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# **Supporting Information**

# I. Experimental Section

All experiments were performed under an atmosphere of dry argon using standard Schlenk techniques. Commercially available reagents were used as received without further purification. Solvents were freshly distilled under argon from sodium/benzophenone (diethyl ether, THF) or from phosphorus pentoxide (dichloromethane). <sup>1</sup>H, <sup>13</sup>C and <sup>31</sup>P NMR spectra were recorded on Bruker DPX200, AV300 or AV400 spectrometers. <sup>1</sup>H and <sup>13</sup>C NMR chemical shifts were reported in parts per million (ppm) relative to Me<sub>4</sub>Si as external standard. <sup>31</sup>P NMR downfield chemical shifts were expressed with a positive sign, in ppm, relative to 85% H<sub>3</sub>PO<sub>4</sub> respectively. Mass analyses and elemental analyses were performed by the CRMPO, University of Rennes 1. 1-Phenyl-2,5-bis(2-pyridyl)phosphole **C** was synthesized according to previously reported procedure.<sup>[Sup1]</sup>

### I.a) Synthesis of the homoditopic connectors 1-4



Scheme S1. Syntheses of the linkers 1-4

I.a.1) Synthesis of the derivative Sup2 Diethyl 4-cyanobenzylphosphonate



4-(Bromomethyl)benzonitrile **Sup1** (1.0 g, 5.1 mmol) and triethyl phosphite (2.2 ml, 12.7 mmol) were refluxed in 20 ml of CHCl<sub>3</sub> for 12 hours. Evaporation of the triethyl phosphite under vacuum gave an oil, which was recrystallized in warm pentane (500 ml) and gave a white solid (1.13 g, 4.5 mmol, 88%). <sup>1</sup>*H NMR* (200 *MHz*, *CDCl*<sub>3</sub>) :  $\delta$  = 1.31 (t, 6H, <sup>3</sup>*J*(H,H) = 7.1 Hz, H OCH<sub>2</sub>CH<sub>3</sub>), 3.23 (d, 2H, <sup>2</sup>*J*(P,H) = 22.3 Hz, H<sub>6</sub>), 4.16 (q, 4H, <sup>2</sup>*J*(P,H) = 7.1 Hz, <sup>3</sup>*J*(H,H) = 7.1 Hz, H OCH<sub>2</sub>CH<sub>3</sub>), 7.51 (AB system, 4H, v<sub>AB</sub> = 38.0 Hz, <sup>3</sup>*J*(H,H) = 8.0 Hz, H<sub>3,4</sub>). <sup>13</sup>*C*[<sup>1</sup>H] *NMR* (75.5 *MHz*, *CDCl*<sub>3</sub>):  $\delta$  = 16.3 (s, C OCH<sub>2</sub>CH<sub>3</sub>), 33.2 (d, <sup>1</sup>*J*(P,C) = 137.7 Hz, C<sub>6</sub>), 62.8 (s, C O<u>C</u>H<sub>2</sub>CH<sub>3</sub>), 111.3 (s, C) = 140.4 (c, C) + 140.4 (c, C

C<sub>2</sub>), 118.4 (s, C<sub>1</sub>), 131.0 (s, C<sub>3</sub>), 132.6 (s, C<sub>4</sub>), 138.1 (s, C<sub>5</sub>).

 $^{31}P{^{1}H} NMR (121.5 MHz, CDCl_3): \delta = +25.6 ppm.$ 

HR-MS (EI) calcd. for  $C_{12}H_{16}NO_3P$ : 253.0867, found: 253.0861.

I.a.2) Synthesis of the linker 1 4,4'-(octa-1,7-diyne-1,8-diyl)dibenzonitrile



To a 100 ml triethylamine solution of one equivalent of 1,8-octadiyne **Sup3** (0.36 ml, 2.74 mmol) and two equivalent of 4-bromobenzonitrile **Sup5** (1000 mg, 5.49 mmol) was added at room temperature a catalytic quantity of Pd(PPh<sub>3</sub>)<sub>2</sub>Cl<sub>2</sub> (77 mg, 0.11 mmol) and CuI (21 mg, 0.11 mmol). This mixture was stirred for 15 hours. An important quantity of precipitate was formed and the solution turned black. The solvent was evaporated under vacuum and the residue was extracted with  $3 \times 80$  ml of diethyl ether. We obtained **1** as a light yellow solid (800 mg, 2.57 mmol, yield 94%) by a column chromatography on silica gel (heptane/ethyl acetate, 80/20).

<sup>1</sup>*H NMR* (300 *MHz*, *CD*<sub>2</sub>*Cl*<sub>2</sub>):  $\delta = 1.82$  (broad s, 4H, H<sub>9</sub>), 2.55 (broad s, 4H, H<sub>8</sub>), 7.56 (AB system, 8H,  $v_{AB} = 31.7$ Hz, <sup>3</sup>*J*(H,H) = 9.0Hz, H<sub>3,4</sub>).

<sup>13</sup> $C{^{1}H}$  NMR (75.5 MHz,  $CD_2Cl_2$ ):  $\delta$  = 19.0 (s, C<sub>9</sub>), 27.6 (s, C<sub>8</sub>), 79.6 (s, C<sub>6</sub>), 94.8 (s, C<sub>7</sub>), 111.0 (s, C<sub>2</sub>), 118.5 (s, C<sub>1</sub>), 128.8 (s, C<sub>5</sub>), 132.0 (s, C<sub>3</sub> or C<sub>4</sub>), 132.1 (s, C<sub>4</sub> or C<sub>3</sub>).

HR-MS (EI) calcd. for C<sub>22</sub>H<sub>16</sub>N<sub>2</sub>Na<sup>+</sup>: 331.12112, found: 331.1211 (0 ppm).

*I.a.3*) Synthesis of the linker **3** 4,4'-(deca-1,9-diyne-1,10-diyl)dibenzonitrile



To a mixed triethylamine/THF solution (40 ml triethylamine, 40 ml THF) of 1,9-decadiyne **Sup4** (0.90 ml, 5,49 mmol) and 4-bromobenzonitrile **Sup5** (1000 mg, 5.49 mmol) was added at room temperature a catalytic quantity of Pd(PPh<sub>3</sub>)<sub>2</sub>Cl<sub>2</sub> (77 mg, 0.11 mmol) and CuI (21 mg, 0.11 mmol). This mixture was stirred over 15 hours. An important quantity of precipitate was formed and the suspension turned brown. The solvent was evaporated under vacuum and the residue was extracted with  $3 \times 80$  ml of diethyl ether. We obtained **3** as a light yellow solid (260 mg, 0.77 mmol, yield 14%) by a column chromatography on silica gel (heptane/ethyl acetate, 80/20).

<sup>1</sup>*H NMR* (200 *MHz*, *CDCl*<sub>3</sub>):  $\delta = 1.46-1.79$  (m, 8H, H<sub>9.10</sub>), 2.38-2.79 (m, 4H, H<sub>8</sub>), 7.53 (AB system, 8H,  $v_{AB} = 22.1$  Hz, <sup>3</sup>*J*(H,H) = 7.8 Hz, H<sub>3,4</sub>).

