Electronic Supplementary Material (ESI) for Journal of Materials Chemistry C.

Supporting Information

Ambipolar transistors based on chloro-substituted tetraphenylpentacene

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General Experimental Procedures

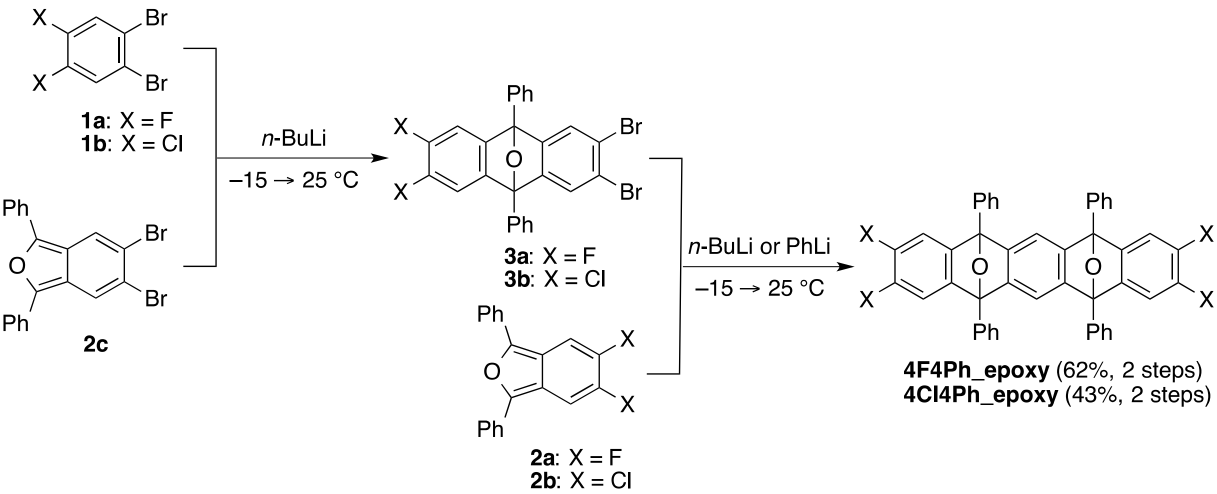
All experiments dealing with air- and moisture-sensitive compounds were conducted under an atmosphere of dry argon. Toluene (anhydrous; Wako Pure Chemical Industries, Ltd.), THF (anhydrous; Wako Pure Chemical Industries, Ltd.) and chlorobenzene (anhydrous; Sigma-Aldrich Co. LLC) were used as received.

For thin-layer chromatography (TLC) analysis, Merck pre-coated plates (silica gel 60 F_{254}, Art 5715, 0.25 mm) were used. For flash column chromatography, silica gel 60 N (spherical, neutral, 63–210 μm) from Kanto Chemical was used.

^{1}H NMR and ^{13}C NMR were measured on a JEOL JNM ECA-400, a JEOL JNM ECX-500II, or a JEOL JNM ECZ-500R spectrometer. Chemical shifts (δ) are expressed in parts per million (ppm) downfield from internal standard (tetramethylsilane, 0.00 ppm) in $CDCl_3$ and coupling constants are reported as hertz (Hz). Splitting patterns are indicated as follows; br, broad; s, singlet; d, doublet; t, triplet; q, quartet; m, multiplet. Attenuated Total Reflectance Fourier Transformation Infrared (ATR-FTIR) spectra were recorded on a JASCO FT/IR-4200 infrared spectrometer. High resolution mass spectra were obtained with a JEOL The AccuTOF LC-plus JMS-T100LP or a JEOL JMS 700 spectrometer. Melting points (Mp) were measured on a Yanako MP-S3 instrument or a MPA100 OptiMelt Automated Melting Point System from Stanford research and are uncorrected.

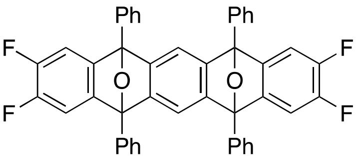
Synthesis of halogen-substituted tetraphenylpentacenes

Scheme S1. Successive [4+2] cycloadditions of haloarynes with isobenzofurans



*One-pot synthesis of diepoxypentacene **4F4Ph_epoxy***:

To a solution of 1,2-dibromo-4,5-difluorobenzene (**1a**) (146 mg, 0.539 mmol) and 5,6-dibromo-1,3-diphenylisobenzofuran (**2c**) (271 mg, 0.633 mmol) in toluene (2.2 mL) was added *n*-BuLi (1.59 M in *n*-hexane, 0.42 mL, 0.67 mmol) at –15 °C. After warmed to 25 °C and stirred for 10 min, 5,6-difluoro-1,3-diphenylisobenzofuran (**2a**) (322 mg, 1.05 mmol) in toluene (3.5 mL) was added to the mixture at –15 °C, to which was slowly added PhLi (1.06 M in cyclohexane–Et_2O, 1.3 mL, 1.4 mmol) at same temperature. After warmed to 25 °C, the reaction was stopped by adding water. The products were extracted with EtOAc (X3), and the combined organic extracts were washed with brine, dried (Na_2SO_4), and concentrated *in vacuo*. The residue was purified by silica-gel flash column chromatography (hexane/toluene = 8/2 → 7/3 → 6/4) to give diepoxypentacene **4F4Ph_epoxy** as a mixture of diastereomers (228 mg, 61.6%, less polar/more polar = 52/48), which were separated by silica-gel flash column chromatography (hexane/toluene = 8/2 → 7/3 → 6/4 → 5/5), affording less polar **4F4Ph_epoxy** and more polar **4F4Ph_epoxy**.



diepoxypentacene **4F4Ph_epoxy** (less polar)

Rf 0.43 (hexane/$CHCl_3$/Et_2O = 90/5/5);

Mp 330.3–330.9 °C (hexane/$CHCl_3$);

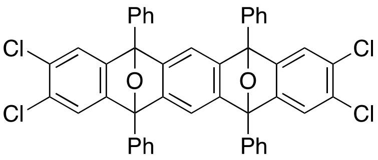
^{1}H NMR (400 MHz, $CDCl_3$, δ) 7.08 (dd, 4H, $J_1 = J_2 = 7.8$ Hz), 7.32 (s, 2H), 7.51 (dd, 4H, $J_1 = J_2 = 7.3$ Hz), 7.59 (dd, 8H, $J_1 = J_2 = 7.3$ Hz), 7.78 (d, 8H, $J = 7.3$ Hz);

^{13}C NMR (100 MHz, $CDCl_3$, δ) 90.3, 110.9 (dd, $J_1 = 7.7$ Hz, $J_2 = 14.4$ Hz), 113.7, 126.4, 128.8,

