

## Supporting Information File

### Halogen-Bonded One-dimensional Chains of Functionalized Ditopic Bipyridines Cocrystallized with Mono-, Di-, and Triiodofluorobenzenes

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## S.1 Experimental

### S.1.1 Materials and Methods

**General methods.** All reagents and solvents employed here were commercially available and used as supplied without further purification. Thin-layer chromatography (TLC) was carried out on silica gel plates (Silica gel 60, F254, Merck) with detection by UV light. Purifications were performed with preparative chromatography using normal-phase silica gel (Silica gel 60, 230-400 mesh, Merck). The pyridine molecular tectons **I**, **II**, **III** and their respective precursors were characterized with nuclear magnetic resonance (NMR) spectroscopy, high-resolution mass spectrometry (HRMS), infra-red spectroscopy (IR), UV-visible spectroscopy (UV-Vis) and elemental analysis. NMR spectra were recorded on a Bruker AM 500 spectrometer (500 MHz for  $^1\text{H}$  / 125 MHz for  $^{13}\text{C}$ ) as solutions in  $\text{CDCl}_3$ . Chemical shifts  $\delta$  were quoted in parts per million (ppm) and were referenced to solvent residual peak as internal standard. The following abbreviations were used to describe peak patterns when appropriate: s = singlet, d = doublet, and m = multiplet. Coupling constants,  $J$ , are reported in the Hertz unit (Hz). Mass spectra were recorded with a Finnigan MAT 95 (70 eV) spectrometer under electron impact (EI) conditions. The molecular fragments were quoted as the relationship between mass and charge ( $m/z$ ). The abbreviation  $[\text{M}^+]$  refers to the molecular ion. IR spectra were recorded with an FTIR Bruker IFS 88 spectrometer, using the attenuated total reflection technique (ATR). The absorption band positions are given in wavenumbers  $\nu$  in  $\text{cm}^{-1}$ . UV-Visible spectra were measured on a Cary 300 UV-Visible Spectrometer, Varian, Agilent Technologies.

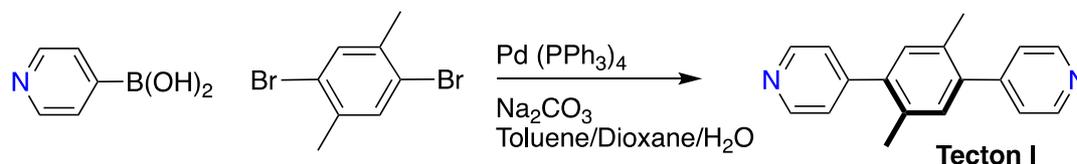
**Elemental analyses** were performed on a Thermo Scientific Flash 2000 by the “Service Commun de Microanalyse” of the University of Strasbourg.

**Crystal Structure Determination:** The single-crystal X-ray diffraction study was carried out on a Bruker APEX8 CCD diffractometer equipped with an Oxford Cryosystem liquid  $\text{N}_2$  device at 173(2) K using graphite-monochromated Mo- $\text{K}\alpha$  ( $\lambda = 0.71073 \text{ \AA}$ ) radiation operating at 50kV and 600  $\mu\text{A}$ . The structures were solved using SHELXS-97 and 2 refined by full-matrix least-squares on F using SHELXL-97 with anisotropic thermal parameters for all non-hydrogen atoms. The hydrogen atoms were introduced at calculated positions and were not refined (riding model).

