Symmetrically Modulated Three Iodocuprate Hybrids by Positional Isomer and Chiral Conformation of N-benzyl-methylpyridinium

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Supporting Information (SI)

Supporting Information Available: Infrared Spectroscopy (Fig. S1), the asymmetric unit diagrams (Fig. S2 for **1**, Fig. S3 for **2** and Fig. S4 for **3**), TG and DSC analyses (Fig. S5), MS for compounds **1**, **2** and **3** (Fig. S6), X-ray powder diffraction (XRPD) patterns (Fig. S7), optical absorption spectra at room temperature (Fig. S8), chiral conformations of **1**, **2** and **3** (Fig. S9, S10 and S11), photoluminescent emissions and excitations of **1**, **2** and **3** (Fig. S12), a summary of the crystal data (Table S1), selected bond lengths (Å) and angles (°) for **1**, **2** and **3** (Table S2), parameters of chiral conformations in the compounds **1-3** (Table S3), and selected TG-DTA-MS data for compounds **1-3** (Table S4).

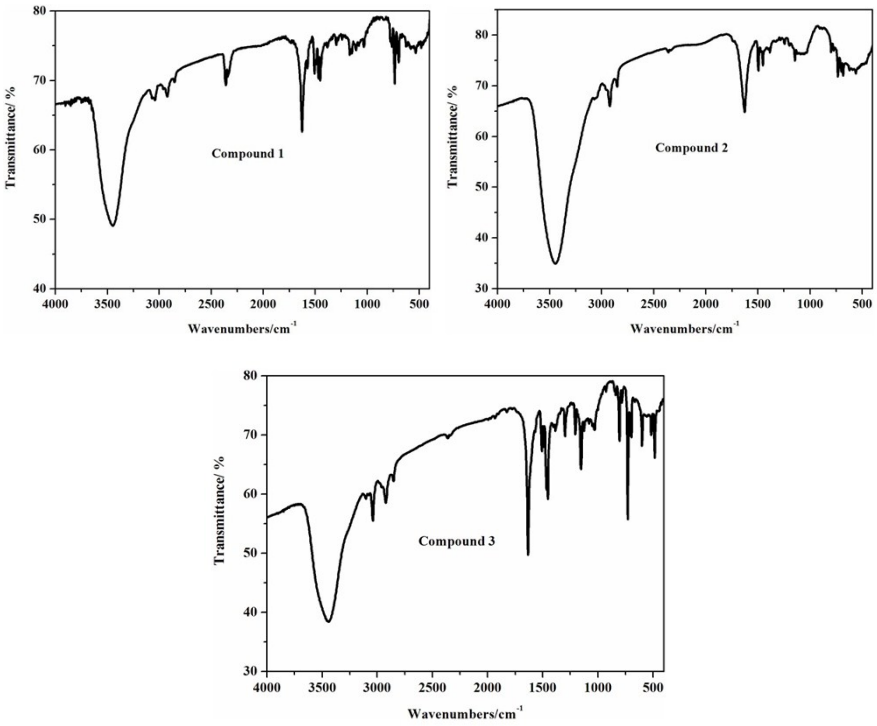

Fig. S1 IR spectra of **1**, **2** and **3**

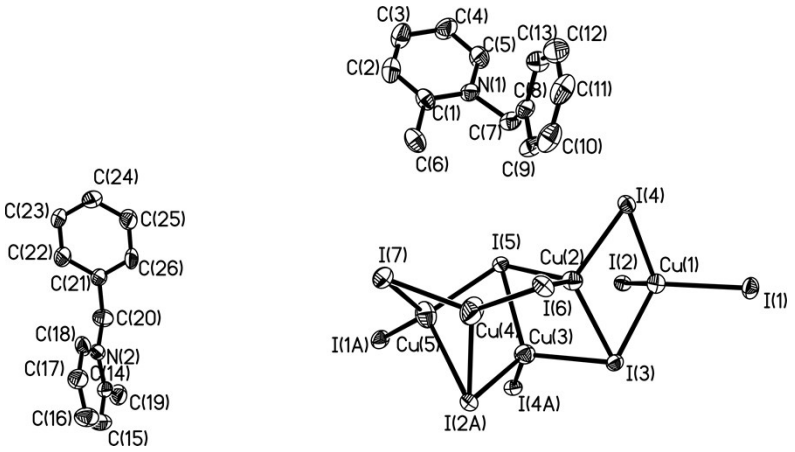

Fig. S2 The asymmetric unit diagram of **1**

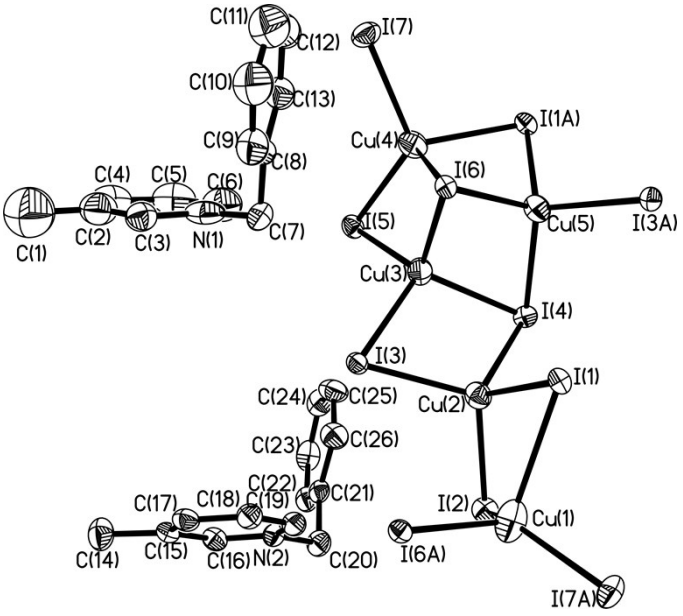

Fig. S3 The asymmetric unit diagram of **2**

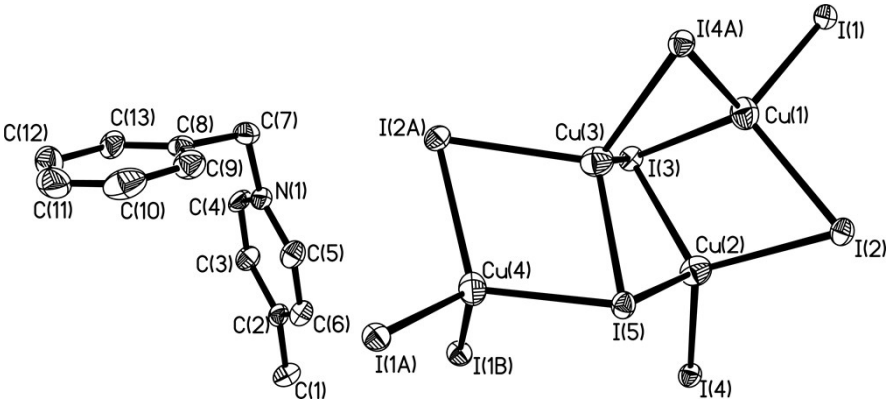

Fig. S4 The asymmetric unit diagram of **3**

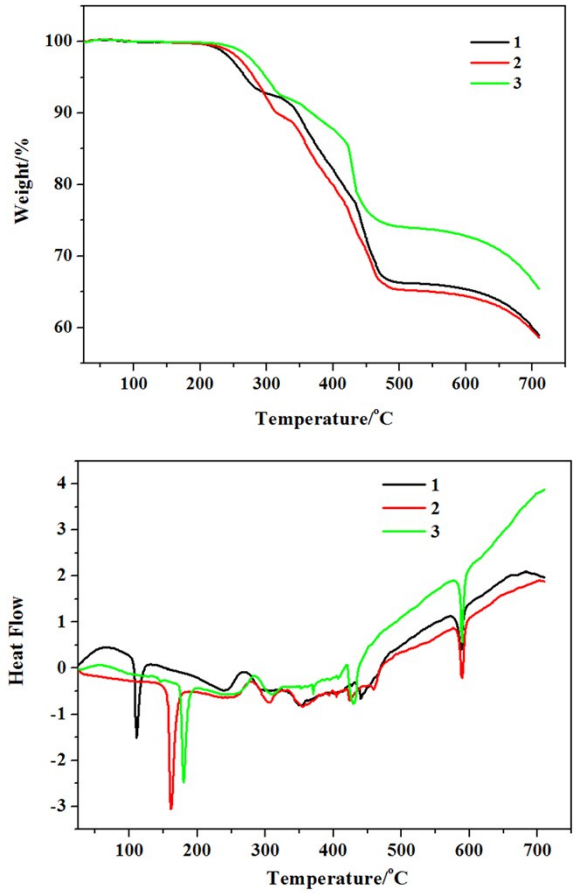

Fig. S5 TG curves (top) and DSC curves (bottom) for compounds **1**, **2** and **3**

