DOI: 10.1002/ejic.201001296

Copper(I) Complexes of Bipyridine and Terpyridine with Fluorous Tails and the Formation of Crystalline Materials with Fluorous Layers

Vedichi Madhu,[a] Yael Diskin-Posner,[b] and Ronny Neumann*[a]

Keywords: Ligand effects / Stacking interactions / Fluorous compounds / Copper / Electron-deficient compounds

Copper(I) complexes with perfluorinated tails, $(Cu^IL^2AcN)BF_4$ and $(Cu^IL^3AcN)BF_4$, where L^2 = 6,6′′-bis(perfluorohexyl)-2,2′:6′,2′′-terpyridine and L^3 = 6,6′-bis(2,2,3,3,4,4,5,5,6,6,7,7,7-tridecafluoroheptyl)-2,2′-bipyridine and AcN = acetonitrile, were synthesized and their rather unique crystal structures were elucidated. $(Cu^IL^2AcN)BF_4$ crystallizes in a low-symmetry space group, $P\bar{1}$, with a very large unit cell that required synchrotron radiation to locate all atoms. The molecular structure of $(Cu^IL^2AcN)BF_4$ has an asymmetric tetrahedrally distorted square-planar coordination sphere around Cu^I. Eight similar but distinct molecular structures were found. The crystal packing of $(Cu^IL^2AcN)(BF_4)$ has a layered structure with a clear segregation between the terpyridine moieties and the fluorous chains. The terpyridine units are arranged in a "back to back" fashion and tilted 20–25° relative to the interlayer plane, and the layered structure is staggered with offsets of approximately 4 Å between layers. The molecular structure of $(Cu^IL^3AcN)(BF_4)$ features a Y-shaped trigonal planar coordination sphere around copper(I). Comparison of the structure with analogous Cu^I(neocuproine)AcN showed that the fluorous tails with the CH_2CH_2 spacers basically have no effect on the bond lengths and angles to Cu^1. The crystal structure of $(Cu^IL^3AcN)(BF_4)$ shows a "herring bone" conformation with an approximately 96° angle in the CubipyAcN units. The "herring bone" conformation leads to an accordion-type fluorous layer.

Introduction

Fluorous chemistry has developed considerably since the original introduction of "fluorous biphase chemistry" in 1994.[1,2] There are, however, only a few reports on fluorous bipyridine-based compounds,[3] and crystal structures have been reported only for Pt^{II} and Pd^{II} complexes of 2,2′-bipyridine with $CH_2OCH_2(CF_2)_5CF_3$ tails at the 4 and 4′ positions.[4] Fluorous pyridene ligands are also known,[5] but we were unable to find reports on terpyridine ligands modified by fluorous "tails". The number of crystal structures for compounds with long fluorous tails $[R_{fn} = (CF_2)_{n-1}CF_3]$ where $n \geq 6$ is likely somewhat limited due to the "oily" nature of the R_{fn} unit. In this manuscript we report on the following: (1) the synthesis of new fluorous bipyridine and terpyridine ligands without a spacer between the bipyridine or terpyridine moiety and the fluorous "tail", that is, 6,6′-bis(perfluorohexyl)-2,2′-bipyridine (L^1) and 6,6′′-bis(perfluorohexyl)-2,2′:6′,2′′-terpyridine (L^2); (2) the synthesis of a fluorous bipyridine ligand with a CH_2CH_2 spacer, 6,6′-bis(2,2,3,3,4,4,5,5,6,6,7,7,7-tridecafluoroheptyl)-2,2′-bipyridine (L^3), and (3) Cu^I complexes of L^2 and L^3. The fluorous bipyridine L^1 ligand was non-coordinating even though the 2,9-bis(trifluoromethyl)-1,10-phenanthroline complex of Cu^I is known.[6] On the other hand, the fluorous terpyridine Cu^IL^2AcN (AcN = acetonitrile) complex was formed and crystallized in a layered fashion showing a parallel "back to back" arrangement of the terpyridine units with pillars of fluorous tails between them. On the molecular level, Cu^IL^2AcN has distorted square-planar coordination, and interestingly eight distinct structures of Cu^IL^2AcN were found. Finally, Cu^IL^3AcN is a trigonal planar complex and shows a "back to back" "herring bone" arrangement of the bipyridine units with fluorous layers between them.