### S.1.2 Synthesis of Molecular Tectons (I-III):

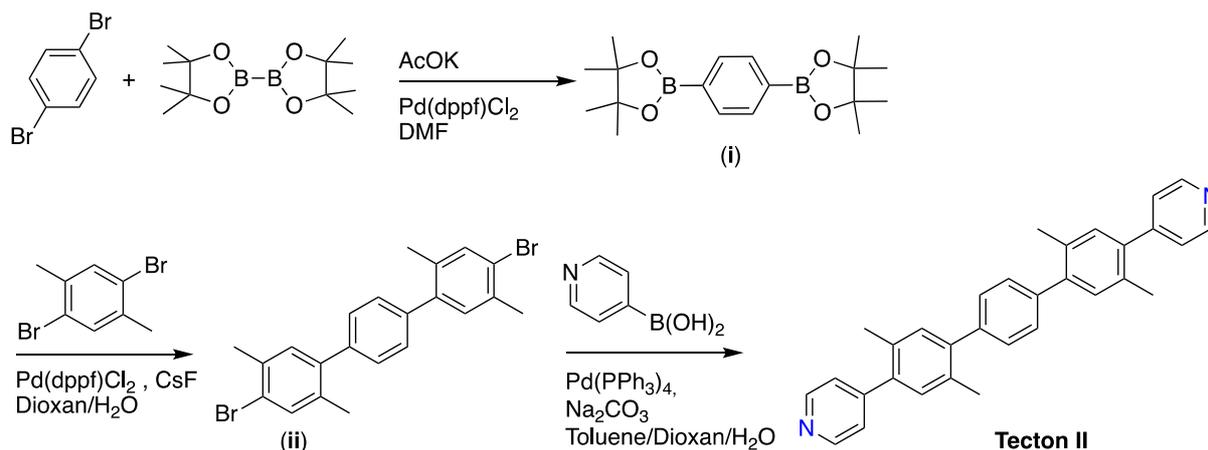
Model ditopic pyridine-bearing molecular tectons with different sizes/length (by including benzene rings as spacer groups) and grafted with photo-responsive azobenzene (-N=N-) moiety were synthesized following modular synthesis procedures by stepwise Mills and Suzuki-Miyaura cross-coupling reaction.<sup>1</sup>

### Synthesis of 4,4'-(2,5-dimethyl-1,4-phenylene)dipyridine (I):



2,5-dibromo-*p*-xylene (0.26 g, 1.00 mmol, 1 eq), 4-pyridylboronic acid (0.37 g, 3.00 mmol, 3 eq), tetrakis(triphenylphosphine)palladium(0) (58 mg, 0.05 mmol, 0.05 eq) and sodium carbonate (0.85 g, 8.00 mmol, 8 eq) were added in a degassed mixture of toluene-dioxane-water (50 mL, 2/2/1) under argon. The mixture was heated at 85°C for 72h under argon. The reaction mixture was cooled to room temperature, then added to water (100 mL) before being extracted with dichloromethane. Combined organic layers were washed with water and brine, then dried over magnesium sulfate and evaporated under reduced pressure. The residue was purified with column chromatography (silica gel, 20% dichloromethane in ethyl acetate) to give **I** as a pale yellow solid (0.24 g, 91%).  $R_{f(EA/DCM:8/2)} = 0.21$ . <sup>1</sup>H-NMR (500 MHz, CDCl<sub>3</sub>):  $\delta = 8.64$  (d, 4H,  $J = 6.0$  Hz,  $CH_{Py}$ ),  $7.27$  (d, 4H,  $J = 6.0$  Hz,  $CH_{Py}$ ),  $7.13$  (s, 4H,  $CH_{Ar}$ ),  $2.26$  (s, 6H,  $ArCH_3$ ) ppm. <sup>13</sup>C-NMR (125 MHz, CDCl<sub>3</sub>):  $\delta = 149.6$  ( $CH_{Py}$ ),  $149.3$  ( $C^{IV}_{Py}$ ),  $139.1$  ( $C^{IV}_{Ar}$ ),  $132.8$  ( $C^{IV}_{Ar}$ ),  $131.6$  ( $CH_{Py}$ ),  $124.2$  ( $CH_{Ar}$ ),  $19.7$  ( $ArCH_3$ ) ppm. IR (ATR):  $\nu = 3023, 2921, 1593, 1543, 1481, 1387, 1216, 1183$  cm<sup>-1</sup>. MS (EI)  $m/z = 260$  (100) [ $M^+$ ],  $245$  (14) [ $M^+ - CH_3$ ]. HRMS (EI):  $m/z$  C<sub>18</sub>H<sub>16</sub>N<sub>2</sub>, calcd.: 260.1313, found: 260.1312. Elemental analysis (%) (C<sub>18</sub>H<sub>16</sub>N<sub>2</sub>): calcd. C: 83.04, H: 6.19, N: 10.76; found C: 82.56, H: 6.21, N: 10.52.