129.1, 133.8, 146.3 (dd, $J_1 = J_2 = 3.8$ Hz), 147.9 (dd, $J_1 = 15.3$ Hz, $J_2 = 250.2$ Hz), 149.3;
IR (ATR) 3061, 3035, 2855, 1617, 1500, 1474, 1450, 1437, 1352, 1308, 1238, 1173, 1121, 1109, 1053, 1030, 1002, 982, 968, 889, 876, 781, 767, 741, 725, 700 cm^{-1};
HRMS (ESI) *m/z* 709.1787 (709.1767 calcd for $C_{46}H_{26}F_4NaO_2$ $[M+Na]^+$).
diepoxypentacene **4F4Ph_epoxy** (more polar)
Rf 0.26 (hexane/$CHCl_3$/Et_2O = 90/5/5);
Mp 339.3–340.1 °C (hexane/$CHCl_3$);
^1H NMR (400 MHz, $CDCl_3$, δ) 7.12 (dd, 4H, $J_1 = J_2 = 7.8$ Hz), 7.29 (s, 2H), 7.47 (m, 4H, $J_1 = J_2 = 7.3$ Hz), 7.55 (dd, 8H, $J_1 = J_2 = 7.3$ Hz), 7.77 (dd, 8H, $J = 7.3$ Hz);
^{13}C NMR (100 MHz, $CDCl_3$, δ) 90.3, 111.0 (dd, $J_1 = 7.7$ Hz, $J_2 = 14.4$ Hz), 113.4, 126.3, 128.7, 129.0, 133.9, 146.7 (dd, $J_1 = J_2 = 3.9$ Hz), 147.8 (dd, $J_1 = 15.3$ Hz, $J_2 = 250.2$ Hz), 149.2;
IR (ATR) 3036, 3010, 1621, 1474, 1449, 1431, 1374, 1310, 1243, 1214, 1185, 1177, 1123, 1107, 1054, 1029, 999, 984, 905, 880, 866, 780, 746 cm^{-1};
HRMS (ESI) *m/z* 709.1782 (709.1767 calcd for $C_{46}H_{26}F_4NaO_2$ $[M+Na]^+$).

One-pot synthesis of diepoxypentacene ***4Cl4Ph_epoxy***:

To a mixture of 1,2-dibromo-4,5-dichlorobenzene (**1b**) (104 mg, 0.341 mmol) and 5,6-dibromo-1,3-diphenylisobenzofuran (**2c**) (154 mg, 0.360 mmol) in chlorobenzene (3.0 mL) was added *n*-BuLi (1.60 M in *n*-hexane, 0.26 mL, 0.42 mmol) at –15 °C. After being warmed to 25 °C and stirred for 10 min, 5,6-dichloro-1,3-diphenylisobenzofuran (**2b**) (180 mg, 0.531 mmol) in chlorobenzene (3.0 mL) was added to the mixture at –15 °C, to which was slowly *n*-BuLi (1.60 M in *n*-hexane, 0.45 mL, 0.72 mmol) at same temperature. After being warmed to 25 °C, the reaction was stopped by adding water. The products were extracted with EtOAc (X3), and the combined organic extracts were washed with brine, dried (Na_2SO_4), and concentrated *in vacuo*. The residue was purified by silica-gel open column chromatography (hexane/CH_2Cl_2/Et_2O = 96/3/1 → 92/6/2) to give cycloadduct **4Cl4Ph_epoxy** as a mixture of diastereomers (111 mg, 43.4%, less polar/more polar = 52/48), which were separated by silica-gel flash column chromatography (hexane/CH_2Cl_2/Et_2O = 96/3/1 → 92/6/2), affording less polar **4Cl4Ph_epoxy** and more polar **4Cl4Ph_epoxy**.



diepoxypentacene **4Cl4Ph_epoxy** (less polar)
Rf 0.43 (hexane/CH_2Cl_2/Et_2O = 92/6/2, X2);
Mp 424.1–425.0 °C (MeOH/$CHCl_3$);
^1H NMR (500 MHz, $CDCl_3$, δ) 7.31 (s, 4H), 7.33 (s, 2H), 7.52 (dd, 4H, $J_1 = J_2 = 7.4$ Hz), 7.60 (dd, 8H, $J_1 = J_2 = 7.4$ Hz), 7.77–7.80 (m, 8H);
^{13}C NMR ($CDCl_3$, δ) 90.2, 114.0, 122.7, 126.4, 128.8, 129.1, 129.6, 133.5, 149.1, 150.2;
IR (ATR) 3035, 1608, 1541, 1506, 1448, 1419, 1339, 1306, 1181, 1146, 1114, 984, 882, 862,

799, 748 cm^{-1};

HRMS (ESI) *m/z* 773.0567 (773.0585 calcd for $C_{46}H_{26}Cl_4NaO_2$ [M+Na]$^+$).

diepoxypentacene **4Cl4Ph_epoxy** (more polar)

Rf 0.28 (hexane/CH_2Cl_2/Et_2O = 92/6/2, X2);

Mp 353.4–354.2 °C (MeOH/$CHCl_3$);

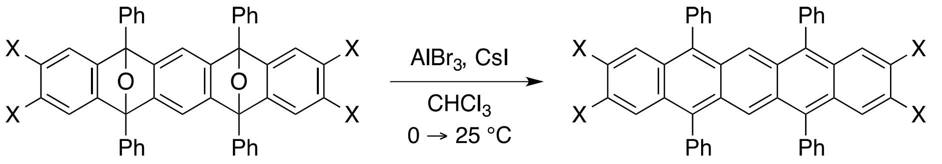
^{1}H NMR (500 MHz, $CDCl_3$, δ) 7.31 (s, 2H), 7.35 (s, 4H), 7.48 (dd, 4H, $J_1 = J_2 = 7.5$ Hz), 7.57 (dd, 8H, $J_1 = J_2 = 7.5$ Hz), 7.75–7.78 (m, 8H);

^{13}C NMR (125 MHz, $CDCl_3$, δ) 90.2, 113.7, 122.8, 126.3, 128.7, 129.0, 129.6, 133.6, 148.9, 150.5;

IR (ATR) 3034, 1607, 1541, 1498, 1449, 1424, 1354, 1306, 1212, 1155, 1111, 999, 983, 878, 805, 750 cm^{-1};

HRMS (ESI) *m/z* 773.0576 (773.0585 calcd for $C_{46}H_{26}Cl_4NaO_2$ [M+Na]$^+$).

Scheme S2. Aromatization of diepoxypentacenes



4F4Ph_epoxy
4Cl4Ph_epoxy

4F4Ph: X = F (51%)
4Cl4Ph: X = Cl (50%)

*Synthesis of pentacene **4F4Ph***:

All manipulations were carried out with a stringent exclusion of air and light. To a mixture of diepoxypentacene **4F4Ph_epoxy** (28.3 mg, 41.2 μmol) and CsI (86.6 mg, 0.334 mmol) in $CHCl_3$ (2.0 mL) was added $AlBr_3$ (1.0 M in dibromomethane, 0.10 mL, 0.11 mmol) at 0 °C, and the reaction was warmed to 25 °C. After 5 h, the reaction was stopped by adding sat. aq. $NaHCO_3$. The aqueous layer was removed with a syringe, and the products were successively washed with sat. aq. $NaHCO_3$ and brine. After removing the aqueous layer, the residue was directly purified by silica-gel column chromatography (hexane/CH_2Cl_2 = 7/3) in argon atmosphere (Figure 1) to give **4F4Ph** (14.0 mg, 51.9%) as a blue solid.

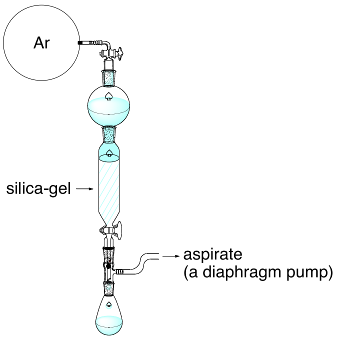
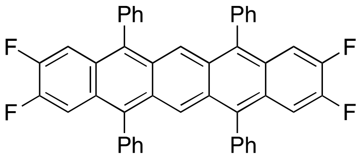


Figure S1. Silica-gel column chromatography in argon atmosphere



pentacene **4F4Ph**

Mp 252.4-253.9 °C (hexane/$CHCl_3$);

^1H NMR (500 MHz, $CDCl_3$, δ) 7.29–7.32 (m, 8H), 7.33 (dd, 4H, $J_1 = J_2 = 10.5$ Hz) 7.42–7.46 (m, 12H), 8.12 (s, 2H);

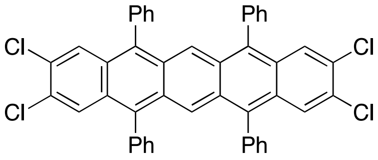
^{13}C NMR (125 MHz, $CDCl_3$, δ) 111.4 (dd, $J_1 = 4.8$ Hz, $J_2 = 14.4$ Hz), 125.7, 126.5, 127.6, 128.4, 128.7, 130.9, 137.0, 137.9, 149.9 (dd, $J_1 = 20.4$ Hz, $J_2 = 255.5$ Hz);

IR (ATR) 3053, 1599, 1555, 1475, 1441, 1378, 1293, 1237, 1137, 1074, 1028, 990, 877, 795, 753 cm^{-1};

HRMS (ESI) *m/z* 654.1985 (654.1971 calcd for $C_{46}H_{26}F_4$, M^+).