Results and Discussion

The reaction of 6,6′-dibromo-2,2′-bipyridine with perfluorohexyl iodide in the presence of copper bronze was expected to yield the corresponding perfluorinated ligand L^1. This was indeed observed; however, quite surprisingly under these conditions there was also a carbon–carbon bond cleavage followed by a rearrangement to yield a perfluorinated terpyridine ligand, L^2 (Figure 1). The perfluorin-

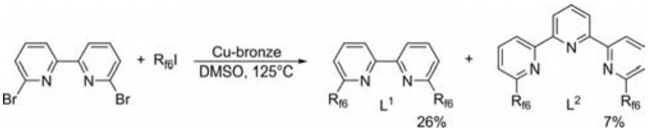

Figure 1. Synthetic pathway for the perfluorinated bipyridine and terpyridine ligands without spacers.

---

[a] Department of Organic Chemistry, Weizmann Institute of Science,
Rehovot 76100, Israel
Fax: +972-8-9343354
E-mail: Ronny.Neumann@weizmann.ac.il
[b] Chemical Research Support Unit, Weizmann Institute of Science,
Rehovot 76100, Israel

ated bipyridine ligand with a CH_2CH_2 spacer, L^3, was prepared by formation of the Zn-activated $R_{f6}CH_2CH_2I$ followed by a Negishi type coupling reaction (Figure 2).

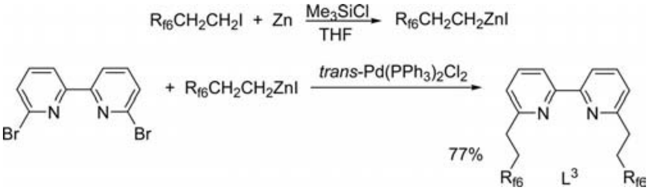

Figure 2. Synthetic pathway for the perfluorinated bipyridine ligand with a CH_2CH_2 spacer.

Attempts at metalation of L^1 failed presumably due to the too low electron density at the nitrogen atoms of L^1. The copper complexes of L^2 and L^3 were prepared by the reaction of the ligands with $[Cu(AcN)_4](BF_4)$ to yield $(Cu^IL^2AcN)(BF_4)$ and $(Cu^IL^3AcN)(BF_4)$, respectively. To the best of our knowledge, the formation of $(Cu^IL^2AcN)(BF_4)$ represents the first example of a nitrogen-based coordination compound with fluorous tails without a spacer unit. The crystal and structural refinement data are presented in Table 2. It should be pointed out that, for $(Cu^IL^2AcN)(BF_4)$ the data was originally collected in house with our Bruker APEX-II diffractometer. However, because of the crystal packing of space group $P\bar{1}$ with eight molecules in the asymmetric unit cell, it was impossible to see all the atoms of the fluorous side chains. Therefore, we decided to collect the data at a synchrotron: although there are limitations regarding the quality of the data and resolution, all atoms are present.

On a molecular level, $(Cu^IL^2AcN)(BF_4)$ was found to form a distorted square-planar coordination sphere with four nitrogen atoms of L^2 and AcN (Figure 3) despite the general tendency of four-coordinate Cu^I complexes to be tetrahedral. Presumably, the interaction between fluorous chains (see below) dictate a coplanar terpyridine conformation, and the bulky nature of the R_{f6} units distorts the square-planar coordination with the AcN ligand pushed out of plane.[7] A closer look at the bond lengths shows that the bond lengths between copper and the nitrogen atoms of the R_{f6}-substituted pyridine rings are longer than those between copper and the nitrogen atoms of acetonitrile and the central pyridine rings.[7] Furthermore, the bond lengths of the former differ very significantly (0.177–0.376 Å), yielding an asymmetric coordination environment around copper. Even more unusual, the crystal structure of $(Cu^IL^2AcN)(BF_4)$ reveals that in fact the molecular unit crystallizes in *eight* distinguishable ways, as can be seen from the interatomic distances shown in Table 1. Thus, the interatomic distances from copper to outer-ring nitrogen atoms vary from 2.156 to 2.215 Å and from 2.383 to 2.534 Å; those from copper to the central ring nitrogen atoms vary from 1.960 to–2.012 Å and those from copper to acetonitrile nitrogen atoms vary from 1.836 to 1.895 Å.