<sup>13</sup>*C*{<sup>1</sup>*H*} *NMR* (75.5 *MHz*, *CDCl*<sub>3</sub>):  $\delta$  = 19.9 (s, C<sub>10</sub>), 28.7 (s, C<sub>9</sub>), 28.8 (s, C<sub>8</sub>), 80.0 (s, C<sub>6</sub>), 95.8 (s, C<sub>7</sub>), 111.3 (s, C<sub>2</sub>), 119.0 (s, C<sub>1</sub>), 129.4 (s, C<sub>5</sub>), 132.4 (s, C<sub>3</sub>), 132.5 (s, C<sub>4</sub>).

HR-MS (Q-Tof 2) calcd. for C<sub>24</sub>H<sub>20</sub>N<sub>2</sub>Na<sup>+</sup>: 359.15242, found: 359.1525 (0 ppm).

I.a.4) Synthesis of the derivative Sup7 4,4'-(octa-1,7-diyne-1,8-diyl)dibenzaldehyde



To a triethylamine/THF solution (30 ml of triethylamine, 30 ml of THF) of one equivalent of 1,8-octadiyne **Sup3** (0.35 ml, 2.7 mmol) and two equivalent of 4-bromobenzaldehyde **Sup6** (1000 mg, 5.4 mmol) was added at room temperature a catalytic quantity of Pd(PPh<sub>3</sub>)<sub>2</sub>Cl<sub>2</sub> (76 mg, 0.11 mmol) and CuI (21 mg, 0.11 mmol). This mixture was stirred for 15 hours. An important quantity of precipitate was formed and the solution turned black. The solvent was evaporated under vacuum and the residue was extracted with  $3 \times 80$  ml of diethyl ether. We obtained **Sup7** a pale yellow solid (730 mg, 2.32 mmol yield 86%) by a column chromatography on silica gel (heptane/ethyl acetate, 80/20).

<sup>1</sup>*H NMR* (200 *MHz*, *CDCl*<sub>3</sub>):  $\delta = 1.84$  (broad s, 4H, H<sub>9</sub>), 2.55 (broad s, 4H, H<sub>8</sub>), 7.69 (AB system, 8H,  $v_{AB} = 52.8$ Hz, <sup>3</sup>*J*(H,H) = 8.3Hz, H<sub>3,4</sub>), 10.01 (s, 2H, H<sub>1</sub>).

<sup>13</sup> $C{^{1}H}$  NMR (75.5 MHz, CDCl<sub>3</sub>):  $\delta$  = 19.5 (s, C<sub>9</sub>), 28.1 (s, C<sub>8</sub>), 80.7 (s, C<sub>6</sub>), 94.9 (s, C<sub>7</sub>), 129.8 (s, C<sub>3</sub>), 130.7 (s, C<sub>5</sub>), 132.4 (s, C<sub>4</sub>), 135.6 (s, C<sub>2</sub>), 191.8 (s, C<sub>1</sub>).

HR-MS (EI) calcd. for C<sub>22</sub>H<sub>18</sub>O<sub>2</sub>: 314.13068, found: 314.1323 (5 ppm).

I.a.5) Synthesis of the derivative **Sup8** 4,4'-(deca-1,9-diyne-1,10-diyl)dibenzaldehyde

To a mixed triethylamine/THF solution (40 ml triethylamine, 40 ml THF) of one equivalent of 1,9-decadiyne **Sup4** (0.44 ml, 2.69 mmol) and two equivalent of 4-bromobenzaldehyde **Sup6** (1000 mg, 5.40 mmol) was added at room temperature a catalytic quantity of Pd(PPh<sub>3</sub>)<sub>2</sub>Cl<sub>2</sub> (76 mg, 0.11 mmol) and CuI (21 mg, 0.11 mmol). This mixture was stirred for 15 hours. An important quantity of precipitate was formed and the suspension turned brown. The solvent was evaporated under vacuum and the residue was extracted with  $3 \times 80$  ml of diethyl ether. We obtained **Sup8** as a yellow solid (780 mg, 2.28 mmol, yield 84%) by a column chromatography on silica gel (heptanes/ethyl acetate, 80/20).

<sup>1</sup>*H NMR* (300 *MHz*, *CDCl*<sub>3</sub>):  $\delta = 1.48-1.74$  (m, 8H, H<sub>9,10</sub>), 2.89-2.57 (m, 4H, H<sub>8</sub>), 7.67 (AB system, 8H, v<sub>AB</sub> = 80.4 Hz, <sup>3</sup>*J*(H,H) = 6.9 Hz, H<sub>3,4</sub>), 10.00 (s, 2H, H<sub>1</sub>).

<sup>13</sup>*C*{<sup>1</sup>*H*} *NMR* (75.5 *MHz*, *CDCl*<sub>3</sub>):  $\delta$  = 19.9 (s, C<sub>10</sub>), 28.7 (s, C<sub>9</sub>), 28.8 (s, C<sub>8</sub>), 80.7 (s, C<sub>6</sub>), 95.4 (s, C<sub>7</sub>), 129.9 (s, C<sub>4</sub>), 130.9 (s, C<sub>5</sub>), 132.5 (s, C<sub>3</sub>), 135.4 (s, C<sub>2</sub>), 191.9 (s, C<sub>1</sub>).

HR-MS (Q-Tof 2) calcd. for C<sub>24</sub>H<sub>22</sub>O<sub>2</sub>Na<sup>+</sup>: 365.15175, found: 365.1518 (0 ppm).

*I.a.6)* Synthesis of the linker **2** 4,4'-(1E,1'E)-2,2'-(4,4'-(octa-1,7-diyne-1,8-diyl)bis(4,1-phenylene))bis(ethene-2,1-diyl)dibenzonitrile



To a THF solution (60 ml) of diethyl 4-cyanobenzylphosphonate **Sup2** (500 mg, 1.97 mmol), was added 5 equivalents of NaH (237 mg, 9.87 mmol). This mixture was stirred for 2 hours and was added 0.5 equivalent of 4,4'-(octa-1,7-diyne-1,8-diyl)dibenzaldehyde **Sup7** (310 mg, 0.99 mmol). This mixture was stirred for 2 hours at room temperature. A yellow solid was obtained after a short column chromatography with THF and a washing with diethyl ether to give **2** as a pale yellow solid (430 mg, 0.84 mmol, yield 79%).

<sup>1</sup>*H NMR* (300 *MHz*, *CD*<sub>2</sub>*Cl*<sub>2</sub>):  $\delta = 1.83$  (broad s, 4H, H<sub>15</sub>), 2.54 (broad s, 4H, H<sub>14</sub>), 7.20 (AB system, 4H, v<sub>AB</sub> = 28.9 Hz, <sup>3</sup>*J*(H,H) = 16.0Hz, H<sub>6,7</sub>), 7.48 (AB system, 8H, v<sub>AB</sub> = 22.2 Hz, <sup>3</sup>*J*(H,H) = 9.0 Hz, H<sub>9,10</sub>), 7.66 (AB system, 8H, v<sub>AB</sub> = 12.0 Hz, <sup>3</sup>*J*(H,H) = 9.0 Hz, H<sub>3,4</sub>).