*Synthesis of pentacene **4Cl4Ph***:

All manipulations were carried out with a stringent exclusion of air and light. To a mixture of diepoxypentacene **4Cl4Ph_epoxy** (28.2 mg, 37.5 μmol) and CsI (78.1 mg, 0.301 mmol) in $CHCl_3$ (1.0 mL) was added $AlBr_3$ (1.0 M in dibromomethane, 90 μL, 90 μmol) at 0 °C, and the reaction was warmed to room temperature. After 18 h, the reaction was stopped by adding sat. aq. $NaHCO_3$. The aqueous layer was removed with a syringe, and the products were washed again with sat. aq. $NaHCO_3$. After removing the upper layer, the product was washed by brine in reactor vessel. After removing the aqueous layer, the residue was directly purified by silica-gel column chromatography (hexane/CH_2Cl_2 = 8/2) in argon atmosphere to give **4Cl4Ph** (13.5 mg, 49.9%) as a blue solid.



pentacene **4Cl4Ph**

Mp 341.9-342.5 °C (MeOH/$CHCl_3$);

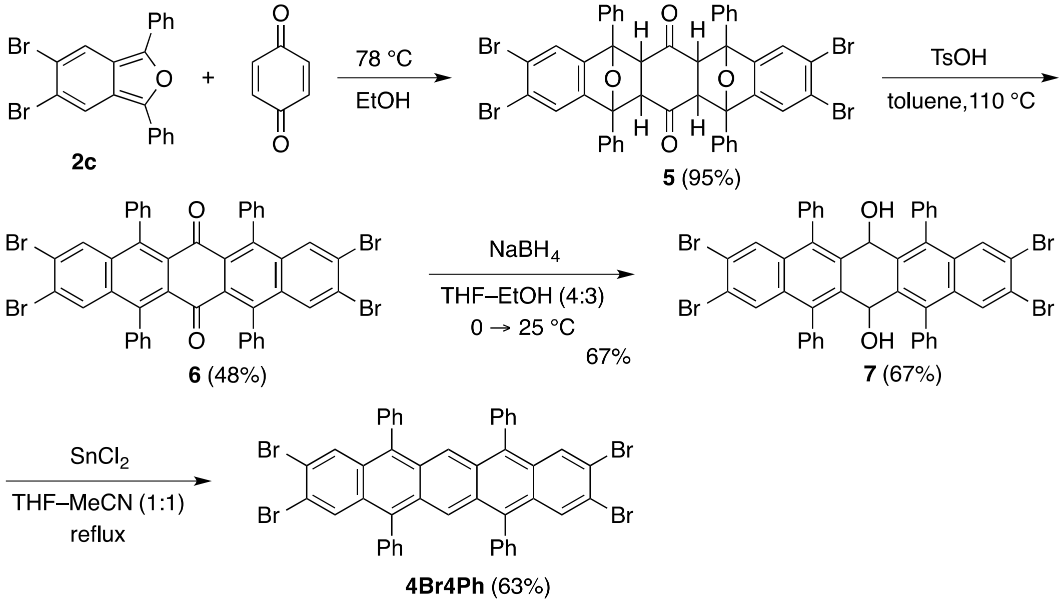
^1H NMR (500 MHz, $CDCl_3$, δ) 7.29–7.31 (m, 8H), 7.43–7.46 (m, 12H), 7.77 (s, 4H), 8.12 (s, 2H);

^{13}C NMR (125 MHz, $CDCl_3$, δ) 126.7, 127.7, 127.9, 128.4, 129.2, 129.5, 131.0, 137.0, 137.4;

IR (ATR) 3021, 1591, 1494, 1441, 1421, 1390, 1375, 1176, 1111, 1072, 987, 903, 886, 754, 731 cm^{-1};

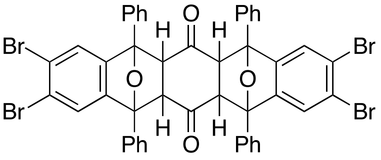
HRMS (ESI) *m/z* 718.0803 (718.0789 calcd for $C_{46}H_{26}Cl_4$, M^+).

Scheme S3. Synthesis of pentacene **4Br4Ph**



Synthesis of cycloadduct ***5***:

A mixture of isobenzofuran **2c** (642 mg, 1.50 mmol) and 1,4-benzoquinone (81.1 mg, 0.750 mmol) in EtOH (20 mL) was heated at 78 °C for 3 h. After being cooled to room temperature, the solvent was removed *in vacuo*. The residue was filtered and washed by hexane (X3) and MeOH (X3) to give essentially pure cycloadduct **5** (690 mg, 95.5%) as a white solid.



cycloadduct **5**

Mp decomposed at 170 °C;

^{1}H NMR (500 MHz, $CDCl_3$, δ) 3.35 (s, 2H), 4.24 (s, 2H), 6.60 (d, 4H, J =7.6 Hz), 7.12 (dd, 4H, J =7.6 Hz), 7.15 (s, 2H), 7.27 (dd, 4H, J =7.6 Hz), 7.41 (s, 2H), 7.63–7.66 (m, 6H), 7.73–7.77 (m, 4H);

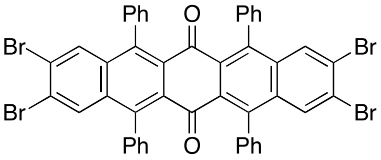
^{13}C NMR (125 MHz, $CDCl_3$, δ) 57.8, 63.2, 88.8, 91.5, 123.0, 124.6, 124.7, 126.5, 127.8, 128.0, 128.1, 128.8, 129.1, 129.4, 132.7, 135.1, 146.4, 147.6, 203.8;

IR (ATR) 3063, 1714, 1605, 1496, 1448, 1355, 1287, 1213, 1177, 1089, 1004, 873, 750 cm^{-1};

HRMS (ESI) m/z 982.8606 (982.8619 calcd for $C_{46}H_{28}Br_4NaO_4$, $[M+Na]^+$).

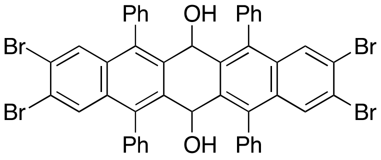
Synthesis of pentacenequinone ***6***:

A mixture of cycloadduct **5** (645 mg, 0.669 mmol) and TsOH (256 mg, 1.35 mmol) in toluene (7.0 mL) was heated at 110 °C for 12 h. After being cooled to 25 °C, the solvent was removed *in vacuo*. The residue was filtered and washed by MeOH (X3) to give essentially pure pentacenequinone **6** (298 mg, 48.0%) as a yellow-brown solid.