Table 1. Interatomic distances (in Å) for the Cu coordination sphere of $(Cu^IL^2AcN)(BF_4)$.

	Outer py 1	Outer py 2	Central py	AcN
Cu1	2.156(8)	2.534(8)	1.982(8)	1.902(10)
Cu2	2.206(9)	2.383(8)	1.959(8)	1.893(9)
Cu3	2.215(9)	2.472(8)	2.012(8)	1.836(9)
Cu4	2.172(8)	2.541(8)	1.995(9)	1.893(10)
Cu5	2.196(8)	2.439(8)	1.984(8)	1.861(10)
Cu6	2.201(8)	2.406(8)	1.974(8)	1.893(9)
Cu7	2.200(8)	2.496(8)	1.960(9)	1.895(11)
Cu8	2.183(8)	2.532(8)	1.973(9)	1.852(10)

The crystal packing of $(Cu^IL^2AcN)(BF_4)$ shows a layered structure (Figure 4). There is a clear segregation between the aromatic terpyridine moieties and the fluorous chains. The terpyridine units are arranged in a "back to back" configuration with a rotation of 180° of the units at the opposite sides of the interlayer. The interlayer Cu–Cu distances are in the approximate range 6–6.2 Å, while the intralayer Cu–Cu distances alternate between approximately 9.8 Å and 12–12.5 Å. The terpyridine units are tilted 20–25° relative to the interlayer plane. The cross-section view (Figure 4, right) shows that the layered structure is staggered with offsets of approximately 4 Å between layers. The perfluorinated side chains all have *anti* $(CF_2)_4$ segments except in one case on Cu1 where the C17–C18–C19–C20 segment

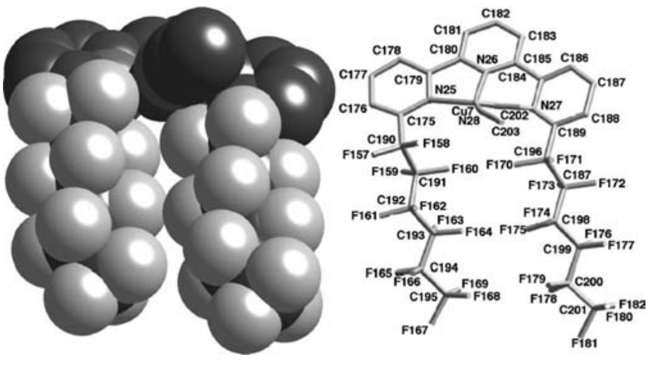

Figure 3. CPK (left) and stick (right) representations of the molecular structure of $(Cu^IL^2AcN)(BF_4)$. The BF_4 anion and H atoms are not shown for clarity.

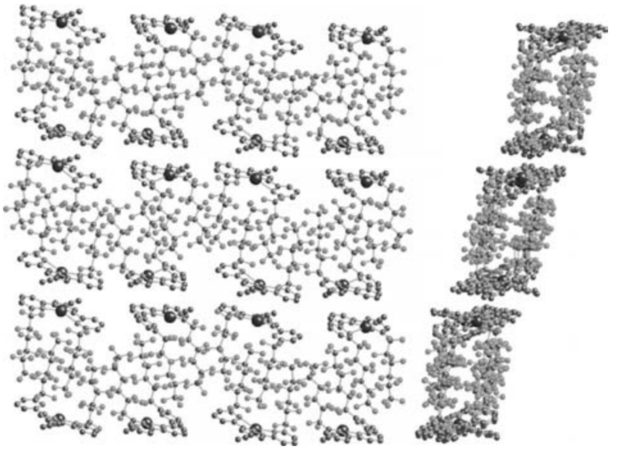

Figure 4. Representations of the crystal structure of $(Cu^IL^2AcN)(BF_4)$ from two different planes. The BF_4 anion and H atoms are not shown for clarity.

has a *gauche* conformation. As can be seen, the perfluorinated chains form intertwining "tail to tail" fluorous layers having an approximate thickness of 8.5 Å. The BF_4 anions are in the interlayer voids.

