## ELECTRONIC SUPPLEMENTARY INFORMATION

Substituent effect on the crystal packing and electronic coupling of tetrabenzocoronenes: a structure-property correlation

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#### **Materials and General Methods**

All chemicals were purchased from *Acros*, *Alfa Aesar*, *Merck*, and *Sigma-Aldrich*. Methylene chloride and toluene were distillated over calcium hydride under nitrogen atmosphere. All reactions were carried out using conventional *Schlenk* technique under nitrogen atmosphere. <sup>1</sup>H NMR spectra were recorded on a *Bruker* AMX 500 spetrometer. Proton chemical shifts ( $\delta$ ) are reported in ppm relative to the methine singlet at 7.24 ppm for the residual CHCl<sub>3</sub> in CDCl<sub>3</sub>, 5.32 ppm for CH<sub>2</sub>Cl<sub>2</sub> in CD<sub>2</sub>Cl<sub>2</sub>, or 2.50 ppm for DMSO in d<sub>6</sub>-DMSO. Molecular weight was determined by HR-FAB/HR-EI on a JMS-700 double focusing mass spectrometer (*JEOL*, Tokyo, Japan). MALDI mass spectrometry was recorded on a DE-PRO mass spectrometer (*Applied Biosystem*). Thermo gravimetric analysis (TGA) was carried out on a *Perkin Elmer* Pyris 1 thermogravimetric analyzer (heating rate: 10 °C / min). Reported decomposition temperatures represent the temperature observed at 5 % mass loss. The HOMO values were measured on a AC-2 photoelectron spectrometer (*Riken Keiki*) in solid state under ambient conditions. UV-Visible spectra were measured using a *Jasco* V-530 double beam spectrophotometer.

#### **Synthetic Details**

All reactions were carried out under similar conditions according to our previously reported publication as summarized in **scheme 1**.<sup>1</sup> The detailed synthetic procedure of dimethyl - substituted derivative **1d** was selected as the demonstrating example.

Scheme 1 Synthesis of tetrabenzocoronenes with unsymmetrical substitution



Reagents and conditions: I) CBr<sub>4</sub>, PPh<sub>3</sub>, 80 °C; II) substituted phenylboronic acid, K<sub>2</sub>CO<sub>3</sub>, Pd(PPh<sub>3</sub>)<sub>4</sub>, toluene, ethanol/H<sub>2</sub>O, reflux; III) I<sub>2</sub>, propylene oxide, benzene, hv; IV) FeCl<sub>3</sub>,CH<sub>2</sub>Cl<sub>2</sub>

#### Synthesis of 9-(Dibromomethylene)-10-(diphenylmethylene)-9,10-dihydroanthracene (2):

A mixture of carbon tetrabromide (11.7 g, 45 mmol), triphenylphosphine (8.32 g, 25 mmol), 9-Benzhydrylidene-10-anthrone (4 g, 11 mmol) was stirred in toluene (100 mL) at 80 °C overnight. After cooling to room temperature, the mixture was filtered, and the filtrate was concentrated, followed by washing with ethanol to give pure product as light yellow solid (4.56 g, 80 %).

<sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) δ 7.76 (d, *J* = 8.0 Hz, 2H), 7.30-7.07 (m, 12H), 6.98-6.86 (m, 4H).

<sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>) δ 141.89, 141.01, 140.87, 137.08, 136.68, 134.25, 129.48, 128.20, 127.03, 126.75, 126.55, 125.34, 88.41.

HRMS (MALDI) (m/z): [M+H]<sup>+</sup> calcd for C<sub>28</sub>H<sub>18</sub>Br<sub>2</sub> : 511.9775, found: 513.9793.

Anal. Calcd. C, 65.40; H, 3.53. Found: C, 65.5636; H, 3.7544.