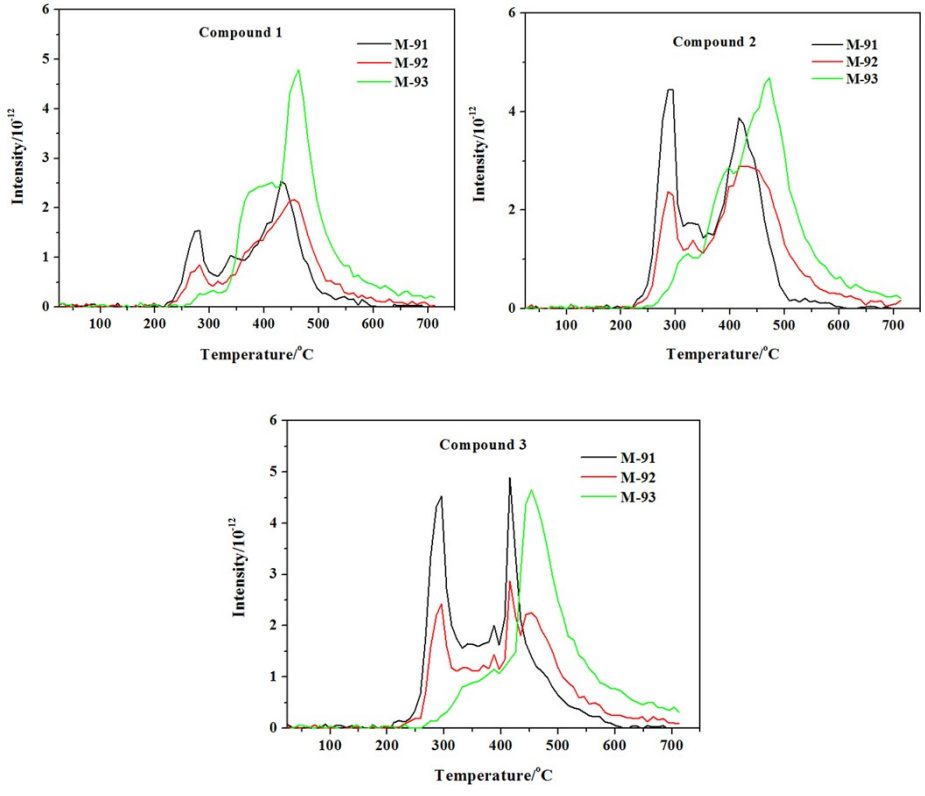

Fig. S6 MS for compounds **1** (top), **2** (middle) and **3** (bottom)