Figure 5 shows the molecular structure of $(Cu^IL^3AcN)(BF_4)$, in which there is a Y-shaped trigonal planar coordination sphere around copper(I). The Cu–N bond lengths [1.8512(17), 2.0111(16), and 2.0182(16) Å] and the N–Cu–N bond angles [82.20(6), 137.24(7), and 140.55(7) Å] are very similar to those reported in the literature for analogous compounds based on 2,9-dimethyl-1,10-phenanthroline, which means that the fluorous tails with the CH_2CH_2 spacers basically have no effect on the coordination of Cu^1.[8] The fluorous tails are at an angle of approximately 130° relative to the plane of the Cu–bipyridine unit. All perfluorinated side chains have *anti* $(CF_2)_4$ segments, except in one case where the C14–C15–C16–C17 segment has a *gauche* conformation. The crystal structure of $(Cu^IL^3AcN)(BF_4)$ (Figure 6) shows a "herring bone" conformation with an approximately 96° angle in the CubipyAcN units. The interlayer Cu–Cu distances are 5.33 Å, whilst the intralayer Cu–Cu distances alternate: 9.467 and 10.292 Å. The "herring bone" conformation leads to an accordion-type, fluorous layer.

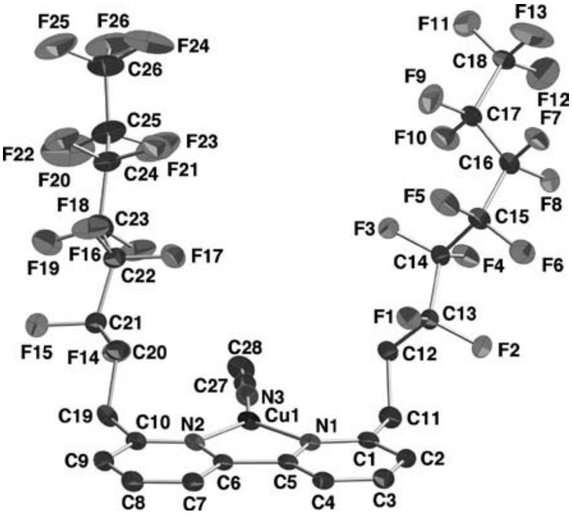

Figure 5. ORTEP (50% probability) representation of the molecular structure of $(Cu^IL^3AcN)(BF_4)$. The BF_4 anion and H atoms are not shown for clarity.

The phase transition behavior of both $(Cu^IL^2AcN)(BF_4)$ and $(Cu^IL^3AcN)(BF_4)$ was investigated by differential scanning calorimetry (DSC), to see whether there were any liquid crystalline phases as may be expected from the crystal packing (Figure 7). $(Cu^IL^3AcN)(BF_4)$ showed the typically observed crystal-to-solid transition at 212 °C, which was reversible with a freezing point depression. Interestingly, $(Cu^IL^2AcN)(BF_4)$ showed a complicated series of phase transitions that were, however, largely irreversible on cooling. These phase transitions are likely crystal-to-liquid crystalline transitions and are the result of the layered structure of $(Cu^IL^2AcN)(BF_4)$.

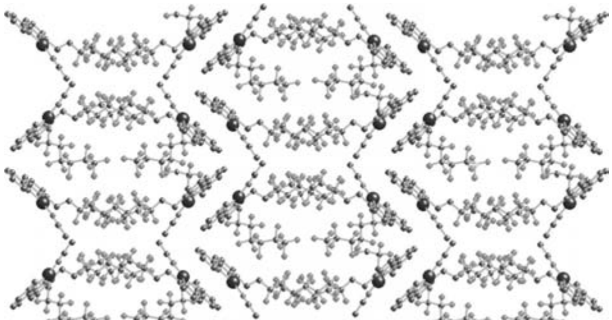

Figure 6. Representation of the crystal structure of $(Cu^IL^3AcN)(BF_4)$. The BF_4 anion and H atoms are not shown for clarity.

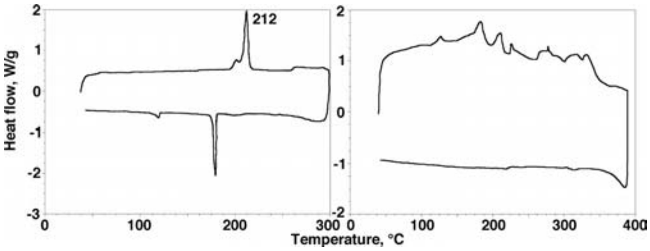

Figure 7. DSC of $(Cu^IL^2AcN)(BF_4)$ and $(Cu^IL^3AcN)(BF_4)$.