#### 9-(Di-p-tolylmethylene)-10-(diphenylmethylene)-9,10-dihydroanthracene (3d):

A mixture of **2** (3 g, 5.8 mmol), tetrakis(triphenylphosphine) palladium(0) (0.34 g, 0.3 mmol), p-tolylboronic acid (2.38 g, 17.5 mmol), and toluene (100 mL), ethanol (2 mL), water (2 mL) was refluxed under nitrogen atmosphere overnight. After cooling to room temperature, the mixture was washed with water, and the organic layer was dried over anhydrous magnesium sulfate. The

crude product was purified by silica-gel column chromatography using hexane: dichloromethane = 2:1 as the eluent to give pure product as white solid (2.88 g, 92 %).

<sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>)  $\delta$  7.39 (d, J = 7.5 Hz, 4H), 7.28-7.24 (m, 8H), 7.17 (t, J = 7.3 Hz, 2H), 7.06 (d, J = 8.0 Hz, 4H), 7.00-6.95 (m, 4H), 6.71-6.69 (m, 4H), 2.28 (s, 6H).

<sup>13</sup>CNMR (125 MHz, CDCl<sub>3</sub>) δ 142.58, 139.91, 139.80, 139.65, 138.09, 137.79, 136.11, 135.79, 135.13, 129.73, 129.53, 128.88, 128.18, 127.96, 127.84, 126.59, 125.11, 124.97, 21.12.

HRMS (MALDI) (m/z): [M+H]<sup>+</sup> cal. For C<sub>42</sub>H<sub>33</sub>: 537.2582, found: 537.2596.

Anal. Calcd. C, 93.99; H, 6.01. Found: C, 93.7045; H, 6.1985.

#### 9-(Bis(4-fluorophenyl)methylene)-10-(diphenylmethylene)-9,10-dihydroanthracene (3b):

<sup>1</sup>H NMR (500MHz, CDCl<sub>3</sub>) δ 7.37-7.19 (m, 14H), 6.99-6.92 (m, 8H), 6.74-6.72 (m, 4H);

<sup>13</sup>CNMR (125 MHz, CDCl<sub>3</sub>) δ 162.69, 160.73, 142.39, 140.13, 137.81, 136.61, 135.39, 131.34, 131.28, 129.62, 128.24, 128.08, 127.77, 126.76, 125.39, 125.29, 115.36, 115.19.

HRMS (FAB+) (m/z):  $[M]^+$  cal. for  $C_{40}H_{26}F_2$ : 544.2003, found: 544.2004.

Anal. Calcd. C, 88.21; H, 4.81. Found C, 88.1831; H, 4.8863.

#### 9-(Bis(4-chlorophenyl)methylene)-10-(diphenylmethylene)-9,10-dihydroanthracene (3c)

<sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) δ 7.42-7.23 (m, 18H), 7.04-6.98 (m, 4H), 6.79-6.75 (m, 4H);

<sup>13</sup>CNMR (125 MHz, CDCl<sub>3</sub>) δ142.33, 140.52, 140.29, 137.76, 137.23, 137.04, 136.83, 135.28, 132.88, 131.09, 129.59, 128.57, 128.27, 128.13, 127.74, 126.80, 125.54, 125.41.

HRMS (FAB+) (m/z):  $[M]^+$  cal. for  $C_{40}H_{26}Cl_2$ : 576.1412; found: 576.1410.

Anal. Calcd. C, 83.19; H, 4.54. Found C: 83.4092; H: 4.7317.

#### 9-(Bis(4-(trifluoromethyl)phenyl)methylene)-10-(diphenylmethylene)-9,10dihydroanthracene (3e):

<sup>1</sup>H NMR (500MHz, CDCl<sub>3</sub>) δ 7.55 (d, *J* = 8.5 Hz, 4H), 7.50 (d, *J* = 8.5 Hz, 4H), 7.38 (d, *J* = 8.0 Hz, 4H), 7.29 (t, *J* = 7.5 Hz, 4H), 7.21 (t, *J* = 7.5 Hz, 2H), 7.02-6.89 (m, 4H), 6.76-6.73 (m, 4H).

<sup>13</sup>CNMR (125 MHz, CDCl<sub>3</sub>) δ 145.39, 142.23, 140.68, 137.72, 136.71, 136.60, 134.99,

130.14, 129.51, 129.34, 129.08, 128.32, 128.27, 127.65, 126.87, 125.81, 125.48, 125.43.