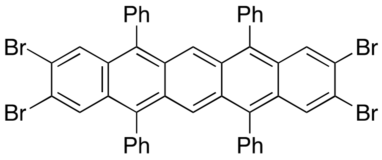
pentacenequinone **6**
Mp decomposed at 350 °C (MeOH/$CHCl_3$);
^{1}H NMR (400 MHz, $CDCl_3$, δ) 7.18–7.22 (m, 8H), 7.37–7.41 (m, 12H), 7.84 (s, 4H);
^{13}C NMR (100 MHz, $CDCl_3$, δ) 125.9, 127.8, 128.2, 129.8, 132.7, 134.2, 135.9, 139.1, 187.7;
IR (ATR) 3058, 1696, 1599, 1493, 1442, 1373, 1327, 1180, 1073, 949, 889, 752 cm^{-1};
HRMS (ESI) *m/z* 946.8419 (946.8408 calcd for $C_{46}H_{24}Br_4NaO_2$, $[M+Na]^+$).

*Synthesis of diol **7***:
To a solution of pentacenequinone **6** (282 mg, 0.304 mmol) in THF–EtOH (4:3, 7.0 mL) was added $NaBH_4$ (57.8 mL, 1.55 mmol) at 0 °C, and the reaction was warmed to 25 °C. After 17 h, the reaction was stopped by adding water. The products were extracted with $CHCl_3$ (X3), and the combined organic extracts were washed with brine, dried (Na_2SO_4), and concentrated *in vacuo*. The residue was purified by silica-gel flash column chromatography (hexane/$CHCl_3$ = 4/6 → 3/7 → 2/8 → $CHCl_3$) to give diol **7** (189 mg, 66.8%) as a white solid.



diol **7**
Mp decomposed at 250 °C (MeOH/$CHCl_3$);
^{1}H NMR (500 MHz, $CDCl_3$, δ) 1.62 (d, 2H, J =5.3 Hz), 5.98 (d, 2H, J =5.3 Hz), 7.24–7.28 (m, 4H), 7.37–7.44 (m, 8H), 7.70 (s, 4H);
^{13}C NMR (125 MHz, $CDCl_3$, δ) 64.7, 122.9, 127.8, 128.3, 128.7, 129.2, 130.8, 131.1, 132.6, 133.3, 137.1, 138.6;
IR (ATR) 3572, 3053, 3006, 2963, 2924, 2851, 1600, 1554, 1494, 1458, 1440, 1404, 1329, 1308, 1216, 1105, 1072, 1029, 958, 906, 881, 753 cm^{-1};
HRMS (ESI) *m/z* 950.8720 (950.8721 calcd for $C_{46}H_{28}Br_4NaO_2$, $[M+Na]^+$).

*Synthesis of pentacene **4Br4Ph***:
All manipulations were carried out with a stringent exclusion of air and light. A mixture of diol **7** (170 mg, 0.182 mmol) and $SnCl_2$ (206 mg, 1.09 mmol) in THF–MeCN (1:1, 18 mL) was refluxed for 1 h. After cooled to 25 °C, the reaction mixture filtered through a Celite® pad and the solvent was removed *in vacuo*. The residue was filtered and washed by MeOH (X5) at 25 °C to give essentially pure **4Br4Ph** (103 mg, 63.2%) as a deep blue solid.



pentacene **4Br4Ph**

Mp 346.0–346.8 °C (MeOH/$CHCl_3$);

^{1}H NMR (500 MHz, $CDCl_3$, δ) 7.28–7.31 (m, 8H), 7.43–7.46 (m, 12H), 7.97 (s, 4H), 8.15 (s, 2H);

^{13}C NMR (125 MHz, $CDCl_3$, δ) 121.6, 126.8, 127.7, 128.4, 128.5, 129.3, 131.0, 131.3, 137.1, 137.3;

IR (ATR) 3056, 1581, 1494, 1440, 1412, 1386, 1176, 1090, 956, 884, 752 cm^{-1};

HRMS (ESI) *m/z* 893.8769 (893.8768 calcd for $C_{46}H_{26}Br_4$, M^+).

CV and UV-Vis measurements

Oxidation potentials were measured by cyclic voltammetry on an ALS620D electrochemical analyzer from BAS Inc., using degassed CH_2Cl_2 as the solvent and n-Bu_4NPF_6 as the supporting electrolyte. The working electrode was glassy carbon, the counter electrode was platinum wire, and the reference electrode was Ag/$AgNO_3$ (0.01 M $AgNO_3$ in MeCN with 0.1 M n-Bu_4NClO_4). The scan rate is 100mV/s. Oxidation and reduction potentials were calculated from the half wave potentials, and HOMO and LUMO levels were calculated by assuming the energy level of ferrocene to be –4.8 eV.[37]

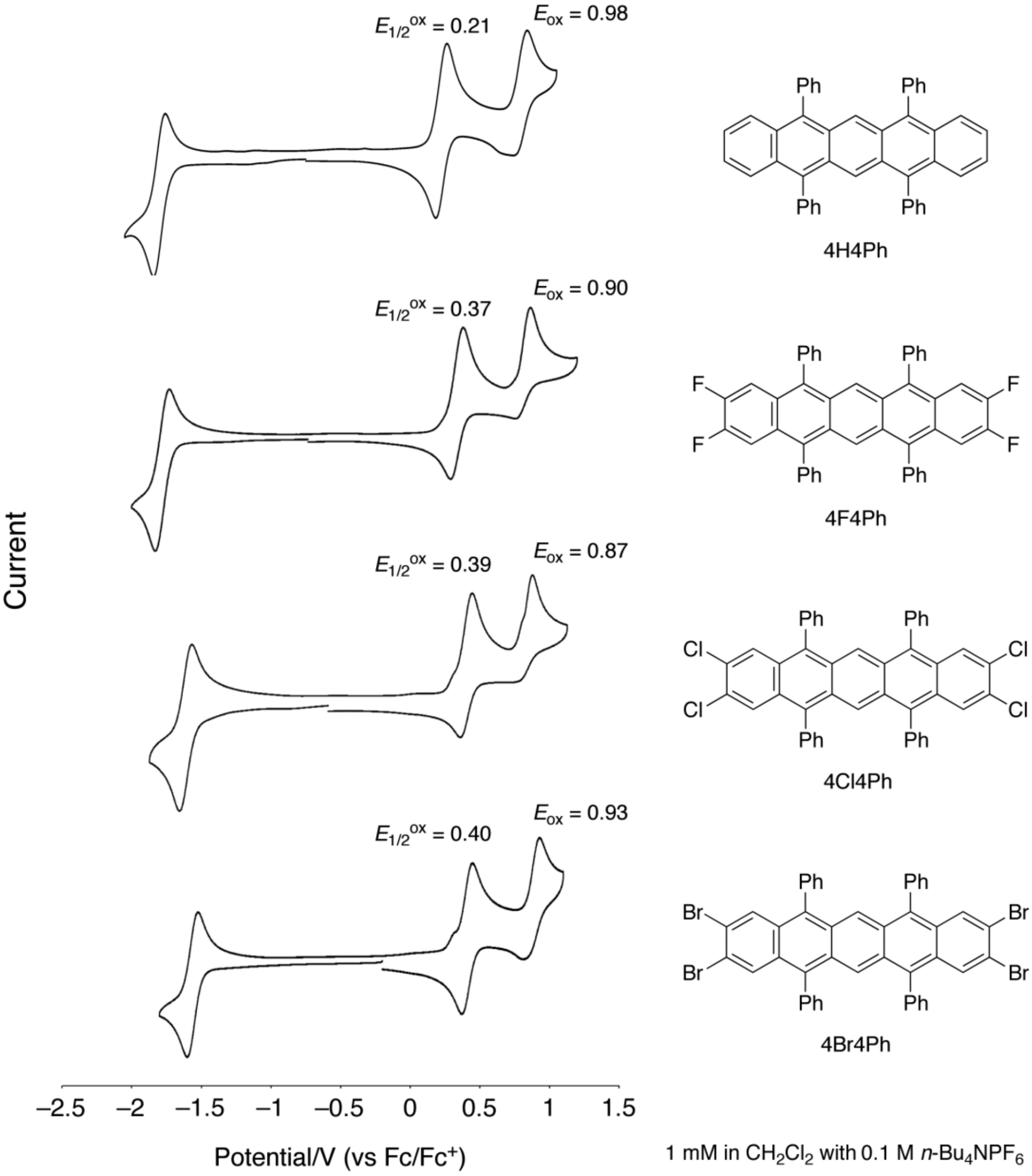


Figure S2. Cyclic voltammetry of **4*X*4Ph** (*X* = H, F, Cl, and Br).