### Synthesis of 4,4'-(2,2'',5,5''-tetramethyl-[1,1':4',1''-terphenyl]-4,4''-diyl)dipyridine (II)



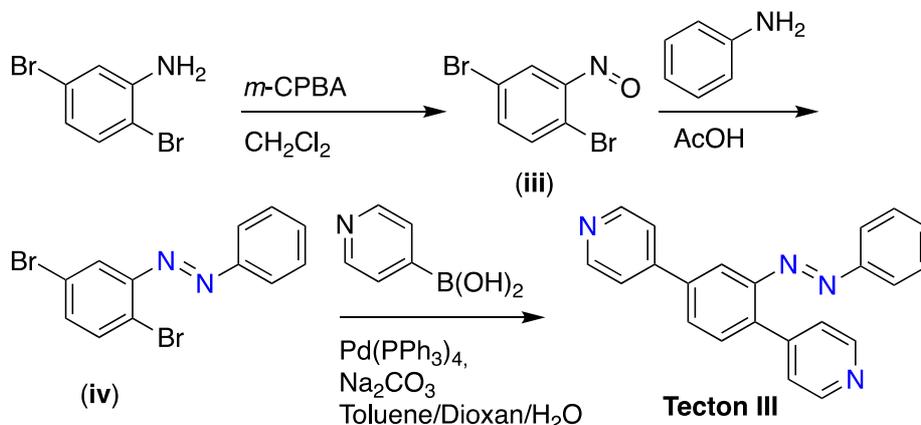
**1,4-bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)benzene (i).** 1,4-dibromobenzene (2.36 g, 10.00 mmol, 1 eq), bis(pinacolato)diboron (7.62 g, 30.00 mmol, 3 eq), [1,1'-bis(diphenylphosphino)ferrocene]dichloropalladium(II) (0.49 g, 0.60 mmol, 0.06 eq), and potassium acetate (5.89 g, 60.00 mmol, 6 eq) were dissolved in degassed dimethylformamide (70 mL) under argon atmosphere. The mixture was heated at 85°C for 48h. The reaction mixture was cooled to room temperature, then added to water (100 mL) before being extracted with dichloromethane (3 x 75 mL). Combined organic layers were washed with water and brine, then dried over sodium sulfate and evaporated under reduced pressure. The crude product was purified by column chromatography (silica gel, 0% to 10% ethyl acetate in *n*-hexane) to give (i) as a pale-green solid (2.89 g, 88%).  $R_{f(m\text{Hx}/\text{EA}:9/1)} = 0.45$ . <sup>1</sup>H-NMR (500 MHz, CDCl<sub>3</sub>):  $\delta = 7.80$  (s, 4H, CH<sub>Ar</sub>), 1.35 (s, 24H, CH<sub>3</sub>(Bpin)) ppm. <sup>13</sup>C-NMR (125 MHz, CDCl<sub>3</sub>):  $\delta = 134.0$  (CH<sub>Ar</sub>), 84.0 (C<sup>IV</sup>), 83.6 (C<sup>IV</sup>), 25.2 (CH<sub>3</sub>(Bpin)) ppm. IR (ATR):  $\nu = 2977, 1522, 1466, 1392, 1328, 1277, 1172$  cm<sup>-1</sup>. MS (EI):  $m/z = 330$  [M<sup>+</sup>], 315 [M<sup>+</sup>-CH<sub>3</sub>]. HRMS (EI):  $m/z$  C<sub>18</sub>H<sub>28</sub>B<sub>2</sub>O<sub>4</sub>, calcd.: 330.2174, found: 330.2174.