HRMS (FAB+) (m/z):  $[M]^+$  cal. for C<sub>42</sub>H<sub>26</sub>F<sub>6</sub>: 644.1939; found: 644.1946.

Anal. Calcd. C, 78.25; H, 4.07. Found: C, 78.2664; H, 4.0574.

# 9-(Bis(4-(tert-butyl)phenyl)methylene)-10-(diphenylmethylene)-9,10-dihydroanthracene (3f):

<sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) δ 7.41 (d, *J* = 7.5 Hz, 4H), 7.31-7.26 (m, 12H), 7.19 (t, *J* = 7.3 Hz, 2H), 6.97-6.93 (m, 4H), 6.69-6.66 (m, 4H), 1.28 (s, 18H).

<sup>13</sup>CNMR (125 MHz, CDCl<sub>3</sub>) δ149.37, 142.69, 139.86, 139.58, 138.07, 136.77, 135.78, 135.09, 129.75, 129.29, 128.21, 128.08, 127.81, 126.58, 125.02, 124.99, 124.85, 34.44, 31.36.

HRMS (MALDI) (m/z): [M+H]<sup>+</sup> cal. for C<sub>48</sub>H<sub>45</sub>: 620.3443; found: 620.3459.

Anal. Calcd. C, 92.86; H, 7.14. Found: C, 92.8569; H, 7.1301.

#### 9-(Bis(3,5-difluorophenyl)methylene)-10-(diphenylmethylene)-9,10-dihydroanthracene (3g):

<sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) δ 7.36 (d, *J* = 8.3 Hz, 4H), 7.28 (t, *J* = 7.5 Hz, 4H), 7.19 (t, *J* = 7.5 Hz, 2H), 7.00-6.70 (m, 14H).

<sup>13</sup>CNMR (125 MHz, CDCl<sub>3</sub>) δ 162.8, 144.45, 142.08, 141.00, 138.36, 137.66, 136.46, 134.93, 134.78, 129.49, 128.33, 128.29, 127.27, 126.92, 126.06, 125.62, 112.93, 102.82.

HRMS (MALDI) (m/z): [M]<sup>+</sup> cal. for C<sub>40</sub>H<sub>24</sub>F<sub>4</sub>: 572.1188; found: 572.1201.

Anal. Calcd. C, 82.75; H, 4.17. Found: C, 82.8586; H, 4.2496.

# 9-(Bis(3,4,5-trifluorophenyl)methylene)-10-(diphenylmethylene)-9,10-dihydroanthracene (3h):

<sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) δ 7.34 (d, *J* = 7.5 Hz, 4H), 7.28 (t, *J* = 7.8 Hz, 4H), 7.20 (t, *J* = 7.5 Hz, 2H), 7.02-6.79 (m, 12H);

<sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>) δ 152.17, 141.94, 141.24, 139.20, 139.12, 137.68, 137.00, 136.19, 134.72, 133.15, 129.42, 128.44, 128.38, 127.12, 127.04, 126.30, 125.76, 114.18.

HRMS (EI+) (m/z):  $[M]^+$  cal. for C<sub>40</sub>H<sub>22</sub>F<sub>6</sub>: 616.1626; found: 616.1628.

Anal. Calcd. C, 77.92; H, 3.60. Found: C: 77.7695; H: 3.7347.

#### Synthesis of 2, 7-Dimethyltetrabenzo[a,d,j,m]coronene (1d):

A mixture of **3d** (1.2 g, 9.31 mmol), iodine (1.7 g, 6.7 mmol), propylene oxide (48 mL) in benzene (700 mL) was stirred under UV- irradiation under nitrogen atmosphere for 16 hours. The solvent was rotary evaporated, and the mixture was filtered, washed with methanol and dried

under vacuum to give crude half-cyclized product. The crude product was dissolved in dry dichloromethane (700 mL), to which a solution of anhydrous iron chloride (4.38 g) in nitromethane (48 mL) was added in dropwisely. After stirring under nitrogen atmosphere for one hour, the reaction was stopped by adding methanol (500 mL). Yellow precipitate was filtered and purified by vacuum sublimation to give pure product as light yellow solid (0.4 g 33 %).