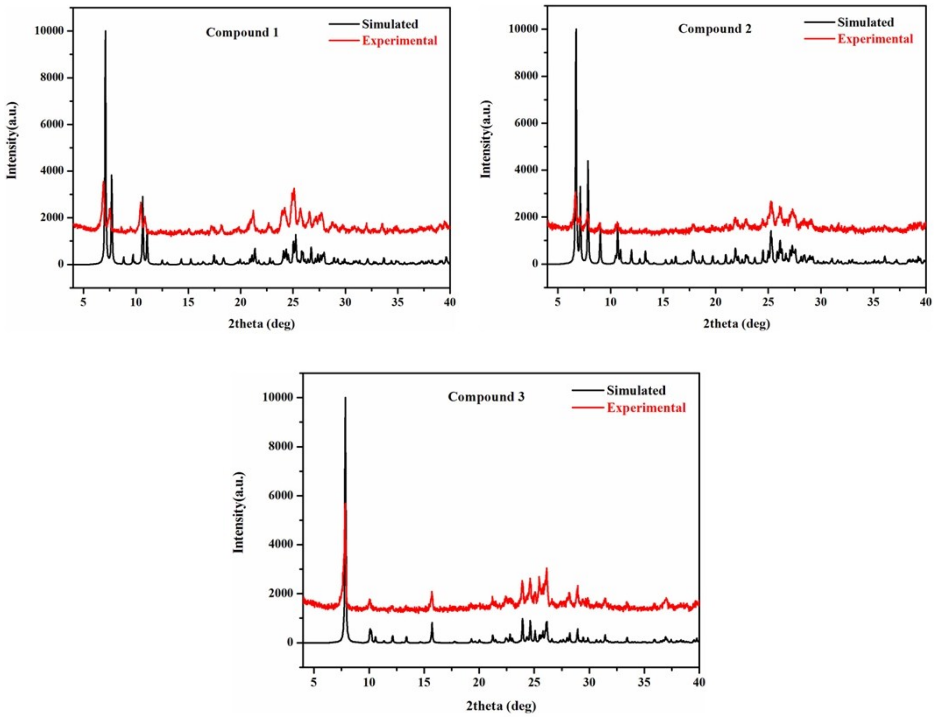

Fig. S7 X-ray powder diffraction (XRPD) patterns of **1**, **2** and **3** at room temperature (RT).

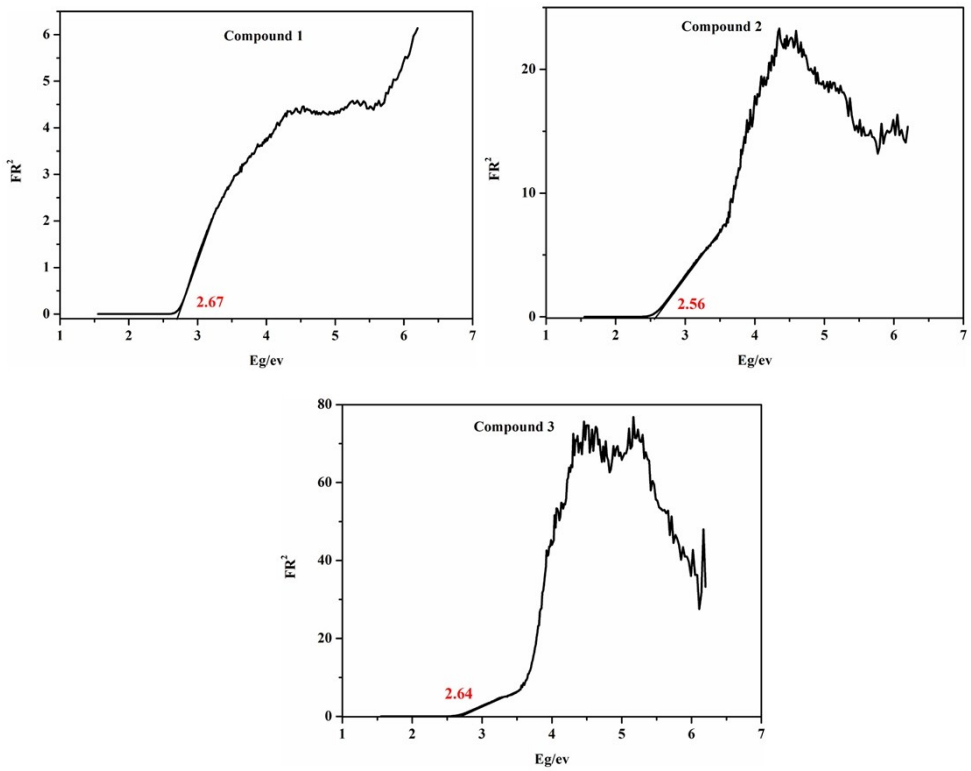

Fig. S8 Optical absorption spectra of **1**, **2** and **3** at room temperature.

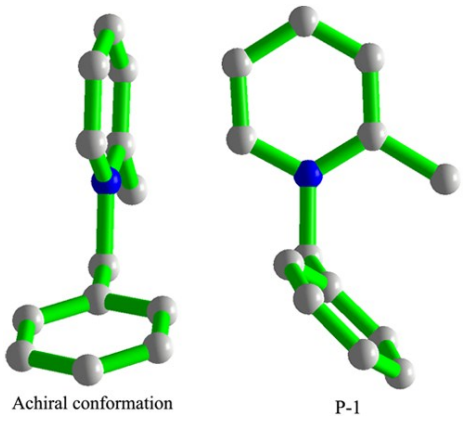

Fig. S9 The two types of conformations in N-Bz-2-MePy^{+}.

