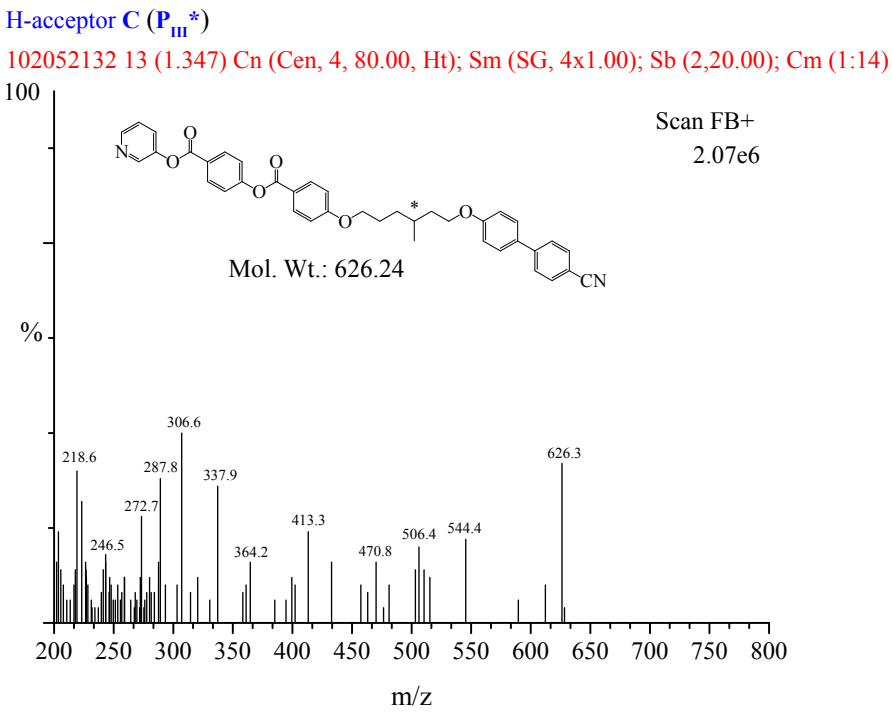


Fig. S4 Mass spectrum of H-acceptor $\mathbf{P_{III}}$*.

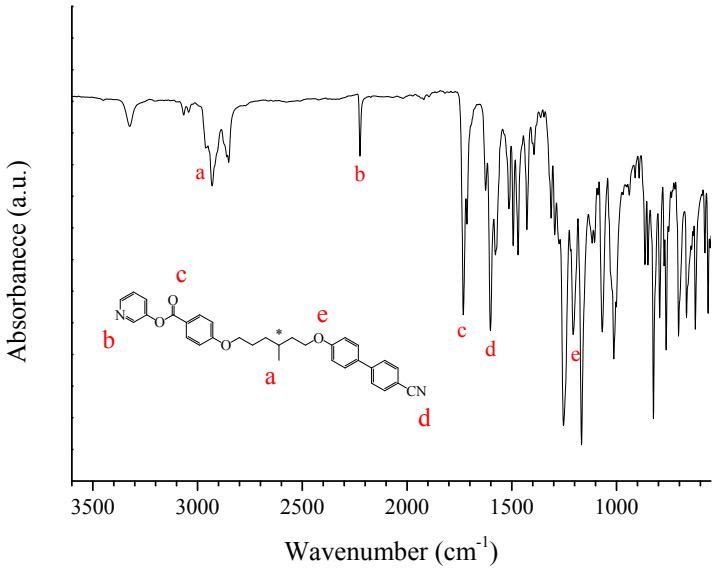


Fig. S5 Infrared spectrum of H-acceptor $\mathbf{P_{II}}$*.

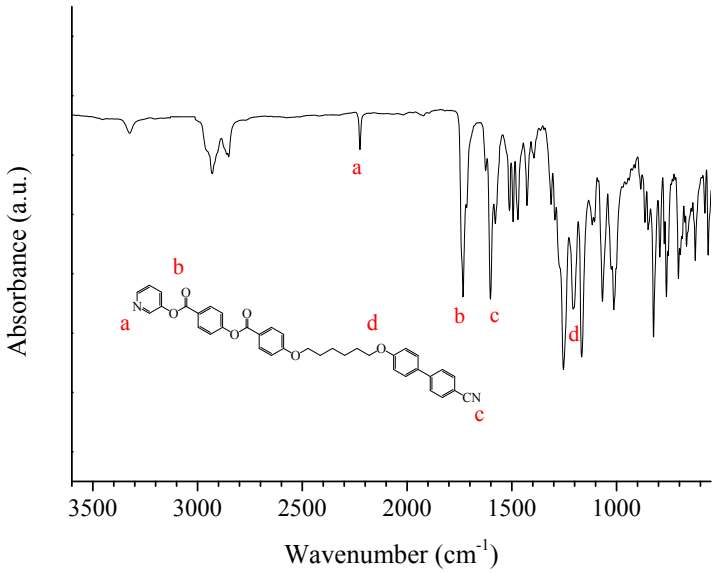


Fig. S6 Infrared spectrum of H-acceptor $\mathbf{P_{III}}$.

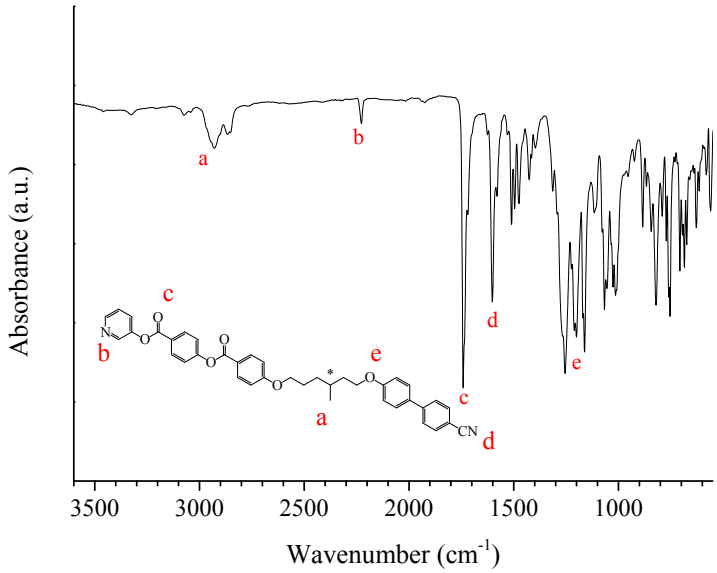


Fig. S7 Infrared spectrum of H-acceptor $\mathbf{P_{III}}$*.