<sup>1</sup>H NMR (500 MHz, CD<sub>2</sub>Cl<sub>2</sub>,) δ 9.37 (s, 4H), 9.24-9.19 (m, 4H), 9.09 (d, *J* = 8.5 Hz, 2H), 8.97 (s, 2H), 7.96-7.85 (m, 4H), 7.69 (d, *J* = 8.0 Hz, 2H), 2.83 (s, 6H).

HRMS (EI+) (m/z): [M]<sup>+</sup> cal. for C<sub>42</sub>H<sub>24</sub> : 528.1878; found: 528.1877.

Anal. Calcd. C, 95.42; H, 4.58. Found: C, 95.3003; H, 4.6171.

#### 2, 7-Difluorotetrabenzo[a,d,j,m]coronene (1b):

HRMS (EI+) (m/z): [M]<sup>+</sup> cal. for C<sub>40</sub>H<sub>18</sub>F<sub>2</sub> : 536.1377; found: 536.1371.

Anal. Calcd. C, 89.54; H, 3.97; F, 3.38. Found C, 89.3063; H, 3.4131.

#### 2, 7-Dichlorotetrabenzo[a,d,j,m]coronene (1c):

HRMS (MALDI) (m/z): [M]<sup>+</sup> cal. for C<sub>40</sub>H<sub>18</sub>Cl<sub>2</sub> : 568.0786; found: 568.0803.

Anal. Calcd. C, 84.36; H, 3.19. Found: C, 84.2955; H, 3.2164.

#### 2, 7-Bis(trifluoromethyl)tetrabenzo[a,d,j,m]coronene (1e)

HRMS (EI+) (m/z): [M]<sup>+</sup> cal. for C<sub>42</sub>H<sub>18</sub>F<sub>6</sub>: 636.1313; found: 636.1314. Anal. Calcd. C, 79.24; H, 2.85. Found C, 79.2738; H, 2.8012.

#### 2, 7-Di-tert-butyltetrabenzo[a,d,j,m]coronene (1f):

<sup>1</sup>H NMR (500 MHz, d<sub>6</sub>-DMSO) δ 9.74 (d, *J* = 9.0 Hz, 2H), 9.66 (d, *J* = 9.0 Hz, 2H), 9.44 (d, *J* = 7.5 Hz, 2H), 9.32 (s, 2H), 9.23-9.17 (m, 4H), 8.09-7.97 (m, 6H), 1.65 (s, 18H).

HRMS (MALDI) (m/z):  $[M]^+$  cal. for C<sub>48</sub>H<sub>36</sub>: 620.3443; found: 620.3459.

Anal. Calcd. C, 94.08; H, 5.92. Found C, 94.0510; H, 5.9396.

#### 1, 3, 6, 8-Tetrafluorotetrabenzo[a,d,j,m]coronene (1g):

HRMS (MALDI) (m/z): [M]<sup>+</sup> cal. for C<sub>40</sub>H<sub>16</sub>F<sub>4</sub>: 572.1188; found: 572.1201. Anal. Calcd. C, 83.91; H, 2.82. Found C, 83.8950; H, 2.7235.

#### 1, 2, 3, 6, 7, 8-Hexafluorotetrabenzo[a,d,j,m]coronene (1h):

HRMS (EI+) (m/z):  $[M]^+$  cal. for  $C_{40}H_{14}F_6$ : 608.1000; found: 608.1003 Anal. Calcd. C, 78.95; H, 2.32. Found C, 78.9268; H, 2.6950.