Optical energy gaps were measured by UV-Vis spectra on a JASCO V-630 spectrophotometer using CH_2Cl_2 as the solvent. The energy gaps are obtained from the absorption edges.

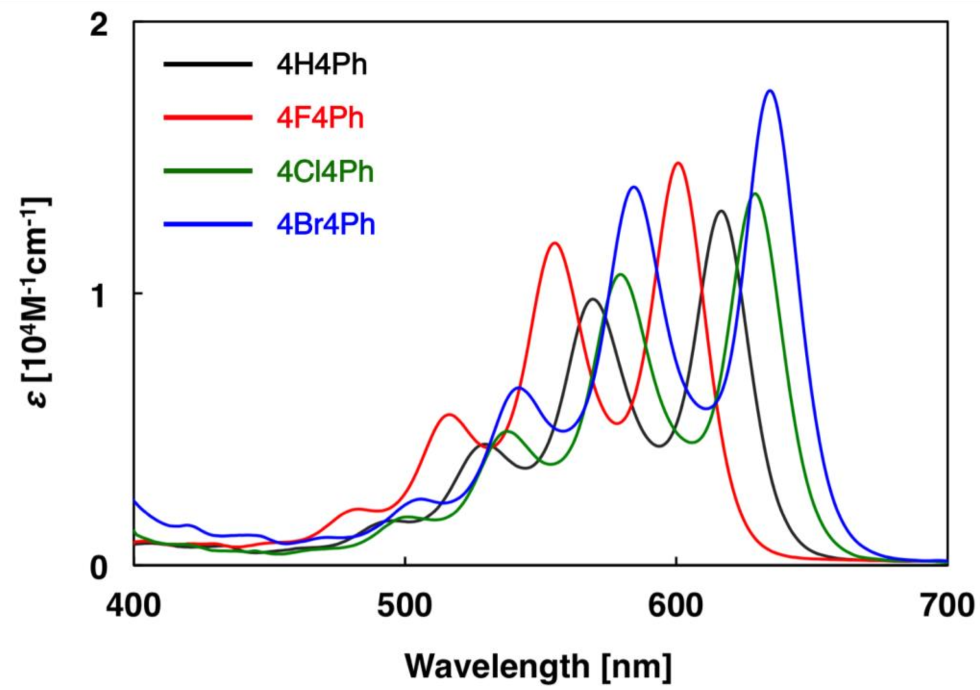


Figure S3. UV-Vis spectra of **4*X*4Ph** (*X* = H, F, Cl, and Br. 10 μM in CH_2Cl_2).

Single crystal structure

The crystal data of **4*X*4Ph** (*X* = F, Cl, and Br) are listed in Table 3.

The diffraction data of **4F4Ph** is collected by a RIGAKU R-AXIS RAPID-II IP Area Detector imaging plate with Cu*Kα* radiation (λ = 1.54186 Å). The structure was solved by direct methods (*SHELXS*97) and refined by the full-matrix least-squares on F^2 (SHELXL-2018/1).[S1] CCDC number is 1887277.

The diffraction data of **4Cl4Ph** is collected by a R-AXIS RAPID IP Area Detector imaging plate with Mo*Kα* radiation (λ = 0.71075 Å). The structure was solved by direct methods (*SHELXT*-2014/5) and refined by the full-matrix least-squares on F^2 (*SHELXL*-2018/1).[S2] CCDC number is 1887276.

The diffraction data of **4Br4Ph** is collected by a RIGAKU R-AXIS RAPID-II IP Area Detector imaging plate with Cu*Kα* radiation (λ = 1.54186 Å). The structure was solved by direct methods (*SHELXT*-2014/5) and refined by the full-matrix least-squares on F^2 (*SHELXL*-2018/1). CCDC number is 1887275.

Table S1. Torsion angles of four phenyl groups from the pentacene skeleton

	1	2	3	4
4H4Ph[15]	76.9°	67.3°	–	–
4F4Ph	60.4°	66.0°	65.9°	58.7°
4Cl4Ph	65.2°	72.9°	70.5°	62.0°
4Br4Ph	67.6°	77.4°	86.7°	68.9°

Transfer integrals

In order to investigate intermolecular interactions, transfer integrals $t = ES$ were calculated from the intermolecular overlaps S for HOMO (t_h) and LUMO (t_e).[39] The HOMO and LUMO were calculated by the MOPAC, AM1 molecular orbital calculation,[S3,S4] and E is assumed to be –10 eV.

In addition, we have estimated transfer integrals using an energy-splitting approach by considering the energy levels of a diad.

$$t_{h[e]}^{eff} = (E_{H[L+1]} - E_{H-1[L]})/2$$

Here $E_{H[L]}$ and $E_{H-1[L+1]}$ are energies of the HOMO and HOMO–1 [LUMO and LUMO+1] levels taken from the neutral state of the intradimer and interdimer diads. These calculations were performed with the MOPAC, AM1 molecular orbital calculation.

Results in Fig. 3 are taken from Ref. 40, and adjusted to the present parameters.