**4,4''-dibromo-2,2'',5,5''-tetramethyl-1,1':4',1''-terphenyl (ii):** The bis-boronic ester derivative (i) (2.50 g, 7.58 mmol, 1 eq), 2,5-dibromo-*p*-xylene (10.00 g, 37.88 mmol, 5 eq), [1,1'-bis(diphenylphosphino)ferrocene]dichloropalladium(II) (0.62 g, 0.76 mmol, 0.1 eq), and CsF (6.90 g, 45.45 mmol, 6 eq) were dissolved in a degassed mixture of dioxane-water (75 mL; 2/1) under argon atmosphere. The mixture was heated at reflux for 72h. The reaction mixture was cooled to room temperature, then added to water (100 mL) before being extracted with dichloromethane (3 x 75 mL). Combined organic layers were washed with water and brine, then dried over magnesium sulfate and evaporated under reduced pressure. The crude product was purified by column chromatography (silica gel, *n*-hexane) to give (ii) as a white solid (1.26 g, 37%).  $R_{f(m\text{Hx})} = 0.37$ . <sup>1</sup>H-NMR (500 MHz, CDCl<sub>3</sub>):  $\delta = 7.47$  (s, 2H, CH<sub>Ar</sub>), 7.32 (s, 4H, CH<sub>Ar</sub>), 7.15 (s, 2H, CH<sub>Ar</sub>), 2.41 (s, 6H, ArCH<sub>3</sub>), 2.27 (s, 6H, ArCH<sub>3</sub>) ppm. <sup>13</sup>C-NMR (125 MHz,

CDCl<sub>3</sub>):  $\delta$  = 140.9 (C<sup>IV</sup>), 139.8 (C<sup>IV</sup>), 135.2 (C<sup>IV</sup>), 134.8 (C<sup>IV</sup>), 134.0 (CH<sub>Ar</sub>), 132.2 (CH<sub>Ar</sub>), 129.0 (CH<sub>Ar</sub>), 123.7 (C<sup>IV</sup>), 22.4 (ArCH<sub>3</sub>), 19.9 (ArCH<sub>3</sub>) ppm. IR (ATR):  $\nu$  = 2954, 2919, 1475, 1442, 1373, 1357, 1177, 1113 cm<sup>-1</sup>. MS (EI):  $m/z$  = 446 (4) – 444 (9) – 442 (4) [M<sup>+</sup>], 365 (95) – 363 (100) [M<sup>+</sup>-Br]. HRMS (EI):  $m/z$  C<sub>22</sub>H<sub>20</sub>Br<sub>2</sub>, calcd.: 441.9932, found: 441.9930.

**4,4'-(2,2'',5,5''-tetramethyl-[1,1':4',1''-terphenyl]-4,4''-diyl)dipyridine (II):** The dibromo derivative (ii) (0.20 g, 0.45 mmol, 1 eq), 4-pyridylboronic acid (0.33 g, 2.70 mmol, 6 eq), tetrakis(triphenylphosphine)palladium(0) (52 mg, 0.045 mmol, 0.1 eq) and sodium carbonate (0.67 g, 6.30 mmol, 14 eq) were added in a degassed mixture of toluene-dioxane-water (50 mL, 2/2/1) under argon. The mixture was refluxed for 72h under argon. The reaction mixture was cooled to room temperature, then added to water (100 mL) before being extracted with dichloromethane. Combined organic layers were washed with water and brine, then dried over magnesium sulfate and evaporated under reduced pressure. The residue was purified with column chromatography (silica gel, 20% dichloromethane in ethyl acetate) to give Tecton (II) as a pale yellow solid (0.17 g, 85%). R<sub>f</sub>(EA/DCM:8/2) = 0.20. <sup>1</sup>H-NMR (500 MHz, CDCl<sub>3</sub>):  $\delta$  = 8.69 (d, 4H,  $J$  = 6.0 Hz, CH<sub>Py</sub>), 7.44 (s, 4H, CH<sub>Ar</sub>), 7.40 (d, 4H,  $J$  = 6.0 Hz, CH<sub>Py</sub>), 7.27 (s, 2H, CH<sub>Ar</sub>), 7.18 (s, 2H, CH<sub>Ar</sub>), 2.37 (s, 6H, ArCH<sub>3</sub>), 2.33 (s, 6H, ArCH<sub>3</sub>) ppm. <sup>13</sup>C-NMR (125 MHz, CDCl<sub>3</sub>):  $\delta$  = 150.8 (C<sup>IV</sup><sub>Py</sub>), 148.8 (CH<sub>Py</sub>), 142.1 (C<sup>IV</sup>), 140.1 (C<sup>IV</sup>), 137.8 (C<sup>IV</sup>), 133.5 (C<sup>IV</sup>), 132.5 (C<sup>IV</sup>), 132.5 (CH<sub>Ar</sub>), 131.6 (CH<sub>Ar</sub>), 129.1 (CH<sub>Ar</sub>), 124.7 (CH<sub>Py</sub>), 20.2 (ArCH<sub>3</sub>), 19.9 (ArCH<sub>3</sub>) ppm. IR (ATR):  $\nu$  = 3025, 2920, 1594, 1540, 1480, 1443, 1210, 1105, 1035 cm<sup>-1</sup>. MS (EI):  $m/z$  = 440 (100) [M<sup>+</sup>]. HRMS (EI):  $m/z$  C<sub>32</sub>H<sub>28</sub>N<sub>2</sub>, calcd.: 440.2252, found: 440.2246. Elemental analysis (%) (C<sub>32</sub>H<sub>28</sub>N<sub>2</sub>): calcd. C: 87.24, H: 6.41, N: 6.36; found C: 85.81, H: 6.58, N: 5.94.

