Electronic Supplementary Information

Spectroscopy, molecular structure and electropolymerization of Ni (II) and Cu (II) complexes containing a thiophene-appending fluorinated Schiff base ligand

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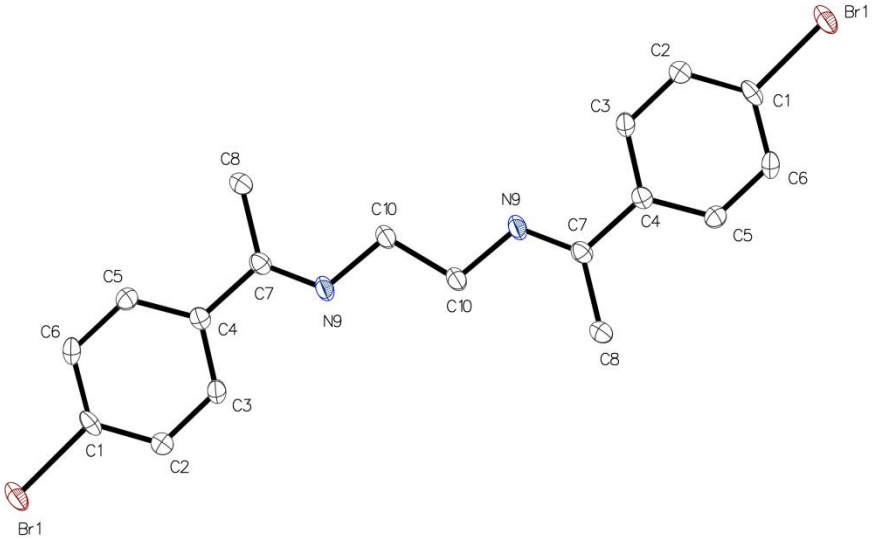

Fig. S1 Molecular structure of the diimine **1** showing the atom labeling scheme. Hydrogen atoms are omitted for clarity. Thermal ellipsoids are drawn at 50% probability. Selected bond distances (Å) and angles (°): C(1)-Br(1) 1.903(3), C(4)-C(7) 1.493(4), N(9)-C(7) 1.275(4), C(7)-C(8) 1.504(4), N(9)-C(10) 1.468(3), C(10)-C(10)$^{\#}$ 1.506(6); N(9)-C(7)-C(4) 116.9(3), N(9)-C(7)-C(8) 124.9(3), C(7)-N(9)-C(10) 119.1(3), N(9)-C(10)-C(10)$^{\#}$ 109.3(3), C(2)-C(1)-Br(1) 118.6(2), C(6)-C(1)-Br(1) 120.0(2). Symmetry transformations used to generate equivalent atoms: # -x, -y, -z.