4F4Ph *c*1

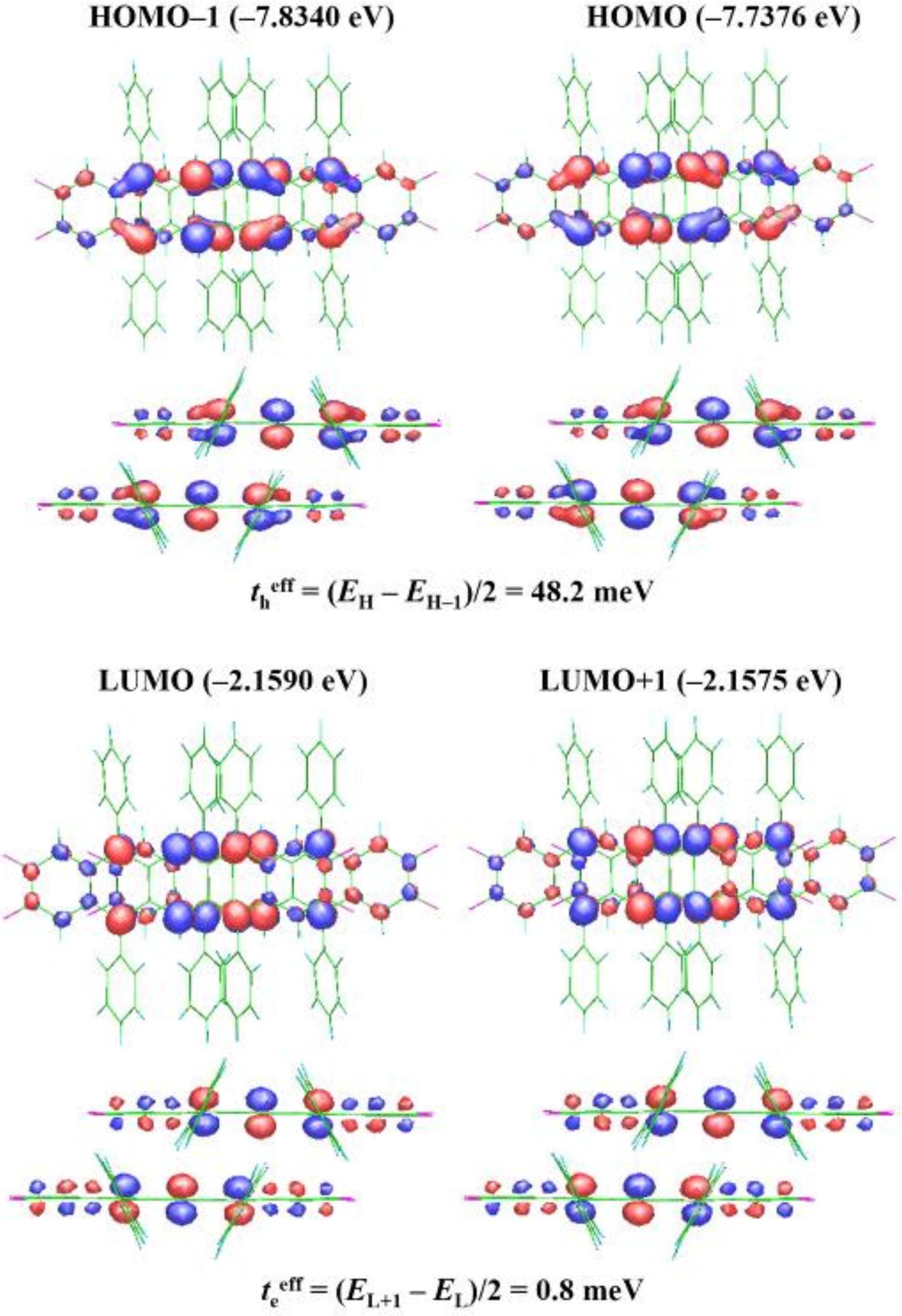


Figure S4. Energy-splitting estimation of the transfer integrals along the stacking direction in the **4F4Ph** intradimer interaction.

4F4Ph *c*2

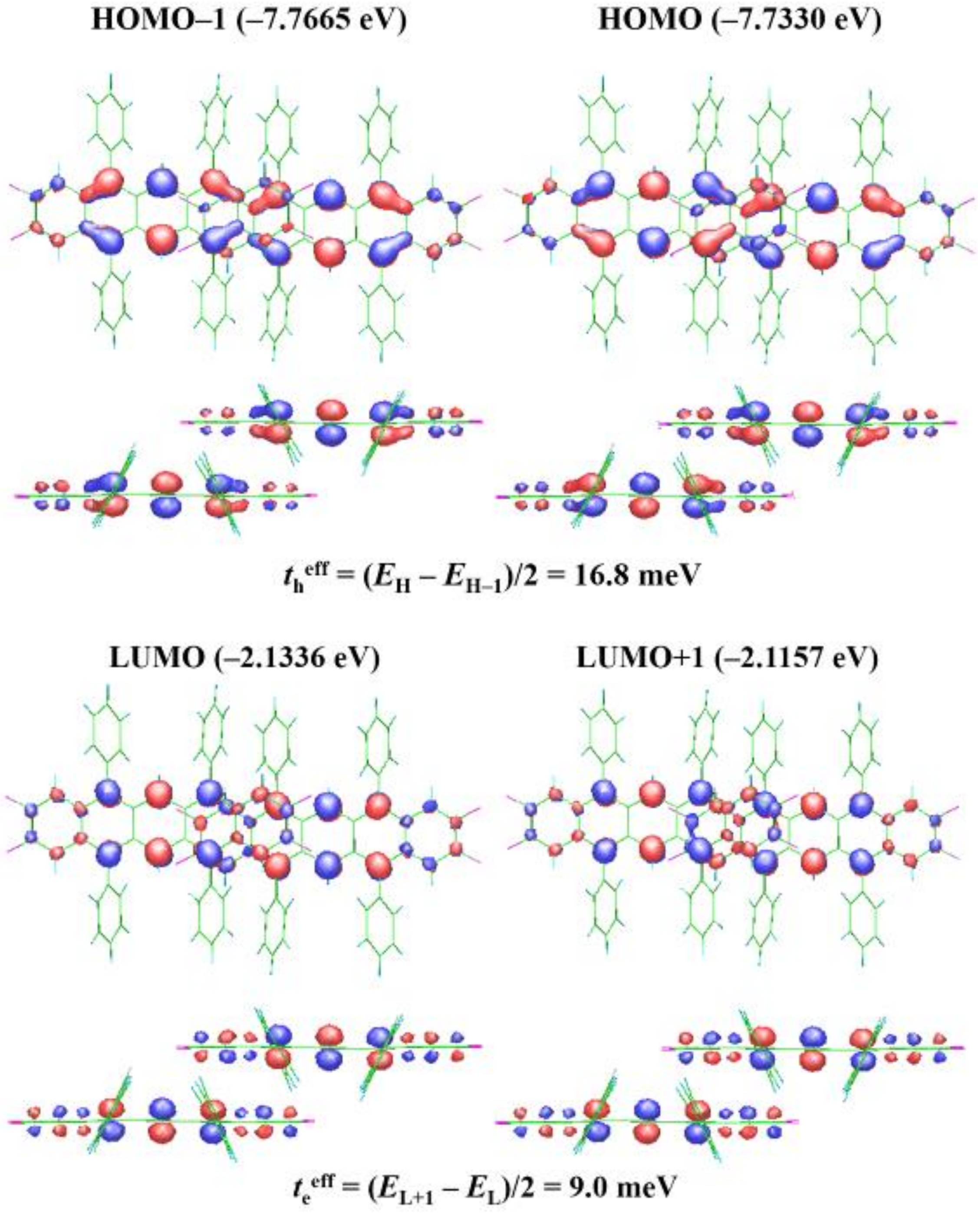


Figure S5. Energy-splitting estimation of the transfer integrals along the stacking direction in the **4F4Ph** interdimer interaction.