### Synthesis of (*E*)-4,4'-(2-(phenyldiazenyl)-1,4-phenylene)dipyridine (III):



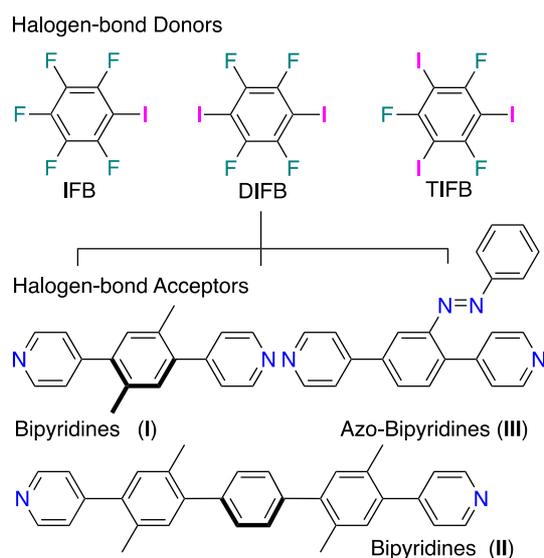
**Synthesis of 1,4-dibromo-2-nitrosobenzene (iii):** 3-chloroperoxybenzoic acid (*m*-CPBA) (70-75%) (4.76 g, 20.00 mmol, 2 eq) was dissolved in dry dichloromethane (60 mL). 2,5-

dibromoaniline (2.51 g, 10.00 mmol, 1 eq) was added at 0°C under argon and the reaction mixture was stirred at 0°C for 1h. A solution of sodium carbonate (2.33 g, 22.00 mmol, 2.2 eq) in water (250 mL) was added and the reaction mixture was allowed to room temperature. Organic layer was separated, washed with water and brine, dried over magnesium sulfate, filtrated and evaporated under reduced pressure. The residue was purified with column chromatography (silica gel, 10% *n*-hexane in dichloromethane) to give **(iii)** as a yellow solid (1.57 g, 59%).  $R_{f(n\text{Hx}/\text{DCM}:9/1)} = 0.45$ .  $^1\text{H-NMR}$  (500 MHz,  $\text{CDCl}_3$ ):  $\delta = 7.88$  (d, 1H,  $J = 8.5$  Hz,  $\text{C}^5\text{H}$ ), 7.65 (dd, 1H,  $J = 8.5$  Hz,  $J = 2.5$  Hz,  $\text{C}^6\text{H}$ ), 6.33 (d, 1H,  $J = 2.5$  Hz,  $\text{C}^3\text{H}$ ) ppm.  $^{13}\text{C-NMR}$  (125 MHz,  $\text{CDCl}_3$ ):  $\delta = 160.2$  ( $\text{C}^2$ ), 138.7 ( $\text{C}^5\text{H}$ ), 136.8 ( $\text{C}^6\text{H}$ ), 131.6 ( $\text{C}^4$ ), 122.4 ( $\text{C}^1$ ), 112.8 ( $\text{C}^3\text{H}$ ) ppm. IR (ATR):  $\nu = 3076, 1566, 1454, 1383, 1260, 1190$   $\text{cm}^{-1}$ . MS (EI):  $m/z = 265$  [ $\text{M}^+$ ], 235 [ $\text{M}^+ - \text{NO}$ ]. HRMS (EI):  $m/z$   $\text{C}_6\text{H}_3\text{Br}_2\text{NO}$ , calcd.: 262.8581, found: 262.8584. Elemental analysis (%) ( $\text{C}_6\text{H}_3\text{Br}_2\text{NO}$ ): calcd. C: 27.20, H: 1.14, N: 5.29; found C: 27.24, H: 1.11, N: 5.44.