Conclusions

The copper(I) complex of a terpyridine ligand with two perfluorinated tails with no spacers, $(Cu^IL^2AcN)(BF_4)$, yields an interesting molecular and crystal structure. Due to the low symmetry and large unit cell, synchrotron irradiation was required to locate all the atoms in the structure. The molecular structure shows a tetrahedrally distorted square-planar coordination around Cu^I with large asymmetry of the bond lengths between Cu^I and the two R_{f6} substituted pyridine rings. Moreover, eight different structural variants of $(Cu^IL^2AcN)(BF_4)$ were observed. The crystal packing showed a "back to back" organization of the terpyridine units with segregated fluorous layers. In the perpendicular plane, one can see that the layers are staggered. Similar complexation of Cu^I to bipyridine required perfluorinated tails with CH_2CH_2 spacers, $(Cu^IL^3AcN)(BF_4)$. In this case, the Y-shaped trigonal planar coordination sphere around Cu^I was almost identical to an analogous 2,9-dimethylphenathroline complex, indicating that the CH_2CH_2 spacers insulate the Cu^I center form the electronic effects of the R_{f6} tail. The fluorous tails were at a 130° angle. The crystal packing showed a "herring bone" organization of the CubipyAcN moieties with an accordion-type fluorous layer.

Experimental Section

6,6′-Bis(perfluorohexyl)-2,2′-bipyridine (L^1) and 6,6′′-Bis(perfluorohexyl)-2,2′:6′,2′′-terpyridine (L^2): A suspension of copper bronze (0.5 g, 7.86 mmol) in dry DMSO (10 mL) was heated at 125 °C for 15 min under an Ar atmosphere. Perfluorohexyl iodide (0.79 mL, 3.66 mmol) was added dropwise, and the reaction mixture was heated for a further 45 min. To this reaction mixture was added a DMSO (7 mL) solution of 6,6′-dibromo-2,2′-bipyridine (0.230 g, 0.73 mmol). The reaction mixture was stirred for 24 h at 125 °C and quenched with cold water (50 mL). Diethyl ether/CH_2Cl_2/$CHCl_3$ (120 mL, 1:1:1 volume ratio) was added, and after shaking the reaction mixture, the organic layer was collected and dried with $MgSO_4$. After filtration, the solvent was evaporated to leave behind a colorless crystalline solid. TLC showed two products that were separated by silica column chromatography with hexane as eluant to give L^1 (150 mg, 26% yield) as a white crystalline solid and also L^2 (40 mg, 7% yield) as a white crystalline solid. Both compounds were separately characterized by ^1H NMR, ^{13}C NMR, ^{19}F NMR spectroscopy, and mass spectrometry. For L^1: ^1H NMR (300 MHz, $CDCl_3$ 25 °C): δ = 8.68 [d, ^3J(H,H) = 9.1 Hz, 2 H, H^3], 8.01 (t, $^3J_{H,H}$ = 9.2 Hz, 2 H, H^4), 7.73 (d, $^3J_{H,H}$ = 9.1 Hz, 2 H, H^5) ppm. ^{13}C NMR (100.58 MHz, $CDCl_3$, 25 °C): δ = 155.55, 153.21, 138.02, 137.54 123.38, 122.20, 99.45 99.13, 99.07, 97.23, 82.54 ppm. ^{19}F NMR (376.31 MHz, $CDCl_3$ 25 °C): δ = –80.95, –113.66, –121.55, –121.86, –122.88, 126.24 ppm. ESI-MS ($CHCl_3$): *m*/*z* = 792.41, 793.47 [M + 1]. $C_{22}H_6F_{26}N_2$ (792.26): calcd. C 33.35, H 0.76, N 3.54; found C 34.12, H 0.55, N 4.13. For L^2: ^1H NMR (300 MHz, $CDCl_3$, 25 °C): δ = 8.78 (d, $^3J_{H,H}$ = 9.0 Hz, 2 H, 2 H, H^3), 8.54 (d, $^3J_{H,H}$ = 9.0 Hz, 2 H, H^9), 7.97 (m, 3 H, H^4, H^7), 7.70 (d, $^3J_{H,H}$ = 9.1 Hz, 2 H, 2 H, H^5) ppm. ^{13}C NMR (100.58 MHz, $CDCl_3$, 25 °C): δ = 155.80, 153.57, 137.97, 137.63, 122.84, 121.84, 121.59, 99.49 99.08, 99.01, 97.19, 82.57 ppm. ^{19}F NMR (376.31 MHz, $CDCl_3$, 25 °C): δ = –81.35, –113.32, –121.22, –121.57, –122.55, 125.92 ppm. ESI-MS ($CHCl_3$): *m*/*z* = 869, 870.11 [M + 1]. $C_{27}H_9F_{26}N_3$ (869.35): calcd. C 37.30, H 1.04, N 4.83; found C 36.23, H 1.84, N 5.38.

