Supporting Information

1:2 Charge-transfer complexes of perylene and coronene with perylene diimide, and the ambipolar transistors

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Synthetis

CyHex-PDI was prepared following the reported method.^{S1} Perylene and coronene were purchased from Tokyo Chemical Industry and used as purchased.

CV measurements

Oxidation potentials were measured by CV on an ALS model 701E electrochemical analyzer using CH_2Cl_2 as the solvent and $Bu_4N \cdot PF_6$ as the electrolyte. The working electrode was glassy carbon, the counter electrode was platinum, and reference electrode was Ag/AgNO₃. 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 $-4.8 \text{ eV}.^{31}$

Single-crystal structures

Single crystals of the charge-transfer complexes were grown by the diffusion method in the chloroform solutions. Perylene or coronene was added in a side arm of an H-cell, and CyHex-PDI was added in another arm. Chloroform was added slowly, and after a one month at room temperature in the dark, black needle-like crystals were harvested (Fig. S1).

The X-ray oscillation photographs of **PEPDI** and **COPDI** were taken using a RIGAKU R-AXIS RAPID II imaging plate with Cu*K* α radiation from a rotation anode source with a confocal multilayer X-ray mirror (RIGAKU VM-Spider, $\lambda = 1.54187$ Å). The structures were solved by the direct method (SHELXT) and refined by the full-

matrix least-squares method by applying anisotropic temperature factors for all nonhydrogen atoms using the SHELXL programs.^{S2,S3} The hydrogen atoms were placed at geometrically calculated positions.



Figure S1. Crystals of (a) PEPDI and (b) COPDI.

Calculations of transfer integrals

Triad and tetrad methods



Figure S2. Estimation of effective transfer integrals along the stacking direction, from the ADA triad and the DAAD tetrad in (a) **PEPDI** and (b) **COPDI**.

Partition method

Direct transfer integrals are also evaluated on the basis of the frozen orbital approximation,^{27,28} and listed in the parentheses in Table 4. These values are, however, considerably smaller than the values obtained from the dimers. This is probably because orbital reorganization in the dimer calculation is significant in the present large molecules.

In order to estimate effective transfers by the partition method,^{29,30} not only the HOMO/LUMO transfers but also transfers to other orbitals are obtained similarly, and added as shown in Table S1.⁵

$$t^{eff} = \sum_{i} \frac{t_{0i} t_{i0}}{E_0 - E_i}$$
(S1)

In perylene, the HOMO–1 and HOMO–2 are nearly degenerate, and particularly the HOMO–1, as well as the HOMO, have large transfers with the PDI LUMO (Table S1) due to the similarity of the orbital symmetry (Fig. S3). These are major contributions to the electron transport. In coronene, pairs of HOMO/HOMO–1 and HOMO–2/ HOMO–3 are nearly degenerate, among which HOMO and HOMO–3 make large contributions to t_e^{eff} . Coronene has a rotation symmetry, and several orbitals are degenerate. This may be a reason to afford large transfers. Although partly canceled by HOMO–3, coronene has potentially larger t_e^{eff} .

Table S1.	Effective	transfers	calculated	by	the	partition	method
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(a) **PEPDI**

Electron				Hole				
$A L \rightarrow$	$E_{\rm A}-E_{\rm D}$	t	$t^2/(E_{\rm A}-E_{\rm D})$	$\rm D~H \rightarrow$	$E_{\rm D}-E_{\rm A}$	t_1	t_2	$t_1^2 t_2 / (E_A - E_D)^2$
DLg	-1520	46	-1.4	A L g	-1183	91	79	0.5
DHu	1183	91	-7.1	ΑHu	1015	124	91	1.3
D H–1 u	2753	130	-6.1					
D H–2 g	2936	33	0.4					
D H–3 g	2948	26	0.2					
D H–4 g	2984	30	0.3					
Total		$t_{\rm e}^{\rm eff}$	-13.7				$t_{\rm h}^{\rm eff}$	1.8

(b) COPDI

Electron				Hole				
$A L \rightarrow$	$E_{\rm A} - E_{\rm D}$	t	$t^2/(E_{\rm A}-E_{\rm D})$	$\rm DH \rightarrow$	$E_{\rm D}-E_{\rm A}$	t_1	t_2	$t_1^2 t_2 / (E_A - E_D)^2$
DLg	-2017	50	-1.3	A L g	-1634	90	32	0.1
DHu	1634	90	-5.0	ΑHu	602	109	127	4.2
D H–1 u	1650	32	-0.6					
D H–2 g	2884	6	0					
D H–3 g	2924	89	2.7					
D H-4 g	3285	50	0.8					
Total		$t_{\rm e}^{\rm eff}$	-3.4				$t_{\rm h}^{\rm eff}$	4.2



Figure S3. (a) Perylene, (b) coronene, and (c) PDI orbitals.

In order to estimate t_{h}^{eff} , we have to use the "second-order" partition method. The energy band of a DAA chain is obtained from the secular equation (Fig. S4).^{S4}

$$\begin{vmatrix} E_D - E & t_1 e^{ik_b b/3} & t_1 e^{-ik_b b/3} \\ t_1 e^{-ik_b b/3} & E_A - E & t_2 e^{ik_b b/3} \\ t_1 e^{ik_b b/3} & t_2 e^{-ik_b b/3} & E_A - E \end{vmatrix} = 0$$
(S2)

To obtain the energy dispersion around $E \sim E_D$, $E_A - E$ is approximated to be $E_A - E_D$, and the solution is

$$E = E_D + \frac{2t_1^2 t_2 \cos k_b b + 2t_1^2 (E_A - E_D)}{(E_A - E_D)^2 - t_2^2}.$$
 (S3)

Here t_h^{eff} is obtained so as to make the coefficient of the cos term afford the bandwidth $4t_h^{eff}$.

$$t_{h}^{eff} = \frac{t_{1}^{2}t_{2}}{\left(E_{A} - E_{D}\right)^{2} - t_{2}^{2}}$$
(S4)

Since $t_2 \sim 0.1$ eV is considerably smaller than $E_A - E_D \sim 1$ eV, t_2^2 in the denominator is neglected.

$$t_{h}^{eff} = \frac{t_{1}^{2}t_{2}}{\left(E_{A} - E_{D}\right)^{2}}$$
(S5)

In the "second-order" partition method mediated by two A molecules, $t_{\rm h}^{\rm eff}$ is by $t_2/(E_{\rm A} - E_{\rm D})$ times smaller than the ordinary trimer-based partition method $t_1^2/(E_{\rm A} - E_{\rm D})$. Accordingly, the former is approximately by one order smaller than the latter.

When more than two bridge orbitals are considered, the sign of eqn S5 does not depend on the sign of $E_A - E_D$, but depends on the sign of t_2 . Inclusion of deep levels is a complicated calculation because we have to consider such process as D HOMO \rightarrow A HOMO-1 \rightarrow A HOMO \rightarrow D HOMO. In **PEPDI**, the transfer between the D HOMO and the A HOMO is the main component, because, owing to the common perylene skeletone, these orbitals have practically the same shape (Fig. S3). **COPDI** has similar orbitals, and these routes are the main pathway of the hole transport.



Figure S4. Transfers in a DAA stack.

References

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- S4 T. Mori, *Electronic Properties of Organic Conductors*, Springer Japan, 2016.