**(E)-1-(2,5-dibromophenyl)-2-phenyldiazene (iv)**: Aniline (320  $\mu\text{L}$ , 3.51 mmol, 1 eq) was added to a solution of 1,4-dibromo-2-nitrosobenzene **(iii)** (1.03 g, 3.86 mmol, 1.1 eq) in acetic acid (25 mL) and the reaction mixture was stirred at 40°C for 24h. The reaction mixture was cooled to room temperature, then concentrated under reduced pressure. Acetic acid (5 mL) was added to the residue and the suspension was filtrated; the solid obtained was washed with a few milliliters of acetic acid and dried to give **(iv)** as a red-orange solid (0.87 g, 73%).  $R_{f(n\text{Hx}/\text{DCM}:9/1)} = 0.49$ .  $^1\text{H-NMR}$  (500 MHz,  $\text{CDCl}_3$ ):  $\delta = 8.00$ -7.98 (m, 2H,  $\text{CH}_{\text{Ph}}$ ), 7.83 (d, 1H,  $J = 2.5$  Hz,  $\text{CH}_{\text{Ar}}$ ), 7.62 (d, 1H,  $J = 8.5$  Hz,  $\text{CH}_{\text{Ar}}$ ), 7.55-7.53 (m, 3H,  $\text{CH}_{\text{Ph}}$ ), 7.44 (dd, 1H,  $J = 8.5$  Hz,  $J = 2.5$  Hz,  $\text{CH}_{\text{Ar}}$ ) ppm.  $^{13}\text{C-NMR}$  (125 MHz,  $\text{CDCl}_3$ ):  $\delta = 152.5$  ( $\text{C}^{\text{IV}}\text{-N=N}$ ), 150.3 ( $\text{C}^{\text{IV}}\text{-N=N}$ ), 135.0 ( $\text{CH}_{\text{Ar}}$ ), 134.5 ( $\text{CH}_{\text{Ar}}$ ), 132.3 ( $\text{CH}_{\text{Ph}}$ ), 129.4 ( $\text{CH}_{\text{Ph}}$ ), 124.6 ( $\text{C}^{\text{IV}}\text{-Br}$ ), 123.8 ( $\text{CH}_{\text{Ph}}$ ), 122.2 ( $\text{C}^{\text{IV}}\text{-Br}$ ), 121.2 ( $\text{CH}_{\text{Ar}}$ ) ppm. IR (ATR):  $\nu = 3080, 1484, 1443, 1368, 1307, 1287, 1068, 1032$   $\text{cm}^{-1}$ . UV-Vis ( $\text{CH}_2\text{Cl}_2$ ):  $\lambda = 323$  nm. MS (EI):  $m/z = 340$  [ $\text{M}^+$ ]. HRMS (EI):  $m/z$   $\text{C}_{12}\text{H}_8\text{Br}_2\text{N}_2$ , calcd.: 337.9054, found: 337.9053. Elemental analysis (%) ( $\text{C}_{12}\text{H}_8\text{Br}_2\text{N}_2$ ): calcd. C: 42.39, H: 2.37, N: 8.24; found C: 41.49, H: 2.19, N: 8.02.

**(E)-4,4'-(2-(phenyldiazenyl)-1,4-phenylene)dipyridine (III)**: **(E)-1-(2,5-dibromophenyl)-2-phenyldiazene (iv)** (0.51 g, 1.50 mmol, 1 eq), 4-pyridylboronic acid (0.55 g, 4.50 mmol, 3 eq), tetrakis(triphenylphosphine)palladium(0) (87 mg, 0.08 mmol, 0.05 eq) and sodium carbonate (1.27 g, 12.00 mmol, 8 eq) were added in a degassed mixture of toluene-dioxane-water (50 mL, 2/2/1) under argon. The mixture was heated at 85°C for 72h under argon. The reaction mixture was cooled to room temperature, organic solvents were removed under reduced pressure. The resulting aqueous suspension was extracted with dichloromethane. The organic phase was