<sup>13</sup>C{<sup>1</sup>H} NMR (75.5 MHz,  $CD_2Cl_2$ ):  $\delta = 19.8$  (s,  $C_{15}$ ), 28.7 (s,  $C_{14}$ ), 80.4 (s,  $C_{12}$ ), 92.4 (s,  $C_{13}$ ), 111.5 (s,  $C_2$ ), 120.8 (s,  $C_1$ ), 124.9 (s,  $C_{11}$ ), 127.5 (s,  $C_9$ ), 127.7 (s,  $C_4$ ), 128.0 (s,  $C_7$ ), 132.3 (s,  $C_6$ ), 132.7 (s,  $C_3$ ), 133.3 (s,  $C_{10}$ ), 136.4 (s,  $C_8$ ), 141.4 (s,  $C_5$ ). HR-MS (Zabspec-Tof ) calcd. for  $C_{38}H_{28}N_2Na^+$ : 535.21502, found: 535.2142 (2 ppm).

I.a.7) Synthesis of the linker **4** 4,4'-(1E,1'E)-2,2'-(4,4'-(deca-1,9-diyne-1,10-diyl)bis(4,1-phenylene))bis(ethene-2,1-diyl)dibenzonitrile



450 mg (1.78 mmol) of diethyl 4-cyanobenzylphosphonate **23** and 105 mg (4.38 mmol) of NaH were mixed in 40ml of anhydrous THF and the reaction mixture was stirred for 2 hours. 300 mg (0.88 mmol) of 4,4'-(deca-1,9-diyne-1,10-diyl)dibenzaldehyde **65** in 20ml anhydrous THF was added and the reaction mixture was stirred for 4 hours at room temperature. We obtained **54** as a white solid after a short column chromatography of the crude solution on silica with THF (450 mg, 0.83 mmol, yield 95%).

<sup>1</sup>*H NMR* (300 *MHz*, *CDCl*<sub>3</sub>) :  $\delta$  = 1.38-1.78 (m, 8H, H<sub>15,16</sub>), 2.39-2.53 (m, 4H, H<sub>14</sub>), 7.14 (AB system, 4H, v<sub>AB</sub> = 30.0 Hz, <sup>3</sup>*J*(H,H) = 16.5 Hz, H<sub>6,7</sub>), 7.44 (AB system, 8H, v<sub>AB</sub> = 11.2 Hz, <sup>3</sup>*J*(H,H) = 8.1 Hz, H<sub>9,10</sub>), 7.62 (AB system, 8H, v<sub>AB</sub> = 18.9 Hz, <sup>3</sup>*J*(H,H) = 8.1 Hz, H<sub>3,4</sub>).

<sup>13</sup>C{<sup>1</sup>H} NMR (75.5 MHz, CDCl<sub>3</sub>):  $\delta$  = 19.4 (s, C<sub>16</sub>), 28.5 (s, C<sub>15</sub>), 28.6 (s, C<sub>14</sub>), 80.6 (s, C<sub>12</sub>), 92.0 (s, C<sub>13</sub>), 110.7 (s, C<sub>2</sub>), 119.0 (s, C<sub>1</sub>), 124.3 (s, C<sub>11</sub>), 126.7 (s, C<sub>9</sub>), 126.9 (s, C<sub>4</sub>), 127.1 (s, C<sub>7</sub>), 131.8 (s, C<sub>6</sub>), 132.0 (s, C<sub>3</sub>), 132.5 (s, C<sub>10</sub>), 135.4 (s, C<sub>8</sub>), 141.6 (s, C<sub>5</sub>).

HR-MS (Q-T of 2) calcd. for  $C_{40}H_{32}N_2Na^+$ : 563.24632, found: 563.2461 (0 ppm).

### *I.b.*) Synthesis of the supramolecular assemblies 5-8 and 11,12.

*I.b.1)* General procedure of the synthesis of supramolecular assemblies:

To a dichloromethane solution (15 ml) of ligand C (40 mg, 0.108 mmol) and  $[Cu(CH_3CN)_4]$ ·BF<sub>4</sub> (34 mg, 0.108 mmol) was added a dichloromethane solution of linker (0.5 equivalent). This reaction solution was stirred overnight and was left upon pentane vapor diffusion to afford desired assembly as a batch of crystals.

#### *I.b.2*) Synthesis of the supramolecular assembly 5.



Following the general procedure, the reaction of ligand C (60 mg, 0.162 mmol) and  $[Cu(CH_3CN)_4]$ ·BF<sub>4</sub> (51 mg, 0.162 mmol) with 0.5 equivalent of **1** (27 mg, 0.081 mmol) in 40 ml of CH<sub>2</sub>Cl<sub>2</sub> afforded after crystallization **5** as an air-stable orange solid (105 mg, 0.038 mmol, yield 95%).

<sup>1</sup>*H NMR* (300 *MHz*, *CDCl*<sub>3</sub>):  $\delta = 1.54$  (broad s, 8H, CCH<sub>2</sub>C*H*<sub>2</sub>), 1.85 (m, 8H, CCH<sub>2</sub>C*H*<sub>2</sub>), 2.53 (m, 8H, H<sub>c</sub>), 2.81 (m, 8H, H<sub>d</sub>), 3.11-3.88 (m, 16H, CC*H*<sub>2</sub>CH<sub>2</sub>), 7.26 (d, 8H, <sup>3</sup>*J*(H,H) = 6.6 Hz, H<sub>5</sub> Py), 7.41 (t, 20H, <sup>3</sup>*J*(H,H) = 8.4 Hz, H<sub>Ph</sub>), 7.61 (d, 8H, <sup>3</sup>*J*(H,H) = 6.6Hz, H<sub>3</sub> Py), 7.61 (broad s, 8H, H<sub>a,b</sub>), 7.95 (dd, 8H, <sup>3</sup>*J*(H,H) = 6.6 Hz, <sup>3</sup>*J*(H,H) = 6.6 Hz, H<sub>4</sub> Py), 8.5 (broad s, 8H, H<sub>a,b</sub>). H<sub>6</sub> Py).

 $^{31}P\{^{1}H\}$  NMR (121.5 MHz, CDCl<sub>3</sub>):  $\delta = +8.9$  (broad s).

Elemental analysis, calcd. (%) for C<sub>143</sub>H<sub>122</sub>B<sub>4</sub>Cl<sub>6</sub>Cu<sub>4</sub>F<sub>16</sub>N<sub>12</sub>P<sub>4</sub>: C 58.29, H 4.17, N 5.70; found: C 58.63, H 4.16, N 5.32.

## *I.b.3*) Synthesis of the supramolecular assembly **6**.



Following the general procedure, the reaction of ligand C (40 mg, 0.108 mmol) and  $[Cu(CH_3CN)_4]$ ·BF<sub>4</sub> (34 mg, 0.108 mmol) with 0.5 equivalent of 2 (28 mg, 0.054 mmol) in 25 ml of CH<sub>2</sub>Cl<sub>2</sub> afforded after crystallization **6** as an air-stable orange solid (46 mg, 0.015 mmol, yield 55%).