4Cl4Ph *c*1

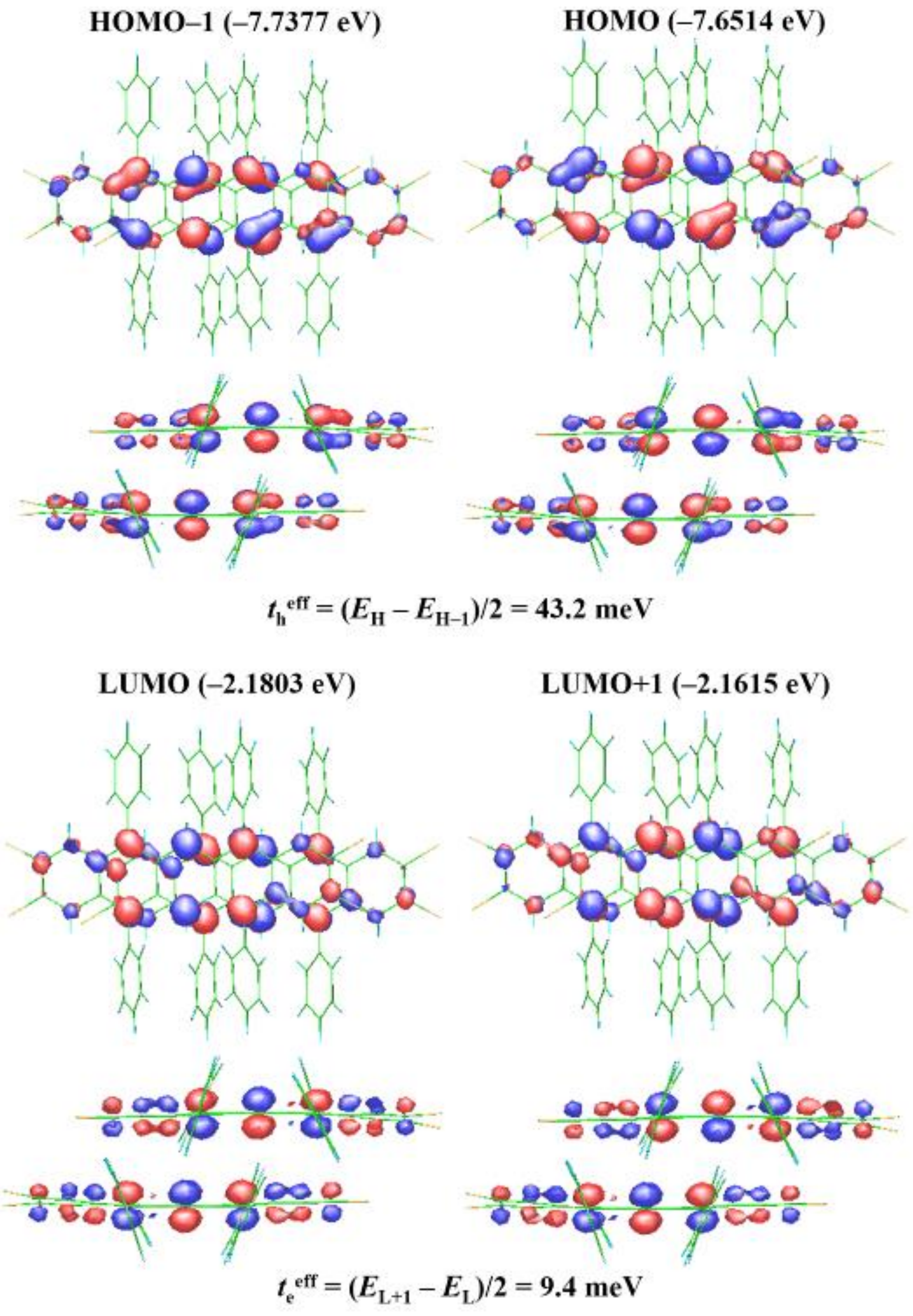


Figure S6. Energy-splitting estimation of the transfer integrals along the stacking direction in the **4Cl4Ph** intradimer interaction.

4Cl4Ph *c*2

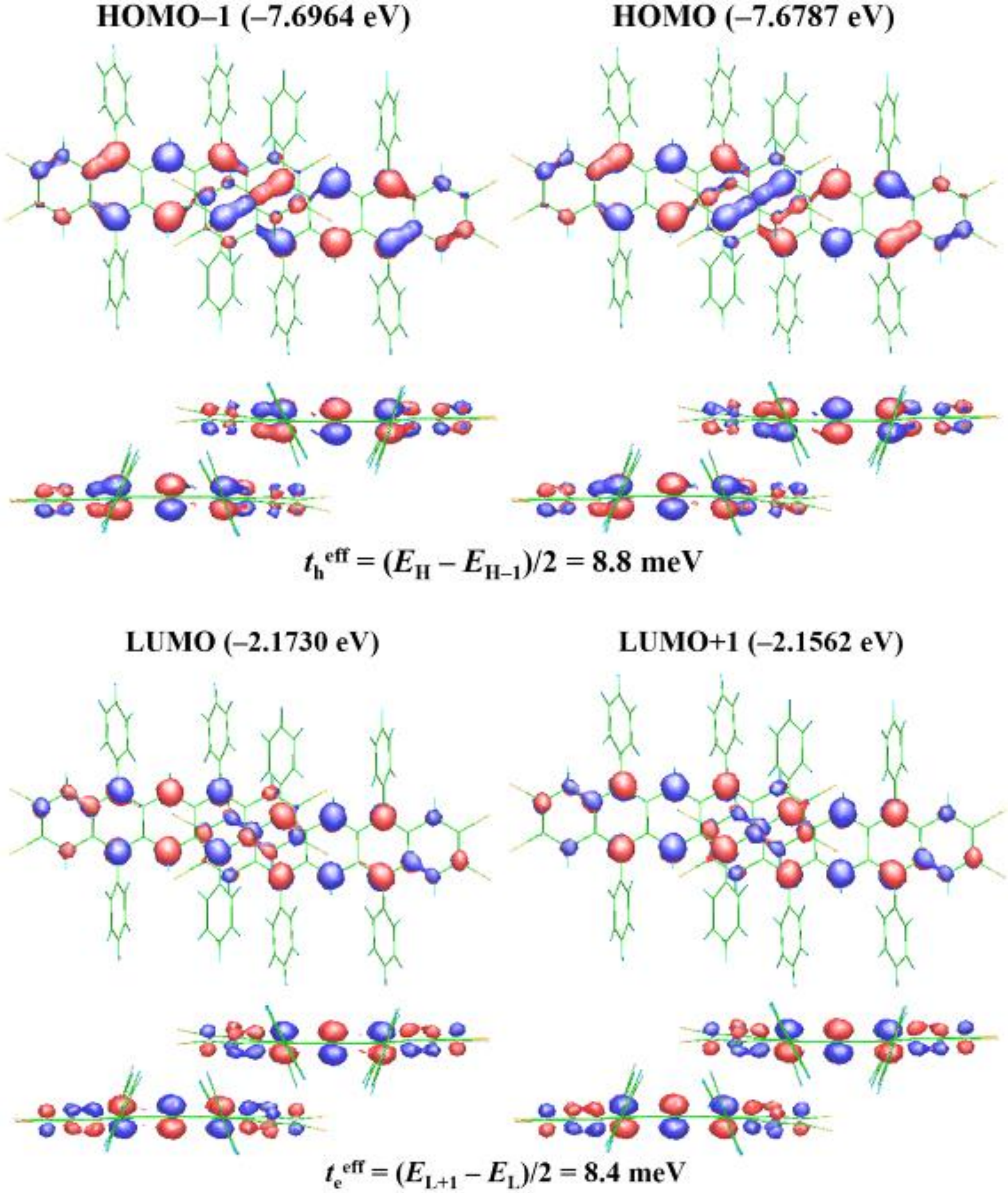


Figure S7. Energy-splitting estimation of the transfer integrals along the stacking direction in the **4Cl4Ph** interdimer interaction.