6,6′-Bis(2,2,3,3,4,4,5,5,6,6,7,7,7-tridecafluoroheptyl)-2,2′-bipyridine (L^3): A Schlenk flask was charged with zinc grains (0.490 g, 7.5 mmol), THF (3 mL), and 1,2-dibromoethane (0.0455 mL, 0.53 mmol). The mixture was gently heated at reflux, by using a heat gun, with stirring and allowed to cool to room temperature (5 times). $(CH_3)_3SiCl$ (0.020 mL, 0.16 mmol) was then added. After 15–20 min, a solution of $I(CH_2)_2R_{f6}$ (1.435 g, 2.5 mmol) in THF (3 mL) was added dropwise. The mixture was stirred for 1 h. A separate Schlenk flask was charged with 6,6′-dibromo-2,2′-dipyridyl (0.314 g, 1.00 mmol), *trans*-$Pd(PPh_3)_2Cl_2$ (0.039 g, 0.056 mmol), and THF (8 mL). The contents of the reaction flask containing $IZnCH_2CH_2R_{f6}$ were added by cannula. The orange solution was stirred at 65 °C for 6 h and then cooled to room temperature. Ether (25 mL) was added. The mixture was washed twice with a solution of KCN in water (15 mL), dried (Na_2SO_4), and concentrated to dryness by rotary evaporation. The product was purified on a silica column by using hexanes/CH_2Cl_2 (3:2 v/v) as eluant. The solvent was removed under vacuum to obtain a white crystalline solid (0.65 g, 77% yield). ^1H NMR (300 MHz, $CDCl_3$, 25 °C): δ = 8.30 (d, $^3J_{H,H}$ = 9.0 Hz, 2 H, 2 H, H^3), 7.74 (t, $^3J_{H,H}$ = 9.1 Hz, 2 H, H^4), 7.20 (d, $^3J_{H,H}$ = 9.2 Hz, 2 H, 2 H, H^5), 3.14 (m, 4 H, H_α), 2.65 (m, 4 H, H_β) ppm. ^{13}C NMR (100.58 MHz, $CDCl_3$, 25 °C): δ = 157.92, 155.61, 137.86, 137.71, 123.22, 119.87, 119.24, 99.49, 99.01, 86.19, 75.57, 30.28, 28.60 ppm. ^{19}F NMR (376.31 MHz, $CDCl_3$, 25 °C): δ = –81.44, –114.92, –122.55, –123.44, –124.13, –127.01 ppm. ESI-MS (CH_2Cl_2): *m*/*z* = 848.16, 849.23 [M + 1]. $C_{27}H_9F_{26}N_3$ (848.37): calcd. C 36.81, H 1.66, N 3.30; found C 36.45, H 1.96, N 3.68.