<sup>1</sup>*H NMR* (300 *MHz*, *CD*<sub>2</sub>*Cl*<sub>2</sub>):  $\delta$  = 1.44-1.78 (m, 16H, CCH<sub>2</sub>C*H*<sub>2</sub>), 1.86 (broad s, 8H, H<sub>h</sub>), 2.21-2.65 (m, 8H, CCH<sub>2</sub>CH<sub>2</sub>), 2.52 (broad s, 8H, H<sub>g</sub>), 2.88-3.14 (m, 8H, CCH<sub>2</sub>CH<sub>2</sub>), 7.09 (AB system, 8H, v<sub>AB</sub> = 54.6 Hz, <sup>3</sup>*J*(H,H) = 16.2 Hz, H<sub>c,d</sub>), 7.23-7.43 (m, 44H, H<sub>Ph</sub>, H<sub>e,f</sub> and H<sub>5</sub> Py), 7.47 (AB system, 16H, v<sub>AB</sub> = 14.9 Hz, <sup>3</sup>*J*(H,H) = 8.4 Hz, H<sub>a,b</sub>), 7.64 (broad s, 8H, H<sub>3</sub> Py), 7.93 (dd, 8H, <sup>3</sup>*J*(H,H) = 7.2 Hz, <sup>3</sup>*J*(H,H) = 7.2 Hz, H<sub>4</sub> Py), 8.51 (broad s, 8H, H<sub>6</sub> Py).

<sup>31</sup> $P{^{1}H}$  NMR (121.5 MHz,  $CD_2Cl_2$ ):  $\delta = +8.2$  (broad s).

Elemental analysis, calcd. (%) for C<sub>177</sub>H<sub>150</sub>B<sub>4</sub>Cl<sub>1</sub>Cu<sub>4</sub>F<sub>16</sub>N<sub>12</sub>P<sub>4</sub>: C 60.31, H 4.29, N 4.77; found: C 60.78, H 4.35, N 4.32.

# I.b.4) Synthesis of the supramolecular assembly 7.



Following the general procedure, the reaction of ligand C (40 mg, 0.108 mmol) and  $[Cu(CH_3CN)_4]$ ·BF<sub>4</sub> (34 mg, 0.108 mmol) with 0.5 equivalent of **3** (18 mg, 0.054 mmol) in 25 ml of CH<sub>2</sub>Cl<sub>2</sub> afforded after crystallization **7** as an air-stable red-orange solid (32 mg, 0.012 mmol, yield 44%).

<sup>1</sup>*H NMR* (300 *MHz*, *CD*<sub>2</sub>*Cl*<sub>2</sub>):  $\delta$  = 1.54-1.73 (m, 16H, H<sub>d,e</sub>), 1.78-1.94 (m, 16H, CCH<sub>2</sub>CH<sub>2</sub>), 2.48-2.56 (m, 8H, H<sub>c</sub>), 2.92-3.09 (m, 16H, CCH<sub>2</sub>CH<sub>2</sub>), 7.26 (d, <sup>3</sup>*J*(H,H) = 6.5 Hz, 8H, H<sub>5</sub> Py), 7.31-7.46 (m, 36H, H<sub>a,b</sub> and H<sub>Ph</sub>), 7.61 (d, 8H, *J*(H,H) = 7.0 Hz, H<sub>3</sub> Py), 7.92 (dd, 8H, <sup>3</sup>*J*(H,H) = 7.0 Hz, <sup>3</sup>*J*(H,H) = 6.5 Hz, H<sub>4</sub> Py), 8.50 (broad s, 8H, H<sub>6</sub> Py). <sup>31</sup>*P*{<sup>1</sup>*H*} *NMR* (121.5 *MHz*, *CD*<sub>2</sub>*Cl*<sub>2</sub>):  $\delta$  = +7.9 (broad s).

 $Elemental \ analysis, \ calcd. \ (\%) \ for \ C_{151}H_{138}B_4Cl_{14}Cu_4F_{16}N_{12}P_4: \ C \ 54.26, \ H \ 4.16, \ N \ 5.03; \ found: \ C \ 54.53, \ H \ 4.08, \ N \ 4.62.$ 

#### *I.b.5*) Synthesis of the supramolecular assembly 8.



Following the general procedure, the reaction of ligand C (40 mg, 0.108 mmol) and  $[Cu(CH_3CN)_4]$ ·BF<sub>4</sub> (34 mg, 0.108 mmol) with 0.5 equivalent of **4** (29 mg, 0.054 mmol) in 25 ml of CH<sub>2</sub>Cl<sub>2</sub> afforded after crystallization **8** as an air-stable orange solid (63 mg, 0.020 mmol, yield 74%).

<sup>1</sup>*H NMR* (300 *MHz*, *CD*<sub>2</sub>*Cl*<sub>2</sub>):  $\delta$  = 1.42-2.04 (m, 32H, CCH<sub>2</sub>C*H*<sub>2</sub> and H<sub>h,i</sub>), 2.53 (broad s, 8H, H<sub>g</sub>), 2.88-3.18 (m, 16H, CC*H*<sub>2</sub>CH<sub>2</sub>), 7.03 (AB system, 8H, v<sub>AB</sub> = 20.8 Hz, <sup>3</sup>*J*(H,H) = 16.2 Hz, H<sub>c,d</sub>), 7.21-7.56 (m, 60H, H<sub>5</sub> Py, H<sub>Ph</sub> and H<sub>a,b,e,f</sub>), 7.64 (d, 8H, <sup>3</sup>*J*(H,H) = 6.5 Hz, H<sub>3</sub> Py), 7.95 (dd, 8H, <sup>3</sup>*J*(H,H) = 7.4 Hz, <sup>3</sup>*J*(H,H) = 6.5 Hz, H<sub>4</sub> Py), 8.50 (broad s, 8H, H<sub>6</sub> Py). <sup>31</sup>*P*{<sup>1</sup>*H*} *NMR* (121.5 *MHz*, *CD*<sub>2</sub>*Cl*<sub>2</sub>):  $\delta$  = + 7.8 (broad s).

Elemental analysis, calcd. (%) for C<sub>180</sub>H<sub>156</sub>B<sub>4</sub>Cl<sub>8</sub>Cu<sub>4</sub>F<sub>16</sub>N<sub>12</sub>P<sub>4</sub>: C 61.84, H 4.17, N 4.81; found: C 61.93, H 4.10, N 4.67.

## I.b.6) Synthesis of the supramolecular assembly 11.



Following the general procedure, the reaction of ligand C (40 mg, 0.108 mmol) and  $[Cu(CH_3CN)_4]$ ·PF<sub>6</sub> (34 mg, 0.092 mmol) with one equivalent of **9** (7.4 mg, 0.108 mmol) in 25 ml of CH<sub>2</sub>Cl<sub>2</sub> afforded after crystallization **11** as an air-stable orange solid (45 mg, 0.038 mmol, yield 71%).