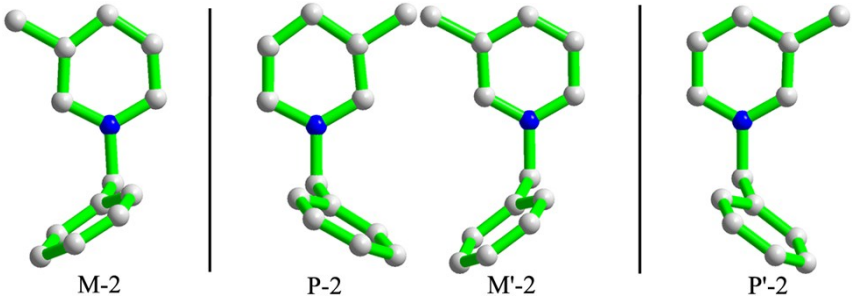

Fig. S10 The four types of chiral conformations (that has mirror symmetry) in N-Bz-3-MePy^{+}.

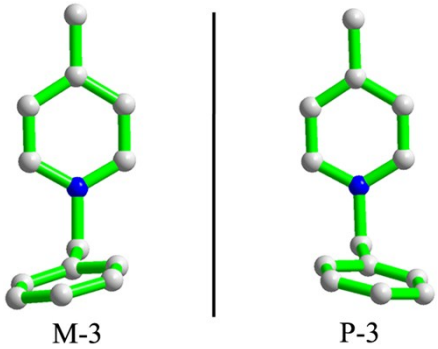

Fig. S11 The two types of chiral conformations (that has mirror symmetry) in N-Bz-4-MePy^{+}.

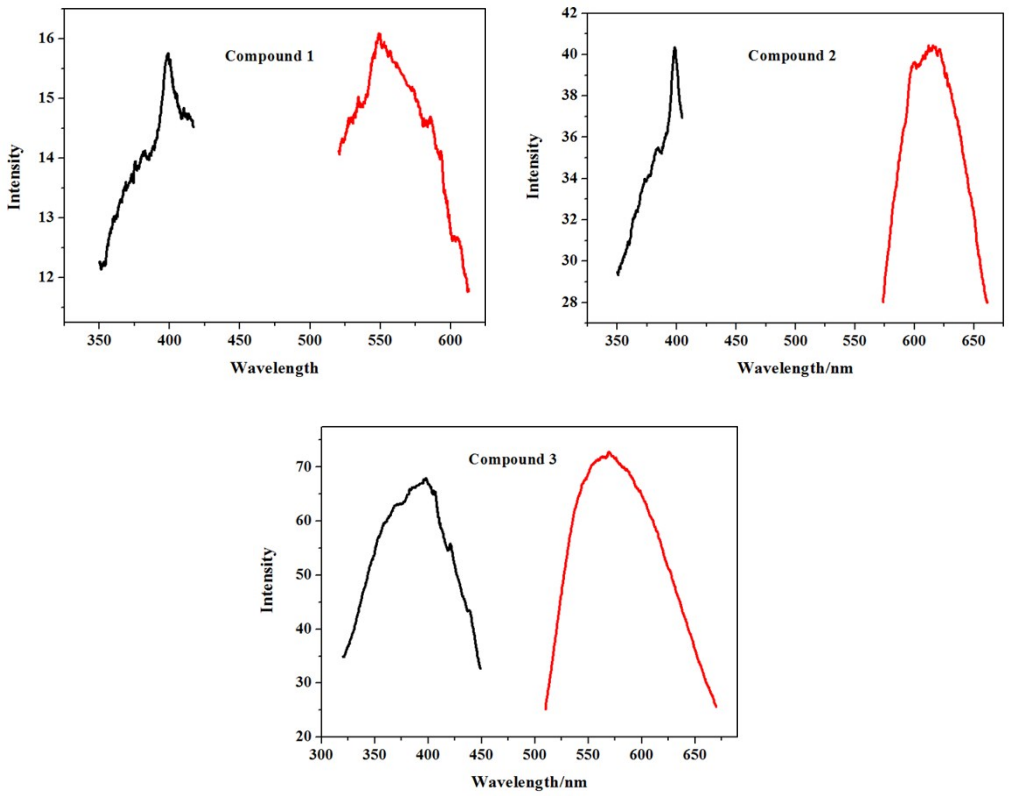

Fig. S12 Photoluminescent emissions (red) and excitations (black) of **1**, **2** and **3**.

Table S1 Crystal data and structure refinement for compounds **1**-**3**.