(Cu^IL^2AcN)(BF_4): L^2 (100 mg, 0.115 mmol) was suspended in deoxygenated CH_2Cl_2 (7 mL); to this mixture was added [Cu-(AcN)$_4$](BF_4) (40 mg, 0.115 mmol), and the reaction mixture was stirred for 3 h at room temperature under an argon atmosphere. The reaction mixture was filtered, and ether was allowed to diffuse into the filtrate. Orange crystals of (Cu^IL^2AcN)(BF_4) formed, which were filtered off, washed with diethyl ether, and dried under vacuum. (90 mg, 81% yield). IR (KBr pellet): $\tilde{\nu}$ = 1585, 1439, 1366, 1202, 1147, 1125, 1086, 993, 836, 778, 767, 746, 738, 634, 582, 533 cm^{-1}. ^1H NMR (300 MHz, CD^3NO_2, 25 °C): δ = 8.68 (d, $^3J_{H,H}$ = 9.0 Hz, 2 H, H^3), 8.56 (d, $^3J_{H,H}$ = 9.1 Hz, 2 H, 2 H, H^7), 8.46 (t, $^3J_{H,H}$ = 9.1 Hz, 2 H, H^4), 8.16 (d, $^3J_{H,H}$ = 9.1 Hz, 2 H, 2 H, H^5); 7.95 (s, 1 H, H^8) ppm. ^{13}C NMR (100.58 MHz, CD_3NO_2, 25 °C): δ = 156.76, 154.81, 148.82, 143.70, 143.16, 128.44, 127.34, 127.03, 120.93, 118.23, 116.01 ppm. ^{19}F NMR (376.31 MHz, CD_3NO_2, 25 °C): δ = –85.17, –117.36, –124.87, –125.60, –130.12, –155.76 ppm. ESI-MS (CH_2Cl_2): *m*/*z* = 973.19, 974.14 [M + 1]. $C_{29}H_{12}BCuF_{30}N_4$ (1060.75): calcd. C 32.84, H 1.14, N 5.28; found C 32.02, H 1.65, N 6.05.

(Cu^IL^3AcN)(BF_4): L^3 (100 mg, 0.117 mmol) was suspended in deoxygenated CH_2Cl_2 (7 mL); to this mixture was added [Cu-(AcN)$_4$](BF_4) (41.6 mg, 0.117 mmol), and the reaction mixture was stirred for 3 h at room temperature under an argon atmosphere. The reaction mixture was filtered, and ether was allowed to diffuse into the filtrate. Pale yellow crystals of (Cu^IL^3AcN)(BF_4) formed, which were collected and washed with diethyl ether and dried under vacuum in 83% yield. IR (KBr pellet): $\tilde{\nu}$ = 1599, 1430, 1241, 1145, 1066, 029, 888, 841, 820, 747, 716, 697, 667, 574 cm^{-1}. ^1H NMR (300 MHz, nitromethane): δ = 8.49 (d, $^3J_{H,H}$ = 9.0 Hz, 2 H, H^3), 8.27 (m, 2 H, H^4), 7.75 (d, $^3J_{H,H}$ = 9.1 Hz, 2 H, 2 H, H^5), 3.00 (m, 2 H, H_α), 2.84 (m, 2 H, H_β) ppm. ^{19}F NMR (376.31 MHz, CD_3NO_2, 25 °C): δ = –85.05, –118.49, –125.33, –126.65, –130.12, –155.76 ppm. ESI-MS (CH_2Cl_2): *m*/*z* = 953.43, 954.56 [M + 1]. $C_{28}H_{17}BCuF_{30}N_3$ (1039.77): calcd. C 32.34, H 1.65, N 4.04; found C 33.02, H 1.34, N 3.75.

X-ray Diffraction Analyses

Crystal data for (Cu^IL^2AcN)(BF_4) was measured at 100(2) K with the European Synchrotron Radiation Facility (ESRF) synchrotron in Grenoble on beamline ID23–1 with a Quantum 315R CCD detector, λ = 0.9000 Å. (Cu^IL^3AcN)(BF_4) was measured at 100(2) K on a Bruker Kappa Apex2 CCD diffractometer [λ(Mo-K_α) = 0.71073 Å] with a graphite monochromator. The data were processed with HKL2000 and Apex2 software, respectively. The structures were solved by direct methods using the program SHELXS-97 and refined with SHELXL-97. All non-hydrogen atoms were

Table 2. Crystal data and structure refinement for (Cu^IL^2AcN)-(BF_4) and (Cu^IL^3AcN)(BF_4).