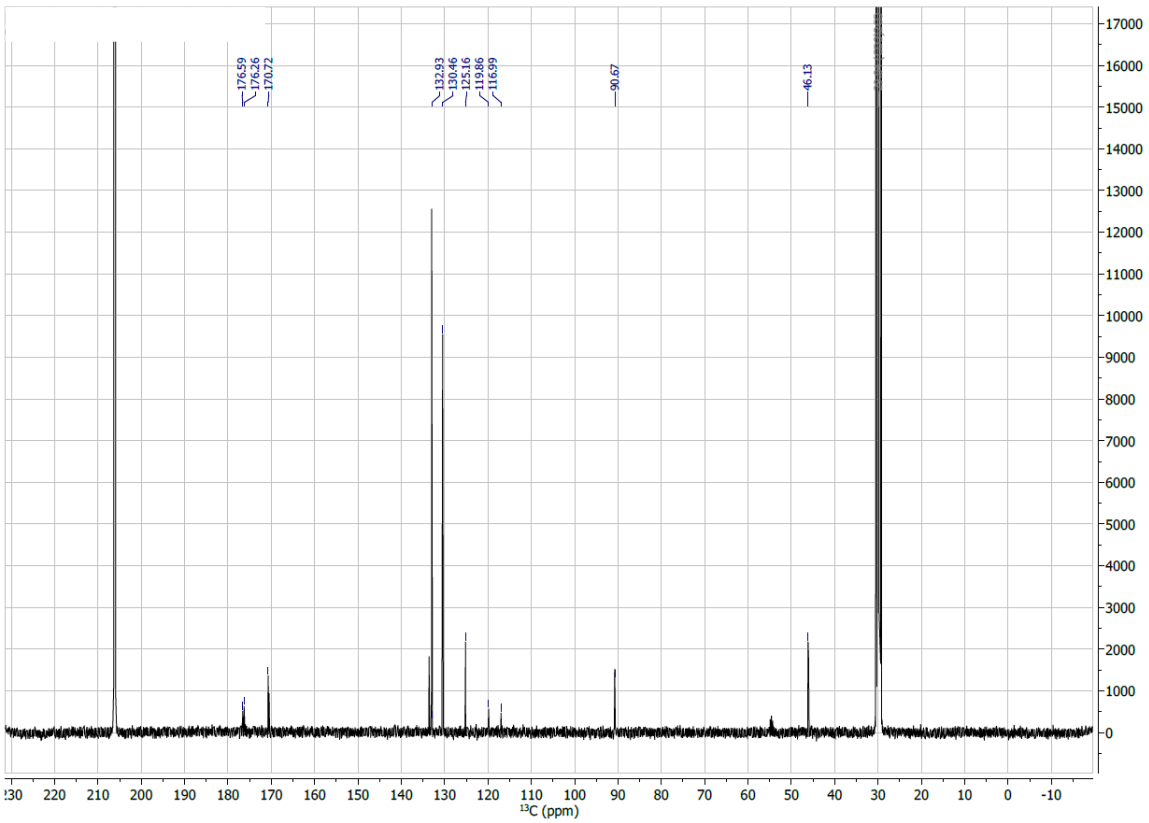

Fig. S2 $^{13}C\{^{1}H\}$ NMR spectrum of the Schiff base proligand **2** recorded in $(CD_3)_2CO$ at 298 K.

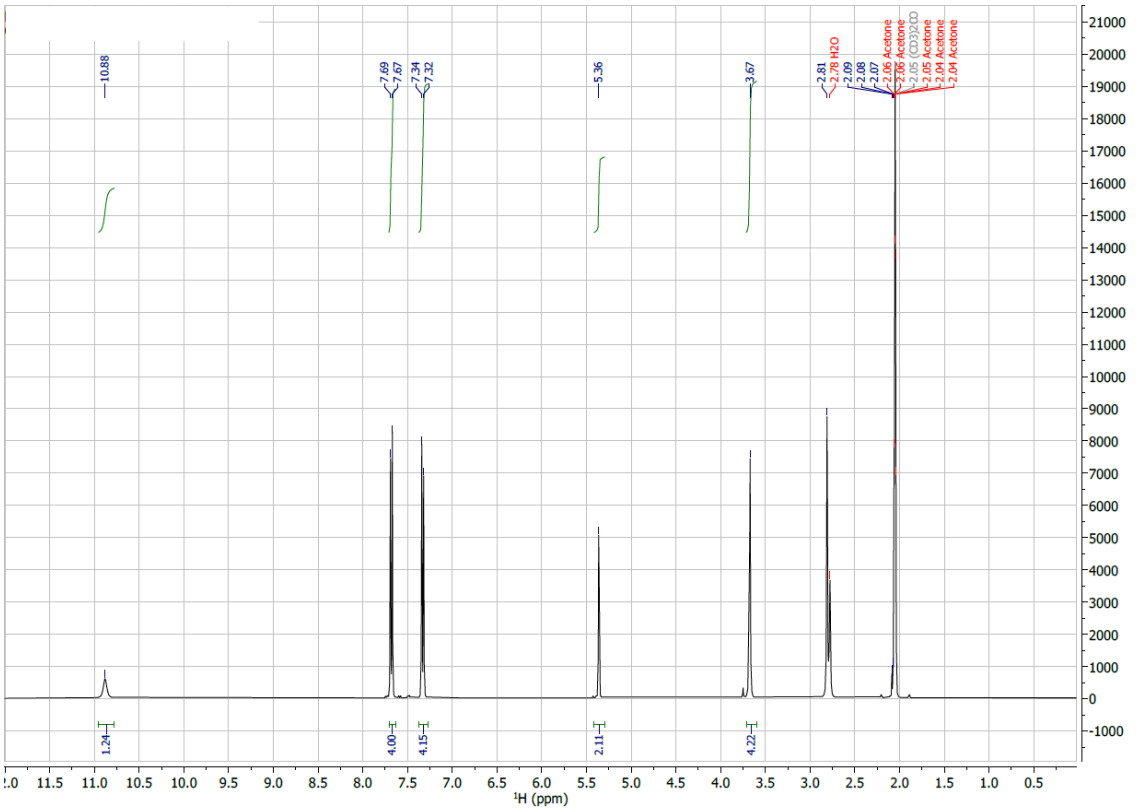

Fig. S3 ^{1}H NMR spectrum of the Schiff base proligand **2** recorded in $(CD_3)_2CO$ at 298 K.