<sup>1</sup>*H NMR* (*300 MHz, CD*<sub>2</sub>*Cl*<sub>2</sub>) :  $\delta$  = 1.24-1.98 (m, 12H, CCH<sub>2</sub>C*H*<sub>2</sub> and H<sub>b</sub>), 2.02-2.34 (m, 4H, CC*H*<sub>2</sub>CH<sub>2</sub>), 2.48 (t, 4H, <sup>3</sup>*J*(H,H) = 6.0 Hz, H<sub>a</sub>), 2.76-3.12 (m, 4H, CC*H*<sub>2</sub>CH<sub>2</sub>), 7.12-7.48 (m, 14H, H<sub>5</sub> Py and H<sub>Ph</sub>), 7.53 (s, 4H, H<sub>3</sub> Py), 7.87 (dd, <sup>3</sup>*J*(H,H) = 6.0 Hz, <sup>3</sup>*J*(H,H) = 6.0 Hz, 4H, H<sub>4</sub> Py), 8.48 (broad s, 4H, H<sub>6</sub> Py). <sup>31</sup>*P*[<sup>1</sup>H] *NMR* (*121.5 MHz, CD*<sub>2</sub>*Cl*<sub>2</sub>) :  $\delta$  = +9.2 (broad s).

Elemental analysis, calcd. (%) for C<sub>109</sub>H<sub>102</sub>B<sub>4</sub>Cl<sub>2</sub>Cu<sub>4</sub>F<sub>16</sub>N<sub>12</sub>P<sub>4</sub>: C 55.09, H 4.33, N 7.07; found: C 55.31, H 4.21, N 6.85.

I.b.7) Synthesis of the supramolecular assembly 12.



Following the general procedure, the reaction of ligand C (40 mg, 0.108 mmol) and  $[Cu(CH_3CN)_4]$ ·BF<sub>4</sub> (34 mg, 0.108 mmol) with 1.4 equivalent of **10** (20.6 mg, 0.15 mmol) in 25 ml of CH<sub>2</sub>Cl<sub>2</sub> afforded after crystallization **12** as an air-stable redorange solid (53 mg, 0.023 mmol, yield 84%).

<sup>1</sup>*H NMR* (*300 MHz, CD<sub>2</sub>Cl<sub>2</sub>*):  $\delta = 0.76-2.02$  (m, 24H, CCH<sub>2</sub>CH<sub>2</sub> and H<sub>b,c</sub>), 2.09 (s, 6H, CH<sub>3</sub>CN), 2.18-2.42 (m, 8H, CCH<sub>2</sub>CH<sub>2</sub>), 2.51 (t, 4H, <sup>3</sup>*J*(H,H) = 6.0 Hz, H<sub>a</sub>), 2.86-3.15 (m, 8H, CCH<sub>2</sub>CH<sub>2</sub>), 7.18-7.47 (m, 28H, H<sub>5</sub> Py and H<sub>Ph</sub>), 7.55 (d, 8H, <sup>3</sup>*J*(H,H) = 6.0 Hz, H<sub>3</sub> Py), 7.88 (dd, <sup>3</sup>*J*(H,H) = 6.0 Hz, <sup>3</sup>*J*(H,H) = 6.0 Hz, 8H, H<sub>4</sub> Py), 8.46 (broad s, 8H, H<sub>6</sub> Py). <sup>31</sup>*P*{<sup>1</sup>*H*} *NMR* (*121.5 MHz, CD<sub>2</sub>Cl<sub>2</sub>): \delta = +7.9 (broad s).* 

Elemental analysis, calcd. (%) for  $C_{114}H_{112}B_4Cl_4Cu_4F_{16}N_{12}P_4$ : C 54.39, H 4.48, N 5.63; found: C 54.76, H 4.35, N 5.07.

# II. X-ray Crystallographic Study.

Single crystals of **5**, **6**, **7**, **8**, **11** and **12** suitable for X-Ray crystal analyses were obtained by slow diffusion of vapors of pentane into dichloromethane solutions. Single crystal data collection were performed at 100 K or at 150 K with an APEX II Bruker-

AXS (Centre de Diffractométrie, Université de Rennes 1, France) with Mo- $K\alpha$  radiation ( $\lambda = 0.71073$  Å). Reflections were indexed, Lorentz-polarization corrected and integrated by the *DENZO* program of the KappaCCD software package. The data merging process was performed using the SCALEPACK program.<sup>[Sup2]</sup> Structure determinations were performed by direct methods with the solving program SIR97,<sup>[Sup3]</sup> that revealed all the non hydrogen atoms. SHELXL program<sup>[Sup4]</sup> was used to refine the structures by full-matrix least-squares based on  $F^2$ . All non-hydrogen atoms were refined with anisotropic displacement parameters. Hydrogen atoms were included in idealised positions and refined with isotropic displacement parameters.

In the crystal lattices of the coordination complexes studied, dichloromethane solvent molecules were found in addition to the cationic coordination complexes and to their counter-anions. These solvent molecules in most cases have a strong tendency to leave the bulk crystal via evaporation once the crystals are removed from their mother solution, a process that induce a rapid degradation of the single-crystal integrity of the crystals investigated. In order to slow down this process, single crystals of all these derivatives were always coated in paratone oil once removed from the mother solution, mount at low temperature (100 K or 150 K) as quickly as possible on the diffractometer gionometer and X-ray data collection were performed at low temperature (100 K or 150 K). In most of the case, X-ray crystal structure resolution revealed the counter-anions and solvent molecules highly disordered. In the case of the supramolecular assembly **5** modelling of the disorder of the counter-anion and solvent molecules was possible leading to rather high anisotropic displacement parameters for some of their atoms. Nevertheless, anisotropic displacement parameters associated to the atoms of the cationic coordination complexes are always satisfactory. This allows a primarily assignment of these modest R factor to an inadequate modelling of the disordered species exterior to this supramolecular assembly and leads confidence to the treatment of the structural resolution of these derivatives. Table S1 gives the crystallographic data for this derivative **5**.

In the case of the supramolecular assemblies 7 and 8, disordered  $CH_2Cl_2$  molecules occupy an important volume of the crystal cell and are found highly disorder. A modelling of these disorders was not possible and we have proceeded to a 'squeeze' treatment in order to remove the scattering contribution of these molecules which can not be satisfactory modelled. In these cases, anisotropic displacement parameters associated to the atoms of the cationic coordination complexes and their counteranions are always satisfactory. Table S1 gives the crystallographic data for the derivatives 7 and 8 after this 'squeeze' treatment. Table S1b gives the crystallographic data for the derivatives 7 and 8 before 'squeeze' treatment. In the case of the supramolecular assemblies 6, 11 and 12, disordered  $CH_2Cl_2$  molecules and disordered counter-anions are highly delocalized and it was not possible to localize them. We have proceeded to a 'squeeze' treatment in order to remove the scattering contribution of these molecules ( $CH_2Cl_2$  molecules and counter-anions) which can not be satisfactory modelled. Table S1 gives the crystallographic data for the derivatives 7 the satisfactory modelled. Table S1 gives the crystallographic data for the derivatives 6, 11 and 12 after this 'squeeze' treatment. Table S1b gives the crystallographic data for the derivatives 6, 11 and 12 before such 'squeeze' treatment. Table S1b gives the crystallographic data for the derivatives 6, 11 and 12 before such 'squeeze' treatment. Finally, in several of these X-ray structures, some of the fused cyclohexyl rings of the phosphole ring of the ligands **B** are disordered over two symmetrical positions. The modelling of this disorder was not possible and consequently these rings appears planar with rather short interatomic distances for  $Csp^3$  atoms (origin of some ALERTs A in the checkcif report).