Compound	**1**	**2**	**3**
CCDC code	1449176	1449177	1449178
Temperature (K)	293(2)	293(2)	293(2)
Formula	$C_{26}H_{28}N_2Cu_5I_7$	$C_{26}H_{28}N_2Cu_5I_7$	$C_{13}H_{14}NCu_4I_5$
formula weight	1574.50	1574.50	1072.91
crystal size (mm)	0.19×0.09 × 0.08	0.18 ×0.15 ×0.04	0.18× 0.16 ×0.14
crystal system	orthorhombic	monoclinic	monoclinic
space group	$P2_12_12_1$	$P2_1/n$	$P2_1/n$
a (Å)	11.1175(3)	14.0832(3)	13.6325(3)
b (Å)	14.8652(5)	10.6623(2)	10.78869(19)
c (Å)	22.9914(7)	25.2274(6)	15.0331(3)
α (°)	90	90	90
β (°)	90	100.572(2)	104.237(2)
γ (°)	90	90	90
V (Å^3)	3799.7(2)	3723.81(15)	2143.11(8)
Z	4	4	4
D_c (g cm^{-3})	2.752	2.808	3.325
F (000)	2856	2856	1920
μ (mm^{-1})	8.460	8.633	11.114
Flack parameter	–0.07(3)	-	-
reflections collected	12950	18438	8669
unique reflections	6845	7314	4215

*R*int	0.0249	0.0260	0.0273
goodness–of–fit on F^2	1.041	1.071	1.048
$R1/wR2$, $[I \geq 2\sigma_I]$[a,b]	0.0321, 0.0532	0.0397, 0.0767	0.0320, 0.0710
$R1/wR2$, (all data)	0.0424, 0.0573	0.0543, 0.0823	0.0418, 0.0765
$\Delta\rho_{max}$, $\Delta\rho_{min}$ (e Å^{-3})	0.990, –0.846	1.811,–0.952	1.280, –1.073

[a] $R_1 = \sum||F_o|-|F_c||/\sum|F_o|$, [b] $wR_2 = [\sum w(F_o^2-F_c^2)^2/\sum w(F_o^2)^2]^{1/2}$

Table S2 Selected bond lengths (Å) and angles (°) for **1**, **2** and **3**.

		Compound **1**	
Cu(1)-I(1)	2.6561(11)	Cu(1)-I(2)	2.7231(13)
Cu(1)-I(3)	2.6892(12)	Cu(1)-I(4)	2.6616(13)
Cu(2)-I(3)	2.6752(12)	Cu(2)-I(4)	2.6557(11)
Cu(2)-I(5)	2.6912(11)	Cu(2)-I(6)	2.6180(14)
Cu(3)-I(2)#2	2.6926(13)	Cu(3)-I(3)	2.6779(11)
Cu(3)-I(4)#2	2.6616(14)	Cu(3)-I(5)	2.6860(12)
Cu(4)-I(2)#2	2.6596(16)	Cu(4)-I(6)	2.4959(14)
Cu(4)-I(5)	3.1720(2)	Cu(4)-I(7)	2.6122(15)
Cu(5)-I(1)#2	2.5246(14)	Cu(5)-I(2)#2	3.0386(15)
Cu(5)-I(5)	2.6762(14)	Cu(5)-I(7)	2.6735(17)
Cu(1)-Cu(2)	2.8451(16)	Cu(1)-Cu(3)#1	2.9265(15)
Cu(1)-Cu(5)#1	2.8691(19)	Cu(2)-Cu(3)	2.8860(16)
Cu(3)-Cu(1)#2	2.9265(15)	Cu(4)-Cu(5)	2.4836(19)
Cu(5)-Cu(1)#2	2.8691(19)		
I(1)-Cu(1)-I(2)	115.43(5)	I(1)-Cu(1)-I(3)	111.37(4)
I(1)-Cu(1)-I(4)	108.10(4)	I(3)-Cu(1)-I(2)	100.21(4)
I(4)-Cu(1)-I(2)	108.26(4)	I(4)-Cu(1)-I(3)	113.44(5)
I(3)-Cu(2)-I(5)	110.19(4)	I(4)-Cu(2)-I(3)	114.09(4)
I(4)-Cu(2)-I(5)	102.61(4)	I(6)-Cu(2)-I(3)	107.76(4)
I(6)-Cu(2)-I(4)	110.07(5)	I(6)-Cu(2)-I(5)	112.16(4)
I(1)#2-Cu(5)-I(2)#2	109.32(5)	I(3)-Cu(3)-I(2)#2	107.31(4)
I(3)-Cu(3)-I(5)	110.26(4)	I(4)#2-Cu(3)-I(3)	112.41(5)
I(4)#2-Cu(3)-I(2)#2	109.18(4)	I(4)#2-Cu(3)-I(5)	105.86(4)
I(5)-Cu(3)-I(2)#2	111.88(5)	I(6)-Cu(4)-I(2)#2	116.54(5)
I(6)-Cu(4)-I(7)	126.92(7)	I(7)-Cu(4)-I(2)#2	108.41(5)
I(1)#2-Cu(5)-I(5)	114.89(6)	I(1)#2-Cu(5)-I(7)	121.08(5)
I(5)-Cu(5)-I(2)#2	102.29(4)	I(7)-Cu(5)-I(2)#2	96.73(5)
I(7)-Cu(5)-I(5)	109.31(5)		
		Compound **2**	
Cu(1)-I(1)	3.0609(19)	Cu(1)-I(2)	2.5278(14)
Cu(1)-I(6)#1	2.6789(16)	Cu(1)-I(7)#1	2.5936(16)
Cu(2)-I(1)	2.7169(13)	Cu(2)-I(2)	2.6598(13)