## **Resutls of theoretical calculation**







**Table.** The ionization potential, electron affinity, reorganization energy, electronic couplings and mobilities of compound **1a**.

dimer	IP (eV) <sup>a</sup>	EA (eV) <sup>a</sup>	$\lambda^+$ (meV)	t+(meV)	$k_{et}$ (s <sup>-1</sup> )	$\mu^{+}(cm^{2}V^{-1}s^{-1})$	$d_{c-c}(A)$
1	6.343	1.135	132	41	2.12×10 <sup>13</sup>	0.58	3.77 <sup>b</sup>
2				2	6.25×10 <sup>10</sup>	0.01	10.67
3				<1	<10 <sup>10</sup>	< 0.01	14.16
4				1	<1010	< 0.01	16.25

<sup>a</sup> B3LYP/6-31+G(d)//B3LYP/6-31G(d,p) with Gaussian 09.

 $^{\rm b}$  For dimer 1,  $d_{\rm c\text{-}c}$  is the same as  $d_{\rm axis}.$ 



**Table.** The ionization potential, electron affinity, reorganization energy, electronic couplings and mobilities of compound **1b**.

dimer	IP (eV) <sup>a</sup>	EA (eV) <sup>a</sup>	$\lambda^+$ (meV)	t <sup>+</sup> (meV)	$k_{et}$ (s <sup>-1</sup> )	$\mu^+(cm^2V^-)^{1}s^{-1}$	d <sub>axis</sub> (Å)
$1 \rightarrow 1'$ (parallel) <sup>b</sup>	6.480	1.279	151	28	7.85x10 <sup>12</sup>	0.22	3.77
$1 \rightarrow 1' (anti-F_{out})^b$				28	7.85x10 <sup>12</sup>	0.22	3.77
$1 \rightarrow 1$ ' (anti- $F_{in}$ ) <sup>b</sup>				22	$4.84 \times 10^{12}$	0.13	3.77

<sup>b</sup> The exact positions of fluorine atoms are not known due to disorders in the X-ray coordinates. Therefore, parallel and antiparallel dimers are both calculated. Because the shift along the long molecular axis, the relationships for the antiparallel dimers along the  $\Box$ -stacking direction are 1) with the fluorine atoms of being farther from another molecule (anti-F<sub>out</sub>) and 2) being closer to another molecule (anti-F<sub>in</sub>). In Table 2, the antiparallel result is presented because it is more likely in terms of the molecular dipole-dipole interaction.



**Table.** The ionization potential, electron affinity, reorganization energy, electronic couplings and mobilities of compound **1c**.

dimer	IP (eV) <sup>a</sup>	EA (eV) <sup>a</sup>	$\lambda^+$ (meV)	t <sup>+</sup> (meV)	$k_{et}$ (s <sup>-1</sup> )	$\mu^{+}(cm^{2}V^{-1}s^{-1})$	$d_{c-c}(A)$
1→1'	6.502	1.379	143	22	5.38x10 <sup>12</sup>	0.15	3.77 <sup>b</sup>
1→2				1	$1.11 \times 10^{10}$	< 0.01	10.79
2→3				2	$4.44 \times 10^{10}$	0.01	12.13
6→9				<1	<10 <sup>10</sup>	< 0.01	14.15
2→5				1	1.11x10 <sup>10</sup>	< 0.01	14.18
3→6				1	$1.11 \times 10^{10}$	< 0.01	14.71
5→8				1	$1.11 \times 10^{10}$	< 0.01	14.75

 $^{\rm b}$  For dimer 1,  $d_{\rm c\text{-}c}$  is the same as  $d_{\rm axis}.$ 



**Table.** The ionization potential, electron affinity, reorganization energy, electronic couplings and mobilities of compound **1d**.

dimer	IP (eV) <sup>a</sup>	EA (eV) <sup>a</sup>	λ⁺(meV) <sup>ь</sup>	t⁺(meV)℃	k <sub>et</sub> (s <sup>-1</sup> )	μ+(cm²V <sup>-1</sup> s <sup>-1</sup> )	d <sub>c-c</sub> (Å) <sup>d</sup>
1→1'	6.203	1.062	134	7	6.14x10 <sup>11</sup>	0.02	4.23
						(0.02) <sup>e</sup>	(3.74) <sup>e</sup>
1→2				2	5.01x10 <sup>10</sup>	0.02	13.21
2→3				2	5.01x10 <sup>10</sup>	0.02	12.80
2'→3				<1	<1010	< 0.01	12.14

<sup>b</sup> Calculated with  $d_{axis}$ .