Atomic scattering factors for all atoms were taken from International Tables for X-ray Crystallography.<sup>[Sup5]</sup> CCDC reference numbers 899323, 899321, 899319, 899322, 899318 and 1063053 contain the supplementary crystallographic data for derivatives **5**, **6**, **7**, **8**, **11** and **12** respectively. These data can be obtained free of charge at www.ccdc.cam.ac.uk/conts/retreving.html or from the Cambridge Crystallographic Data Center, 12 union Road, Cambridge CB2 1EZ, UK; Fax: (internat.) + 44-1223-336-033; E-mail: deposit@ccdc.cam.ac.uk]

	5.4BF4.6CH2Cl2	6
Molecular formula	$C_{146}H_{128}B_4Cl_{12}Cu_4F_{16}N_{12}P_4\\$	$C_{172}H_{140}Cu_4N_{12}P_4$
CCDC number	899323	899321
Molecular weight	3201.28	2753.00
<i>a</i> (Å)	13.887(2)	15.705(2)
<i>b</i> (Å)	15.375(2)	17.816(2)
<i>c</i> (Å)	18.799(2)	21.535(2)
α(°)	101.562(4)	107.871(4)
β(°)	105.589(4)	104.457(4)
γ(°)	101.967(4)	97.386(4)
$V(\text{\AA}^3)$	3639.7(8)	5413.8(11)
Ζ	1	1
<i>D</i> c (g cm <sup>-3</sup> )	1.461	0.844
Crystal system	Triclinic	Triclinic
Space group	P-1	P-1
Temperature (K)	100(2)	100(2)
Wavelength Mo-Ka (Å)	0.71069	0.71069
Crystal size (mm)	0.3 * 0.15 * 0.08	0.4 * 0.2 * 0.1
$\mu$ (mm <sup>-1</sup> )	0.916	0.456
<i>F</i> (000)	1632	1432
$\theta$ limit (°)	1.17 -26.46	1.04 - 26.42
Index ranges hkl	$-17 \le h \le 17,$	$-19 \le h \le 19,$
	$-18 \le k \le 19$ ,	$-22 \le k \le 22,$

Table S1. Crystal data and structure refinement for 5, 6, 7, 8, 11 and 12

	$-23 \le l \le 23$	$-26 \le l \le 26$
Reflections collected	36995	45854
Independant reflections	14600	21982
Reflections $[I > 2\sigma(I)]$	9708	9948
Data/restraints/parameters	14600 / 0 / 893	21982 / 0 / 866
Goodness-of-fit on $F^2$	1.122	0.931
Final <i>R</i> indices $[I > 2\sigma(I)]$	R1 = 0.0672	<i>R</i> 1=0.843
	<i>wR</i> 2= 0.1683	wR2= 0.2170
R indices (all data)	<i>R</i> 1= 0.1133	<i>R</i> 1= 0.1413
	wR2= 0.1992	wR2= 0.2346
Largest diff peak and hole (e ${\rm \AA}^{-3})$	1.794 and -1.337	0.657 and -0.485

	7.4BF4	8.4BF4	
Molecular formula	$C_{144}H_{124}B_4Cu_4F_{16}N_{12}P_4\\$	$C_{176}H_{148}B_4Cu_4F_{16}N_{12}P_4\\$	
CCDC number	899319	899322	
Molecular weight	2747.83	3156.34	
<i>a</i> (Å)	15.189(2)	15.582(3)	
<i>b</i> (Å)	15.957(2)	17.047(2)	
<i>c</i> (Å)	23.446(2)	22.619(2)	
α (°)	107.923(4)	102.262(3)	
β(°)	101.304(4)	104.435(3)	
γ(°)	104.447(4)	102.171(3)	
$V(\text{\AA}^3)$	5001.2(10)	5460.5(13)	
Ζ	1	1	
<i>D</i> c (g cm <sup>-3</sup> )	0.912	0.960	
Crystal system	Triclinic	Triclinic	
Space group	P-1	P-1	
Temperature (K)	150(2)	100(2)	
Wavelength Mo-Kα (Å)	0.71069	0.71069	
Crystal size (mm)	0.2 * 0.14 * 0.09	0.2 * 0.14 * 0.06	
$\mu$ (mm <sup>-1</sup> )	0.503	0.468	
<i>F</i> (000)	1412	1628	
$\theta$ limit (°)	0.96 - 26.88	1.27 – 26.60	
Index ranges hkl	$-19 \le h \le 18,$	$-19 \le h \le 18,$	
	$-20 \le k \le 20,$	$-19 \le k \le 21,$	
	$-29 \le l \le 29$	$-23 \le l \le 28$	
Reflections collected	55607	40112	
Independant reflections	20832	21964	
Reflections $[I > 2\sigma(I)]$	9974	13244	
Data/restraints/parameters	20832 / 0 / 838	21964 / 0 / 974	

Largest uni peak and note (e A )	0.005 and -0.851	1.022 and -0.704
I argost diff peak and hole (a $Å^{-3}$ )	0.665 and 0.851	1.022 and 0.764
	<i>wR</i> 2= 0.1614	wR2= 0.1976
R indices (all data)	R1 = 0.1048	<i>R</i> 1= 0.1014
	wR2 = 0.14/6	wR2 = 0.1874
		<b>P2</b> 0 1974
Final <i>R</i> indices $[I > 2\sigma(I)]$	R1 = 0.0598	<i>R</i> 1= 0.0723
Goodness-of-fit on $F^2$	0.883	1. 097