Cu(2)-I(3)	2.6628(13)	Cu(2)-I(4)	2.6536(13)
Cu(3)-I(3)	2.6657(12)	Cu(3)-I(4)	2.6832(13)
Cu(3)-I(5)	2.5995(13)	Cu(3)-I(6)	2.7713(14)
Cu(4)-I(1)#2	2.7004(16)	Cu(4)-I(5)	2.5081(14)
Cu(4)-I(6)	3.0590(17)	Cu(4)-I(7)	2.6140(15)
Cu(5)-I(1)#2	2.7018(13)	Cu(5)-I(3)#2	2.6509(13)
Cu(5)-I(4)	2.6484(13)	Cu(5)-I(6)	2.6865(13)
Cu(1)-Cu(2)	2.998(2)	Cu(1)-Cu(4)#1	2.5248(19)
Cu(2)-Cu(3)	2.9974(17)	Cu(2)-Cu(5)#1	2.8526(17)
Cu(3)-Cu(4)	2.8506(19)	Cu(3)-Cu(5)	2.8341(17)
Cu(4)-Cu(1)#2	2.5248(19)	Cu(5)-Cu(2)#2	2.8526(17)
I(2)-Cu(1)-I(1)	104.99(6)	I(2)-Cu(1)-I(6)#1	113.90(6)
I(2)-Cu(1)-I(7)#1	127.59(6)	I(6)#1-Cu(1)-I(1)	99.44(5)
I(7)#1-Cu(1)-I(1)	97.13(5)	I(7)#1-Cu(1)-I(6)#1	108.26(6)
I(2)-Cu(2)-I(1)	111.53(5)	I(2)-Cu(2)-I(3)	111.61(5)
I(3)-Cu(2)-I(1)	111.01(4)	I(4)-Cu(2)-I(1)	102.41(4)
I(4)-Cu(2)-I(2)	109.36(4)	I(4)-Cu(2)-I(3)	110.55(5)
I(3)-Cu(3)-I(4)	109.55(4)	I(3)-Cu(3)-I(6)	99.27(4)
I(4)-Cu(3)-I(6)	109.70(4)	I(5)-Cu(3)-I(3)	110.58(5)
I(5)-Cu(3)-I(4)	112.33(5)	I(5)-Cu(3)-I(6)	114.62(5)
I(1)#2-Cu(4)-I(6)	99.01(5)	I(5)-Cu(4)-I(1)#2	118.21(6)
I(5)-Cu(4)-I(6)	108.19(5)	I(5)-Cu(4)-I(7)	123.05(6)
I(7)-Cu(4)-I(1)#2	106.21(5)	I(7)-Cu(4)-I(6)	97.42(5)
I(3)#2-Cu(5)-I(6)	104.63(4)	I(3)#2-Cu(5)-I(1)#2	111.86(4)
I(4)-Cu(5)-I(1)#2	106.96(4)	I(4)-Cu(5)-I(3)#2	111.04(5)
I(4)-Cu(5)-I(6)	113.45(5)	I(6)-Cu(5)-I(1)#2	108.97(5)
Compound **3**			
Cu(1)-I(1)	2.6495(11)	Cu(1)-I(2)	2.7157(11)
Cu(1)-I(3)	2.6592(11)	Cu(1)-I(4)#1	2.6694(10)
Cu(2)-I(2)	2.7367(11)	Cu(2)-I(3)	2.6796(11)
Cu(2)-I(4)	2.6415(10)	Cu(2)-I(5)	2.6488(10)
Cu(3)-I(2)#1	2.7801(11)	Cu(3)-I(3)	2.6842(10)
Cu(3)-I(4)#1	2.6495(10)	Cu(3)-I(5)	2.6448(11)
Cu(4)-I(1)#1	2.6756(11)	Cu(4)-I(1)#4	2.6802(10)
Cu(4)-I(2)#1	2.7114(11)	Cu(4)-I(5)	2.6042(10)
Cu(1)-Cu(2)	2.9111(14)	Cu(1)-Cu(3)	2.8907(13)
Cu(1)-Cu(4)#2	3.0180(13)	Cu(2)-Cu(3)	2.8760(13)
Cu(2)-Cu(3)#2	2.7356(12)	Cu(3)-Cu(2)#1	2.7356(12)
Cu(4)-Cu(1)#1	3.0180(13)	Cu(4)-Cu(4)#3	2.6532(18)
I(1)-Cu(1)-I(2)	107.10(3)	I(1)-Cu(1)-I(3)	109.77(4)