**Table.** The ionization potential, electron affinity, reorganization energy, electronic couplings and mobilities of compound **1e**.

dimer	IP (eV) <sup>a</sup>	EA (eV) <sup>a</sup>	$\lambda^+$ (meV)	t <sup>+</sup> (meV)	$k_{et}$ (s <sup>-1</sup> )	$\mu^{+}(cm^{2}V^{-1}s^{-1})$	$d_{c-c}(A)$
1→1'	6.720	1.624	148	35	$1.27 \times 10^{13}$	0.33 <sup>b</sup>	3.65 <sup>b</sup>
1→2				<1	<10 <sup>10</sup>	< 0.01	13.20
1'→2				2	4.16x10 <sup>10</sup>	0.02	13.99
2→3				1	$1.04 \times 10^{10}$	< 0.01	15.07
2'→3				3	9.36x10 <sup>10</sup>	0.04	14.08

<sup>b</sup> Calculated with  $d_{axis}$ .



**Table.** The ionization potential, electron affinity, reorganization energy, electronic couplings and mobilities of compound **1f**.

dimer	IP (eV) <sup>a</sup>	EA (eV) <sup>a</sup>	λ⁺(meV) <sup>ь</sup>	t⁺(meV)⁰	k <sub>et</sub> (s <sup>-1</sup> )	μ+(cm <sup>2</sup> V <sup>-1</sup> s <sup>-1</sup> )	d <sub>c-c</sub> (Å) <sup>d</sup>
3→1'	6.170	1.078	136	79	7.61x10 <sup>13</sup>	3.43	4.83
						(2.17) <sup>e</sup>	(3.84) <sup>e</sup>
1→2				56	3.82x10 <sup>13</sup>	3.14	6.52
						(1.09) <sup>e</sup>	(3.84) <sup>e</sup>
2→3				40	1.95x10 <sup>13</sup>	1.54	6.39
						(0.56) <sup>e</sup>	(3.84) <sup>e</sup>



**Table.** The ionization potential, electron affinity, reorganization energy, electronic couplings and mobilities of compound **1g**.

dimer	IP (eV) <sup>a</sup>	EA (eV) <sup>a</sup>	$\lambda^+$ (meV)	t <sup>+</sup> (meV)	$k_{et}$ (s <sup>-1</sup> )	$\mu^{+}(cm^{2}V^{-1}s^{-1})$	d <sub>axis</sub> (Å)
$1 \rightarrow 1$ ' (parallel) <sup>b</sup>	6.627	1.513	135	46	$2.61 \times 10^{13}$	0.71	3.75
$1 \rightarrow 1$ ' (anti-F <sub>out</sub> ) <sup>b</sup>				41	$2.08 \times 10^{13}$	0.56	3.75
$1 \rightarrow 1$ ' (anti- $F_{in}$ ) <sup>b</sup>				43	2.28x10 <sup>13</sup>	0.62	3.75

<sup>b</sup> The exact positions of fluorine atoms are not known due to disorders in the X-ray coordinates. Therefore, parallel and antiparallel dimers are both calculated. Because the shift along the long molecular axis, the possible relationships for the antiparallel dimers are 1) with the fluorine atoms of being farther from another molecule (anti- $F_{out}$ ) and 2) being closer to another molecule (anti- $F_{in}$ ).