4Br4Ph *c*1

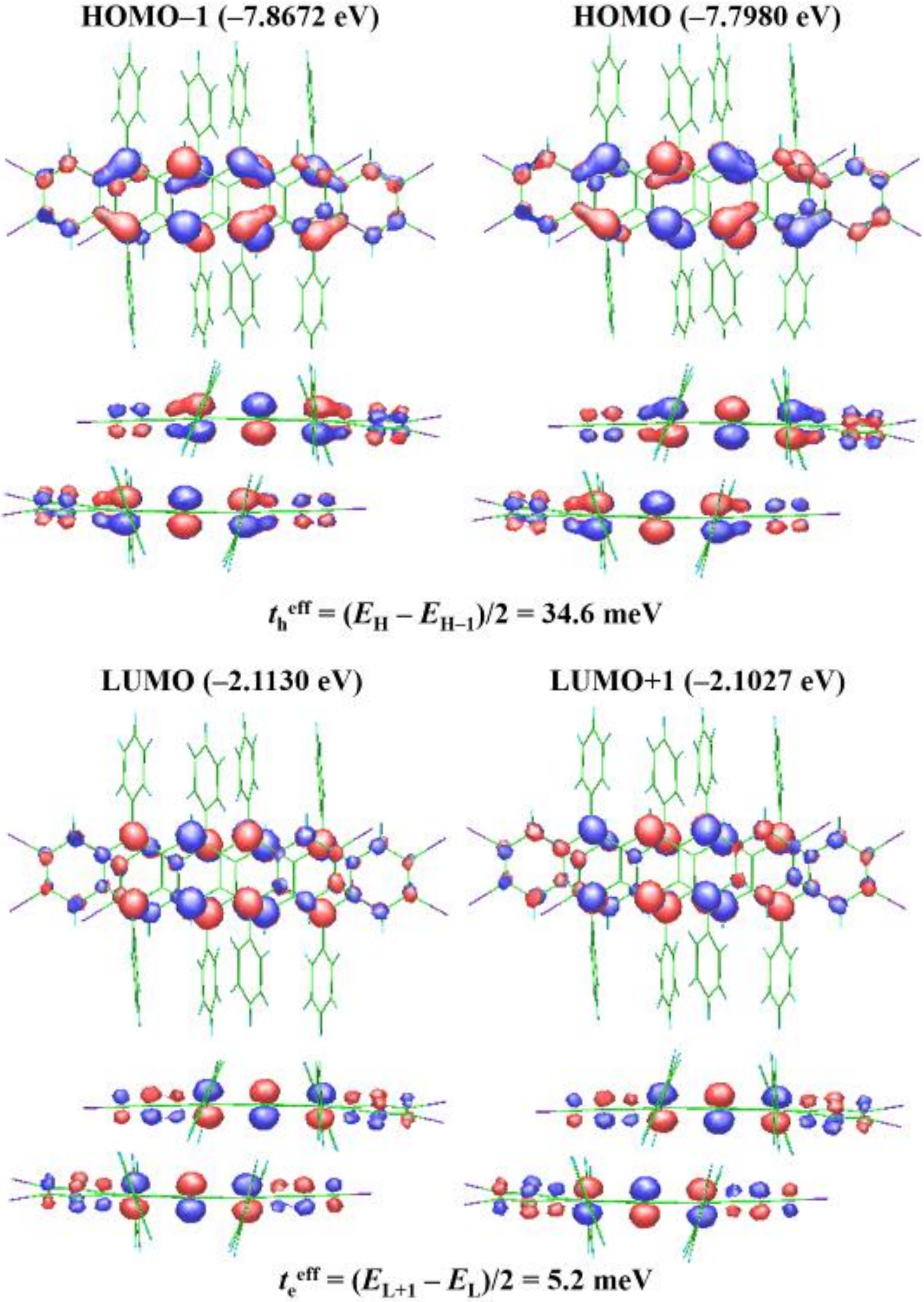
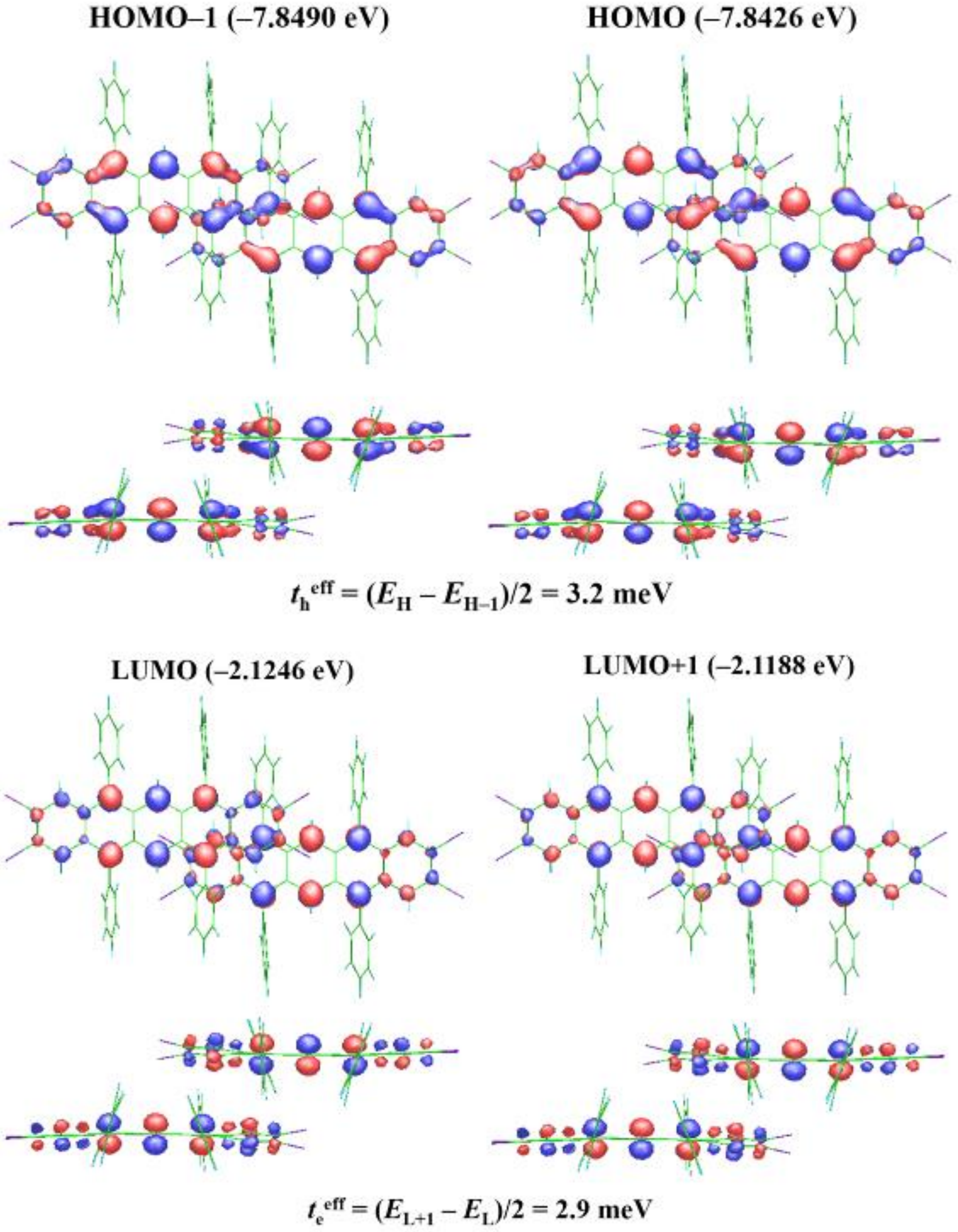


Figure S8. Energy-splitting estimation of the transfer integrals along the stacking direction in the **4Br4Ph** intradimer interaction.

4Br4Ph *c*2



HOMO–1 (–7.8490 eV)

HOMO (–7.8426 eV)

$t_{\mathrm{h}}^{\mathrm{eff}} = (E_{\mathrm{H}} - E_{\mathrm{H-1}})/2 = 3.2$ meV

LUMO (–2.1246 eV)

LUMO+1 (–2.1188 eV)

$t_{\mathrm{e}}^{\mathrm{eff}} = (E_{\mathrm{L+1}} - E_{\mathrm{L}})/2 = 2.9$ meV

Figure S9. Energy-splitting estimation of the transfer integrals along the stacking direction in the **4Br4Ph** interdimer interaction.

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