I(1)-Cu(1)-I(4)#1	110.70(4)	I(3)-Cu(1)-I(2)	112.69(4)
I(3)-Cu(1)-I(4)#1	106.18(3)	I(4)#1-Cu(1)-I(2)	110.44(4)
I(3)-Cu(2)-I(2)	111.39(4)	I(4)-Cu(2)-I(2)	116.48(4)
I(4)-Cu(2)-I(3)	103.40(4)	I(4)-Cu(2)-I(5)	114.42(4)
I(5)-Cu(2)-I(2)	100.06(4)	I(5)-Cu(2)-I(3)	111.41(3)
I(3)-Cu(3)-I(2)#1	102.29(4)	I(4)#1-Cu(3)-I(2)#1	114.74(3)
I(4)#1-Cu(3)-I(3)	106.03(4)	I(5)-Cu(3)-I(2)#1	107.60(4)
I(5)-Cu(3)-I(3)	111.39(3)	I(5)-Cu(3)-I(4)#1	114.18(4)
I(1)#1-Cu(4)-I(1)#4	120.61(3)	I(1)#1-Cu(4)-I(2)#1	106.48(3)
I(1)#4-Cu(4)-I(2)#1	103.85(4)	I(5)-Cu(4)-I(1)#1	110.08(4)
I(5)-Cu(4)-I(2)#1	110.90(3)	I(5)-Cu(4)-I(1)#4	104.69(3)

Symmetry code:

1: #1 x-1/2, -y+1/2, -z ; #2 x+1/2, -y+1/2, -z.

2: #1 -x+3/2, y+1/2, -z+1/2; #2 -x+3/2, y-1/2, -z+1/2.

3: #1 -x+1/2, y-1/2, -z+3/2; #2 -x+1/2, y+1/2, -z+3/2; #3 -x+1, -y+1, -z+2; #4 x+1/2, -y+3/2, z+1/2; #5 x-1/2, -y+3/2, z-1/2.

Table S3 The angles that two aromatic rings make with the C-C-N plane and the angles between two aromatic rings in the compounds **1**-**3**

	N-Bz-2-MePy$^+$ in **1**	N-Bz-3-MePy$^+$ in **2**	N-Bz-4-MePy$^+$ in **3**
The angles between the pyridine rings and C-C-N reference plane	8.309(920)° 76.485(862)°	74.727(625)° 71.971(628)°	77.642(462)°
The angles between the phenyl rings and C-C-N reference plane	83.928(819)° 52.775(710)°	64.964(785)° 60.035(523)°	79.316(431)°
The angles between the phenyl and pyridine rings	88.189(391)° 80.262(366)°	82.409(380)° 80.823(228)°	82.168(178)°

Table S4 Selected TG-DTA-MS data for compounds **1-3**.

	1	**2**	**3**
Decomposition Temp. (°C)	210	230	245
Total weight loss (%)	37.8	38.1	28.2
Endothermic peaks (°C)	112, 350, 440, 588	161, 305, 355, 424, 589	180, 429, 588
Exothermic peaks (°C)	269	280	284
Range of temp. for loss of benzyl group in MS (°C)	245-580	230-585	230-575
Range of temp. for loss of methylpyridine in MS (°C)	282-620	275-630	295-660