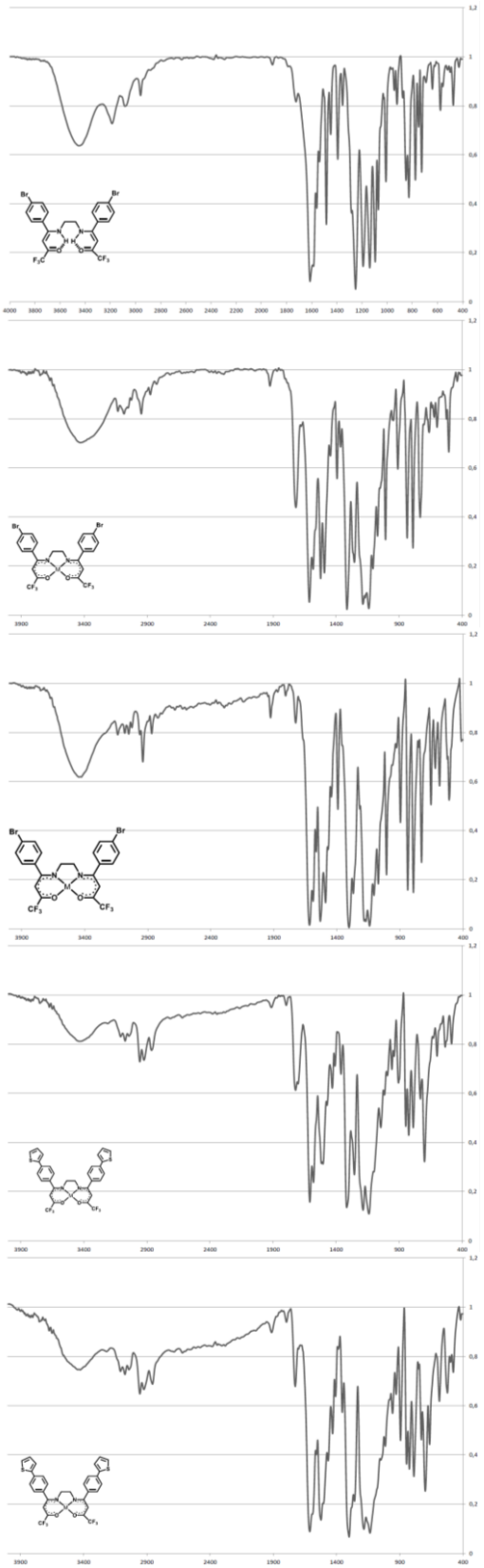

Fig. S4 FT-IR solid-state spectra (KBr disk) of compounds **2-6** (from top to bottom).