washed with water, then dried over magnesium sulfate and evaporated under reduced pressure. The residue was purified with column chromatography (silica gel, 25% dichloromethane in ethyl acetate) to give **III** as a red solid (0.33 g, 65%).  $R_f(\text{EA/DCM:8/2}) = 0.14$ .  $^1\text{H-NMR}$  (500 MHz,  $\text{CDCl}_3$ ):  $\delta = 8.74$  (d, 2H,  $J = 6.0$  Hz,  $\text{CH}_{\text{Py}}$ ),  $8.71$  (d, 2H,  $J = 6.0$  Hz,  $\text{CH}_{\text{Py}}$ ),  $8.09$  (d, 1H,  $J = 2.0$  Hz,  $\text{CH}_{\text{Ph}}$ ),  $7.87$  (dd, 1H,  $J = 8.0$  Hz,  $J = 2.0$  Hz,  $\text{CH}_{\text{Ph}}$ ),  $7.83$ - $7.81$  (m, 2H,  $\text{CH}_{\text{Ph}}$ ),  $7.71$  (d, 1H,  $J = 8.0$  Hz,  $\text{CH}_{\text{Ph}}$ ),  $7.64$  (d, 2H,  $J = 6.0$  Hz,  $\text{CH}_{\text{Py}}$ ),  $7.53$ - $7.50$  (m, 3H,  $\text{CH}_{\text{Ph}}$ ),  $7.46$  (d, 2H,  $J = 6.0$  Hz,  $\text{CH}_{\text{Py}}$ ) ppm.  $^{13}\text{C-NMR}$  (125 MHz,  $\text{CDCl}_3$ ):  $\delta = 152.7$  ( $\text{C}^{\text{IV-N=N}}$ ),  $150.6$  ( $\text{CH}_{\text{Py}}$ ),  $150.0$  ( $\text{C}^{\text{IV-N=N}}$ ),  $149.3$  ( $\text{CH}_{\text{Py}}$ ),  $147.3$  ( $\text{C}^{\text{IV}}$ ),  $146.4$  ( $\text{C}^{\text{IV}}$ ),  $139.6$  ( $\text{C}^{\text{IV}}$ ),  $139.0$  ( $\text{C}^{\text{IV}}$ ),  $131.9$  ( $\text{CH}_{\text{Ar}}$ ),  $131.4$  ( $\text{CH}_{\text{Ph}}$ ),  $129.5$  ( $\text{CH}_{\text{Ar}}$ ),  $129.4$  ( $\text{CH}_{\text{Ph}}$ ),  $125.7$  ( $\text{CH}_{\text{Py}}$ ),  $123.6$  ( $\text{CH}_{\text{Ar}}$ ),  $121.8$  ( $\text{CH}_{\text{Py}}$ ),  $114.9$  ( $\text{CH}_{\text{Ph}}$ ) ppm. IR (ATR):  $\nu = 3025, 1589, 1546, 1467, 1381, 1201, 1152$   $\text{cm}^{-1}$ . UV-Vis ( $\text{CH}_2\text{Cl}_2$ ):  $\lambda = 276, 323$  nm. MS (EI):  $m/z = 336$  [ $\text{M}^+$ ],  $231$  [ $\text{M}^+ - \text{C}_6\text{H}_5\text{N}_2$ ]. HRMS (EI):  $m/z$   $\text{C}_{22}\text{H}_{16}\text{N}_4$ , calcd.: 336.1375, found: 336.1374. Elemental analysis (%) ( $\text{C}_{22}\text{H}_{16}\text{N}_4$ ): calcd. C: 78.55, H: 4.79, N: 16.66; found C: 78.06, H: 4.69, N: 16.09.



**Scheme 1.** Bipyridine molecular tectons (**I-III**) cocrystallized with **IFB**, **DIFB**, and **TIFB** as halogen-bond donors in supramolecular systems

### S.1.3 Co-crystallization:

For crystallographic data, see CCDC 2076758-2076764.

Liquid-liquid diffusions were conducted in glass crystallization tubes (height~15-17 cm, diameter = 0.4 cm) at ambient temperature.

For the vapour diffusion technique, a solution of the reagent contained in a glass vial (height

= 4.7 cm, diameter = 1.1 cm) was placed into another closed vial (height = 6.3 cm, diameter 1.9 cm) containing the volatile solvent at ambient temperature.