	11	12	
Molecular formula	$C_{54}H_{50}B_4Cu_2N_6P_2\\$	$C_{108}H_{102}Cu_4N_{12}P_4$	
CCDC number	899318	1063053	
Molecular weight	972.02	1946.06	
<i>a</i> (Å)	26.589(1)	25.7551(14)	
<i>b</i> (Å)	17.564(1)	20.5086(8)	
<i>c</i> (Å)	29.171(1)	24.6987(14)	
α(°)	90	90	
β(°)	106.352(2)	95.409(2)	
γ(°)	90	90	
$V(\text{\AA}^3)$	13072.1(10)	12987.8(11)	
Ζ	8	4	
$Dc (g cm^{-3})$	0.988	0.995	
Crystal system	Monoclinic	Monoclinic	
Space group	C2/c	C2/c	
Temperature (K)	100(2)	100(2)	
Wavelength Mo-Kα (Å)	0.71069	0.71069	
Crystal size (mm)	0.21 * 0.08 * 0.07	0.24 * 0.15 * 0.11	
$\mu$ (mm <sup>-1</sup> )	0.731	0.736	
<i>F</i> (000)	4032	4040	
$\theta$ limit (°)	2.78 - 27.16	1.27 – 26.45	
Index ranges hkl	$-33 \le h \le 33,$	$-32 \le h \le 32,$	
	$-19 \le k \le 22,$	$-14 \le k \le 25,$	
	-37 ≤ <i>l</i> ≤ 37	$-30 \le l \le 23$	
Reflections collected	25063	34353	
Independant reflections	14411	13049	
Reflections $[I > 2\sigma(I)]$	6337	7048	
Data/restraints/parameters	14411 / 0 / 577	13049/ 0 / 579	
Goodness-of-fit on $F^2$	0.895	0.900	
Final <i>R</i> indices $[I > 2\sigma(I)]$	<i>R</i> 1= 0.0864	<i>R</i> 1= 0.0660	
	<i>wR</i> 2= 0.2221	wR2= 0.1768	

R indices (all data)	<i>R</i> 1= 0.1636	<i>R</i> 1= 0.1053		
	<i>wR</i> 2= 0.2523	wR2=0.1932		
Largest diff peak and hole (e $Å^{-3}$ )	0.544 and -0.417	1.312 and -0.737		

# $Table\ S1b$ . Crystal data and structure refinement for $6,\,7$ and 8 before the 'squeeze' treatment

	6.4BF <sub>4</sub> .22CH <sub>2</sub> Cl <sub>2</sub>	7.4BF4.24CH2Cl2
Molecular formula	$C_{194}H_{172}B_4Cl_{44}Cu_4F_{16}N_{12}P_4\\$	$C_{168}H_{128}B_4Cl_{50}Cu_4F_{16}N_{12}P_4\\$
Molecular weight	4956.52	4812.60
<i>a</i> (Å)	15.705(2)	15.189(2)
<i>b</i> (Å)	17.816(2)	15.957(2)
<i>c</i> (Å)	21.535(2)	23.446(2)
α(°)	107.871(4)	107.923(4)
$\beta$ (°)	104.457(4)	101.304(4)
γ(°)	97.386(4)	104.447(4)
$V(\text{\AA}^3)$	5413.8(11)	5001.2(10)
Ζ	1	1
<i>D</i> c (g cm <sup>-3</sup> )	1.520	1.598
Crystal system	Triclinic	Triclinic
Space group	P-1	P-1
Temperature (K)	100(2)	150(2)
Wavelength Mo-Kα (Å)	0.71069	0.71069
Crystal size (mm)	0.4 * 0.2 * 0.1	0.2 * 0.14 * 0.09
$\mu$ (mm <sup>-1</sup> )	1.027	1.187
<i>F</i> (000)	2508	2410
$\theta$ limit (°)	1.04 - 26.42	0.96 - 26.88
Index ranges hkl	$-19 \le h \le 190,$	$-19 \le h \le 18$ ,
	$-22 \le k \le 22,$	$-20 \le k \le 20,$
	$-26 \le l \le 26$	$-29 \le l \le 29$
Reflections collected	45854	55607
Independant reflections	21982	20832
Reflections $[I > 2\sigma(I)]$	11769	10738
Data/restraints/parameters	21982 / 0 / 1232	20832 / 0 / 1226
Goodness-of-fit on $F^2$	1.658	1.204

Final <i>R</i> indices $[I > 2\sigma(I)]$	R1 = 0.1799	R1 = 0.1150	
	wR2= 0.4593	wR2= 0.3093	
R indices (all data)	<i>R</i> 1= 0.2547	<i>R</i> 1= 0.2016	
	wR2= 0.4994	<i>wR</i> 2= 0.3738	
Largest diff peak and hole (e $Å^{-3}$ )	2.375 and -1.592	1.856 and -1.218	

	8·4BF4·20CH2Cl2	11. 2PF6·3CH2Cl2	12. 4BF4·7.5CH2Cl2
Molecular formula	$C_{196}H_{176}B_4Cl_{40}Cu_4F_{16}N_{12}P_4\\$	$C_{60}H_{56}Cl_6Cu_2F_{12}N_6P_4$	$C_{115}H_{106}B_4Cl_{15}Cu_4F_{16}N_{12}P_4\\$
Molecular weight	4842.77	1552.81	2913.15
<i>a</i> (Å)	15.582(3)	26.589(1)	25.7551(14)
<i>b</i> (Å)	17.047(2)	17.564(1)	20.5086(8)
<i>c</i> (Å)	22.619(2)	29.171(1)	24.6987(14)
α(°)	102.262(3)	90	90
β(°)	104.435(3)	106.352(2)	95.409(2)
γ(°)	102.171(3)	90	90
$V(\text{\AA}^3)$	5460.5(13)	13072.1(10)	12987.8(11)
Ζ	1	8	4
$Dc (g cm^{-3})$	1.473	1.468	1.490
Crystal system	Triclinic	Monoclinic	Monoclinic
Space group	P-1	C2/c	C2/c
Temperature (K)	100(2)	100(2)	100(2)
Wavelength Mo-Kα (Å)	0.71069	0.71069	0.71069
Crystal size (mm)	0.2 * 0.14 * 0.06	0.21 * 0.08 * 0.07	0.24 * 0.15 * 0.11
$\mu$ (mm <sup>-1</sup> )	0.969	1.067	1.078
<i>F</i> (000)	2456	5808	5900
$\theta$ limit (°)	1.27 - 26.60	2.78 - 27.16	1.27 – 26.45
Index ranges hkl	$-19 \le h \le 18,$	$-33 \le h \le 33,$	$-32 \le h \le 32,$
	$-19 \le k \le 21,$	$-19 \le k \le 22$ ,	$-14 \le k \le 25$ ,
	$-23 \le l \le 28$	$-37 \le l \le 37$	$-30 \le l \le 23$
Reflections collected	40112	25063	34353
Independant reflections	21964	14411	13049
Reflections $[I > 2\sigma(I)]$	14408	6923	7294
Data/restraints/parameters	21964 / 0 / 1325	14411 / 0 / 866	13049/ 0 / 579
Goodness-of-fit on $F^2$	1.260	0.895	0.900
Final <i>R</i> indices $[I > 2\sigma(I)]$	R1= 0.1018	<i>R</i> 1= 0.1492	R1 = 0.1230
	wR2= 0.3030	wR2= 0.3790	wR2=0.3534
R indices (all data)	R1 = 0.1469	<i>R</i> 1= 0.2510	<i>R</i> 1= 0.1926
	w <b>R</b> 2=0.3411	wR2= 0.4366	wR2= 0.4060
Largest diff peak and hole (e Å-3)	1.493 and -1.651	1.603 and -1.138	1.917 and -1.335

**Table S2**. Selected bond lengths [Å], angles [°] and torsion angle of the  $Cu_2(N\mu$ -PN) moieties in the derivatives **6-10** and **11,12**, in the molecular clip **A** and in a selection of metallocyclophanes  $C^{[sup6]}$  and  $D^{[sup7]}$ 