	(Cu^IL^2AcN)(BF_4)	(Cu^IL^3AcN)(BF_4)
Empirical formula	$C_{29}H_{12}BCuF_{30}N_4$	$C_{28}H_{17}BCuF_{30}N_3$
Molecular weight	1060.78	1039.80
Crystal system	triclinic	monoclinic
Space group	$P\bar{1}$	$C2/c$
a /Å	11.242(2)	38.095(2)
b /Å	34.007(7)	15.6106(8)
c /Å	41.339(8)	12.0960(6)
α /°	66.25(3)	90
β /°	87.72(3)	91.229(4)
γ /°	84.27(3)	90
Volume /Å^3; Z	14394(5); 16	7191.7(6); 8
Density$_{calc}$ /g cm^{-3}	1.958	1.921
μ /mm^{-1}	0.795	0.792
Reflections	455897	12503
Unique reflections	32860	8954
R_{int}	0.00	0.0405
R_1; wR_2 [$I > 2\sigma(I)$][a]	0.1548; 0.4076	0.0460; 0.1065
R_1; wR_2 (all data)[a]	0.1582; 0.4100	0.0757; 0.1240

[a] $R_1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$; $wR_2 = \{\Sigma[w(F_o^2 - F_c^2)^2]/\Sigma w(F_o^2)^2\}^{1/2}$.

refined anisotropically, using weighted full-matrix least-squares on F^2. Crystal data collection and refinement parameters are given in Table 2. Further details, also concerning disorder, where present, are given in the crystallographic files, which are available at the Cambridge Crystallographic Data Centre.

CCDC-806042 [for $(Cu^IL^2AcN)(BF_4)$] and -806043 [for $(Cu^IL^3AcN)(BF_4)$] contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Acknowledgments

This research was supported by the Israel Science Foundation (ISF) grant 1073/10 and the Helen and Martin Kimmel Center for Molecular Design. Dr. Linda Shimon is thanked for data collection at the European Synchrotron Radiation Facility (ESRF) synchrotron in Grenoble. R. N. is the Rebecca and Israel Sieff Professor of Chemistry.

---

[1] a) I. T. Horváth, J. Rábai, *Science* **1994**, *266*, 72–74; b) I. T. Horváth, *Acc. Chem. Res.* **1998**, *31*, 641–645.

[2] J. A. Gladysz, D. P. Curron, I. T. Horváth, *Handbook of Fluorous Chemistry*, Wiley/VCH, Weinheim, **2004**.

[3] a) B. Betzemeier, M. Cavazzini, S. Quici, P. Knochel, *Tetrahedron Lett.* **2000**, *41*, 4343–4346; b) S. Quici, M. Cavazzini, S. Ceragioli, F. Montanari, G. Pozzi, *Tetrahedron Lett.* **1999**, *40*, 3647–3650; c) N. Garelli, P. Vierling, *Inorg. Chim. Acta* **1992**, *194*, 247–253; d) N. Garelli, P. Vierling, *J. Org. Chem.* **1992**, *57*, 3046–3051.

[4] a) N. Lu, W.-H. Tu, Y.-S. Wen, L.-K. Liu, C.-Y. Chou, J.-C. Jiang, *CrystEngComm* **2010**, *12*, 538–542; b) N. Lu, Y.-N. Lin, J.-Y. Chen, T.-C. Chen, S.-C. Chen, Y.-S. Wen, L.-K. Liu, *Polyhedron* **2007**, *26*, 3045–3053; c) N. Lu, W.-H. Tu, H.-C. Hou, C.-T. Lin, C.-K. Li, L.-K. Liu, *Polyhedron* **2010**, *29*, 1123–1129.

[5] C. Rocaby, F. Hampel, J. A. Gladysz, *J. Org. Chem.* **2002**, *67*, 6863–6870.

[6] a) A. Y. Kovalevsky, M. Gembicky, P. Coppens, *Inorg. Chem.* **2004**, *43*, 8282–8289; b) M. T. Miller, P. K. Gantzel, T. B. Karpishin, *Angew. Chem.* **1998**, *110*, 1659; *Angew. Chem. Int. Ed.* **1998**, *37*, 1556–1558.

[7] A. Onoda, K. Kawakita, T. Okamura, H. Yamamoto, N. Ueyama, *Acta Crystallogr., Sect. E* **2003**, *59*, m266–m267.

[8] a) M. Munakata, M. Maekawa, S. Kitagawa, S. Matsuyama, H. Masuda, *Inorg. Chem.* **1989**, *28*, 4300–4302; b) S. Mutrofin, E. J. Chan, P. C. Healy, A. Marinelli, J. Ngoune, C. Pettinari, R. Pettinari, N. Somers, B. W. Skelton, A. H. White, *Inorg. Chim. Acta* **2008**, *361*, 2365–2374.

Received: December 9, 2010