**Tecton I-(IFB)<sub>2</sub>**: To 0.6 mL of H<sub>2</sub>O few drops of iodopentafluorobenzene (**IFB**) were added. To the mixture was added an EtOH solution of tecton **I** ( $C = 2 \cdot 10^{-2}$  M) in 1 mL of EtOH.

**Tecton II-(IFB)<sub>2</sub>**: To 0.6 mL of H<sub>2</sub>O few drops of iodopentafluorobenzene (**IFB**) were added. An EtOH solution of tecton **II** ( $C = 1 \cdot 10^{-2}$  M) in 1 mL of EtOH was added to the mixture.

**Tecton I-(DIFB)**: To a solution of tecton **I** ( $C = 3 \cdot 10^{-3}$  M) in 1 mL of CHCl<sub>3</sub> was added a solution of 1,4-diiodo-tetrafluoro benzene ( $C = 3 \cdot 10^{-3}$  M) in 1 mL of EtOH. Upon slow evaporation of solvents, crystals appeared within 3-4 days.

**Tecton II-(DIFB)**: To a solution of tecton **II** ( $C = 3 \cdot 10^{-3}$  M) in 1 mL of CHCl<sub>3</sub> was added a solution of 1,4-diiodo-tetrafluoro benzene ( $C = 3 \cdot 10^{-3}$  M) in 1 mL of EtOH. Upon slow evaporation of solvents, crystals appeared within 3-4 days.

**Tecton I-(TIFB)**: To a solution of tecton **I** ( $C = 3 \cdot 10^{-3}$  M) in 0.5 mL of CHCl<sub>3</sub> was added a solution of 1,3,5-trifluoro-2,4,6-triiodobenzene ( $C = 6 \cdot 10^{-3}$  M) in 0.5 mL of EtOH. Upon slow evaporation of solvents crystals appeared within 3-4 days.

**Tecton II-(TIFB)<sub>2</sub>**: To a solution of tecton **II** ( $C = 3 \cdot 10^{-3}$  M) in 0.5 mL of CHCl<sub>3</sub> was added a solution of 1,3,5-trifluoro-2,4,6-triiodobenzene ( $C = 6 \cdot 10^{-3}$  M) in 0.5 mL of EtOH. Upon slow evaporation of solvents crystals appeared within 3-4 days.

**Tecton III-(DIFB)**: To a solution of tecton **III** ( $C = 3 \cdot 10^{-3}$  M) in 1 mL of CHCl<sub>3</sub> was added a solution of 1,4-diiodo-tetrafluoro benzene ( $C = 3 \cdot 10^{-3}$  M) in 1 mL of EtOH. Upon slow evaporation of solvents, crystals appeared within 3-4 days.

**Table 1.** Py<sub>mp</sub>-pyridine mean plane, Xy<sub>mp</sub>-xylene moiety mean plane, Bz<sub>mp</sub>-benzene moiety mean plane, HBdonor<sub>mp</sub>- mean plane of the DIFB moiety.

Comp	Angle Py <sub>mp</sub> / Xy <sub>mp</sub> (deg)	Angle Py <sub>mp</sub> / HBdonor <sub>mp</sub> (deg)	AngleN ---I-C (deg)	Comp	Angle Py <sub>mp</sub> / Xy <sub>mp</sub> (deg)	Angle Xy <sub>mp</sub> / Bz <sub>mp</sub> (deg)	Angle Py <sub>mp</sub> / HBdonor <sub>mp</sub> (deg)	Angle N---I-C (deg)
I	-	-	-	II	58	-	-	-
IFB	47	23	170	IFB	40 40	44	18	174
DIFB	66	77	176	DIFB	43	51	31	176
TIFB (1:2 ligand: TIFB)	86	83	171	TIFB (1:2 ligand: TIFB)	52	42	46	174
TIFB (3:2 ligand: TIFB)	50 42	43 46	167 178	TIFB (3:2 ligand: TIFB)	-	-	-	-

### References:

- (a) S. Grosjean, Z. Hassan, C. Wöll, S. Bräse, *Eur. J. Org. Chem.*, **2019**, 1446–1460;  
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