	Cu-µP	Cu–N	Cu⋯Cu	N-Cu-µP	Cu-µP- Cu	μP-Cu-Cu	Cu-NC-	CN-Cu-Cu-
10								NC
$\mathbf{A}^{[1]}$	2.3487(8)	2.056(2)	2.5638(10)	83.86(6)	66.11(3)	57.00(3)	1.989(2)	33.46
	2.2540(10)	2.047(2)		84.80(6)		56.89(2		
5	2.2907(12)	2.064(4)	2.5946(11)	84.93(11)	67.33(5)	58.22(4)	2.048(4)	32.91
	2.3915(14)	2.044(4)		82.67(12)		54.51(3)	1.986(4)	
6	2.309(3)	2.056(9)	2.6306(19)	84.9(3)	67.92(9)	57.66(8)	2.059(12)	32.55
	2.398(3)	2.039(9)		83.4(3)		54.42(7)	2.003(10)	
7	2.387(2)	2.030(7)	2.6071(16)	85.0(2)	67.94(7)	54.02(5)	1.992(7)	32.06
	2.276(2)	2.043(7)		84.27(19)		58.04(6)	2.056(6)	
8	2.3786(17)	2.034(5)	2.6095(12)	84.77(15)	67.91(5)	54.47(4)	1.979(5)	37.51
	2.2919(17)	2.052(5)		84.72(15)		57.63(5)	2.064(6)	
11	2.3473(17)	2.041(5)	2.5538(11)	85.72(16)	66.83(4)	55.49(5)	1.982(5)	35.46
	2.2891(16)	2.026(5)		84.30(17)		57.67(5)	2.061(5)	
12	2.3069(11)	2.037(4)	2.5740(8)	84.23(10)	67.08(3)	55.64(3)	1.978(4)	33.7
	2.3511(11)	2.057(4)		84.71(10)		57.28(3)	2.039(4)	
C1	2.3118(13)	2.096(4)	2.5622(10)	81.10(11)	66.16(3)	58.23(4)	2.035(4)	36.0
	2.3815(13)	2.037(4)		84.46(11)		55.62(3)	2.042(4)	
C2	2.2935(10)	2.052(3)	2.6117(9)	84.24(9)	67.82(3)	57.77(3)	2.089(3)	28.0
	2.3858(11)	2.049(3)		84.44(9)		54.41(2)	1.998(3)	
C3	2.3994(11)	2.077(3)	2.6294(6)	83.87(9)	68.21(3)	53.87(3)	1.997(3)	27.0
	2.2871(11)	2.061(3)		85.94(10)		57.92(3)	2.058(4)	
C4	2.440(3)	2.086(6)	2.661(2)	85.90(18)	67.99(8)	53.79(6)	2.028(6)	30.0
	2.315(3)	2.117(7)		85.9(2)		58.22(8)	2.058(6)	
C5	2.2987(16)	2.040(4)	2.6019(12)	83.99(11)	67.33(5)	54.60(4)	2.002(4)	28.7
	2.3932(14)	2.070(4)		85.93(15)		58.07(4)	2.040(5)	
C6 <sup>[a]</sup>	2.347(2)	2.036(6)	2.5659(13)	85.3(2)	67.17(6)	55.39(5)	1.921(8)	33.3
	2.291(2)	2.034(7)		85.32(19)		57.44(6)	2.065(8)	
C7 <sup>[b]</sup>	2.3659(19)	2.032(6)	2.5947(12)	85.06(15)	67.44(6)	55.21(5)	1.978(6)	30.6
	2.307(2)	2.029(6)		85.32(18)		57.36(5)	2.055(6)	
	2.4045(19)	2.069(6)	2.6100(12)	84.38(15)	67.64(6)	53.93(5)	1.961(6)	30.2
	2.281(2)	2.057(6)		84.13(17)		58.43(5)	2.024(6)	
C8	2.3128(13)	2.050(4)	2.5736(9)	84.95(11)	66.45(3)	58.09(4)	2.035(4)	28.7
	2.3831(13)	2.056(4)		83.53(11)		55.47(3)	2.004(4)	
C9[c]	2.328(2)	2.075(6)	2.6131(12)	85.37(19)	67.91(5)	56.45(5)	2.075(6)	35.6
	2.3502(19)	1.985(6)		85.86(17)		55.64(5)	2.041(6)	
	2.403(2)	2.031(6)	2.6121(14)	84.26(18)	67,74(6)	53.91(5)	1.983(5)	33.8
	2.2809(19)	2.071(7)	. ,	85.71(18)		58.35(6)	2.069(6)	
C10	2.3578(17)	2.042(4)	2.5820(9)	84.50(15)	67.27(4)	55.35(3)	1.984(5)	26.0
	2.3028(13)	2.023(5)		83.83(11)		57.38(4)	2.023(5)	
C11	2.2745(17)	2.064(6)	2.5539(11)	85.03(14)	67.08(6)	57.81(6)	1.967(7)	30.1
	2.347(2)	2.036(5)	. ,	83.40(19)	. /	55.11(4)	1.947(8)	
D1	2.2988(11)	2.055(3)	2.6118(9)	83.41(10)	67.74(3)	57.72(3)	2.016(3)	16.8
	2.3860(13)	2.071(4)		85,73(10)		54,54(3)	1.968(3)	
D2	2.288(4)	2.060(11)	2,604(3)	85,5(3)	67.85(11)	57.68(11)	2.003(11)	28.5
	2 376(4)	2 058(15)		83 3(4)		54 47(10)	1.967(11)	

[a] twisted-ribbon geometry, [b] two independent supramolecular rectangles in the unit cell, [c] These supramolecular assemblies are non centrosymetric, [e] value observed for CH- $\pi$  distance, [f] BF4<sup>-</sup> salt

Scheme S2. Labelling scheme adopted for the atoms of the molecular clips in the supramolecular assemblies 5, 6, 7, 8, 11 and 12.



Figure S1. Molecular structure of the cationic part of the complex 5 (thermal ellipsoids 50% probability). Hydrogen atoms have been omitted for clarity.



Figure S2. Molecular structure of the cationic part of the complex 6 (thermal ellipsoids 50% probability). Hydrogen atoms have been omitted for clarity.



**Figure S3**. Molecular structure of the cationic part of the complex 7 (thermal ellipsoids 50% probability). Hydrogen atoms have been omitted for clarity.



Figure S4. Molecular structure of the cationic part of the complex 8 (thermal ellipsoids 50% probability). Hydrogen atoms have been omitted for clarity.



Figure S5 . Molecular structure of the cationic part of the complex 11 (thermal ellipsoids 50% probability). Hydrogen atoms have been omitted for clarity.



Figure S6 . Molecular structure of the cationic part of the complex 12 (thermal ellipsoids 50% probability). Hydrogen atoms have been omitted for clarity.



**Figure S7**. 'Side' and 'lateral' views of the stacking patterns of  $\pi$ -stacked assemblies **5-8** observed in single crystals.



# **III.** References for the supplementary information part.

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