**Table.** The ionization potential, electron affinity, reorganization energy, electronic couplings and mobilities of compound **1h**.

dimer	IP (eV) <sup>a</sup>	EA (eV) <sup>a</sup>	$\lambda^+$ (meV)	t <sup>+</sup> (meV)	$k_{et}$ (s <sup>-1</sup> )	$\mu^{+}(cm^{2}V^{-1}s^{-1})$	$d_{c-c}(A)$
1→3	6.736	1.630	147	75	5.93x10 <sup>13</sup>	1.47 <sup>b</sup>	3.58 <sup>b</sup>
3→5				59	$3.67 \times 10^{13}$	0.91 <sup>b</sup>	3.58 <sup>b</sup>
2→3				<1	<1010	< 0.01	11.73
4→5				2	$4.22 \times 10^{10}$	0.01	12.05
3→7				2	$4.22 \times 10^{10}$	0.01	13.29
1→7				<1	<10 <sup>10</sup>	< 0.01	14.93

 $^{b}$  Calculated with  $d_{axis}$ .

# TFTBC



**Table.** The ionization potential, electron affinity, reorganization energy, electronic couplings and mobilities of compound **TFTBC**.

dimer	IP (eV) <sup>a</sup>	EA (eV) <sup>a</sup>	$\lambda^{\!\!+\!}(meV)$	t <sup>+</sup> (meV)	$k_{et}$ (s <sup>-1</sup> )	$\mu^{+}(cm^{2}V^{-1}s^{-1})$	$d_{c-c}(A)$
1 <b>→</b> 1'	6.618	1.424	169	41	$1.34 \times 10^{13}$	0.36	3.72 <sup>b</sup>
1→2				3	7.15x10 <sup>10</sup>	0.02	11.31
1→3				<1	<10 <sup>10</sup>	< 0.01	14.97

<sup>a</sup>B3LYP/6-31+G(d)//B3LYP/6-31G(d,p) with Gaussian 09.

<sup>b</sup>  $d_{c-c}$  is the same as  $d_{axis}$ .

# тствс



**Table.** The ionization potential, electron affinity, reorganization energy, electronic couplings and mobilities of compound **TCTBC**.

dimer	IP (eV) <sup>a</sup>	EA (eV) <sup>a</sup>	$\lambda^+$ (meV)	t <sup>+</sup> (meV)	$k_{et}$ (s <sup>-1</sup> )	$\mu^{+}(cm^{2}V^{-1}s^{-1})$	$d_{c-c}(A)$
1 <b>→</b> 1'	6.652	1.609	154	51	2.50×10 <sup>13</sup>	0.68	3.75 <sup>b</sup>
1→3				10	9.63×10 <sup>11</sup>	0.36	13.87
1→3'				4	1.54×10 <sup>11</sup>	0.06	14.31
1 <b>→</b> b				4	1.54×10 <sup>11</sup>	0.06	14.39

<sup>a</sup>B3LYP/6-31+G(d)//B3LYP/6-31G(d,p) with Gaussian 09.

<sup>b</sup>  $d_{c-c}$  is the same as  $d_{axis}$ .

## TMTBC





top layer and black ones are at the bottom layer.

**Table.** The ionization potential, electron affinity, reorganization energy, electronic couplings and mobilities of compound **TMTBC**.

Dimer	IP (eV) <sup>a</sup>	EA (eV) <sup>a</sup>	□+(meV)	t <sup>+</sup> (meV)	$k_{et}$ (s <sup>-1</sup> )	$\mu^{+}(cm^{2}V^{-1}s^{-1})$	$d_{c-c}(A)$
1→1'	6.091	0.990	136	20	4.88x10 <sup>12</sup>	0.13 <sup>b</sup>	3.66 <sup>b</sup>
1→3				2	4.88x10 <sup>10</sup>	0.02	13.68
1'→3'				9	9.87x10 <sup>11</sup>	0.24	11.32
1→2				<1	<10 <sup>10</sup>	< 0.01	12.99
1'→2				1	$1.22 \times 10^{10}$	0.01	14.96

<sup>a</sup> B3LYP/6-31+G(d)//B3LYP/6-31G(d,p) with Gaussian 09.

<sup>b</sup> Calculated with  $d_{axis}$ .

### Reference

<sup>&</sup>lt;sup>1</sup> Pola, S.; Kuo, C. –H.; Peng, W. –T., Islam, Md. M.; Chao, I.; Tao, Y. T. *Chem. Mater.* **2012**, *24*, 2566.