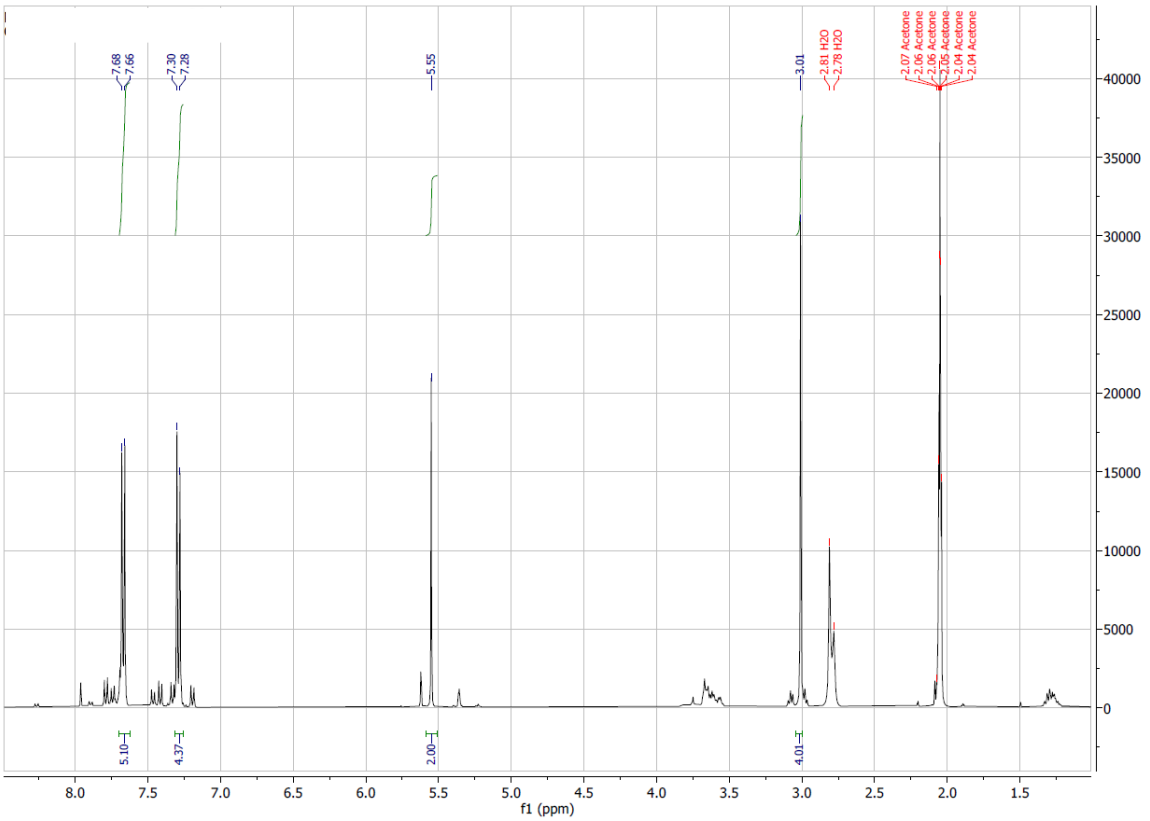

Fig. S5 ^{1}H NMR spectrum of the Schiff base complex **3** recorded in $(CD_3)_2CO$ at 298 K.

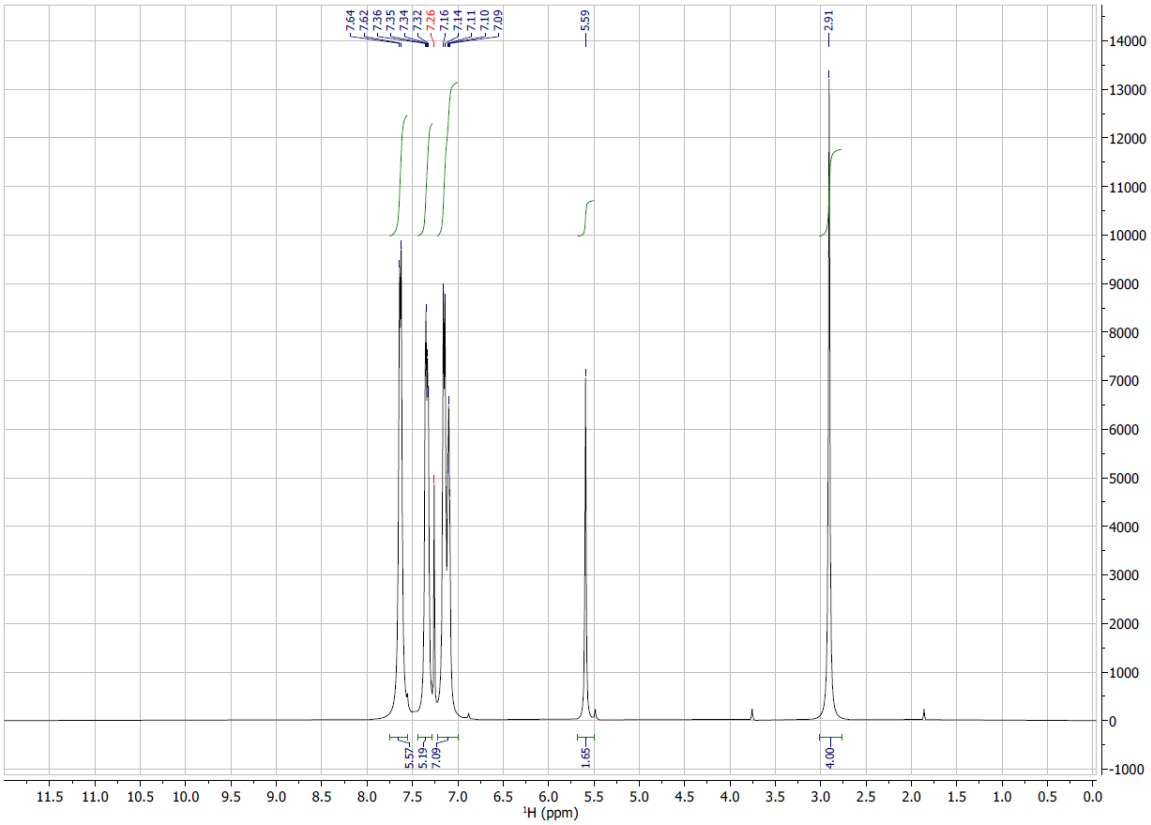

Fig. S6 ^{1}H NMR spectrum of the thiophene-appending Schiff base complex **5** recorded in $CDCl_3$ at 298 K.

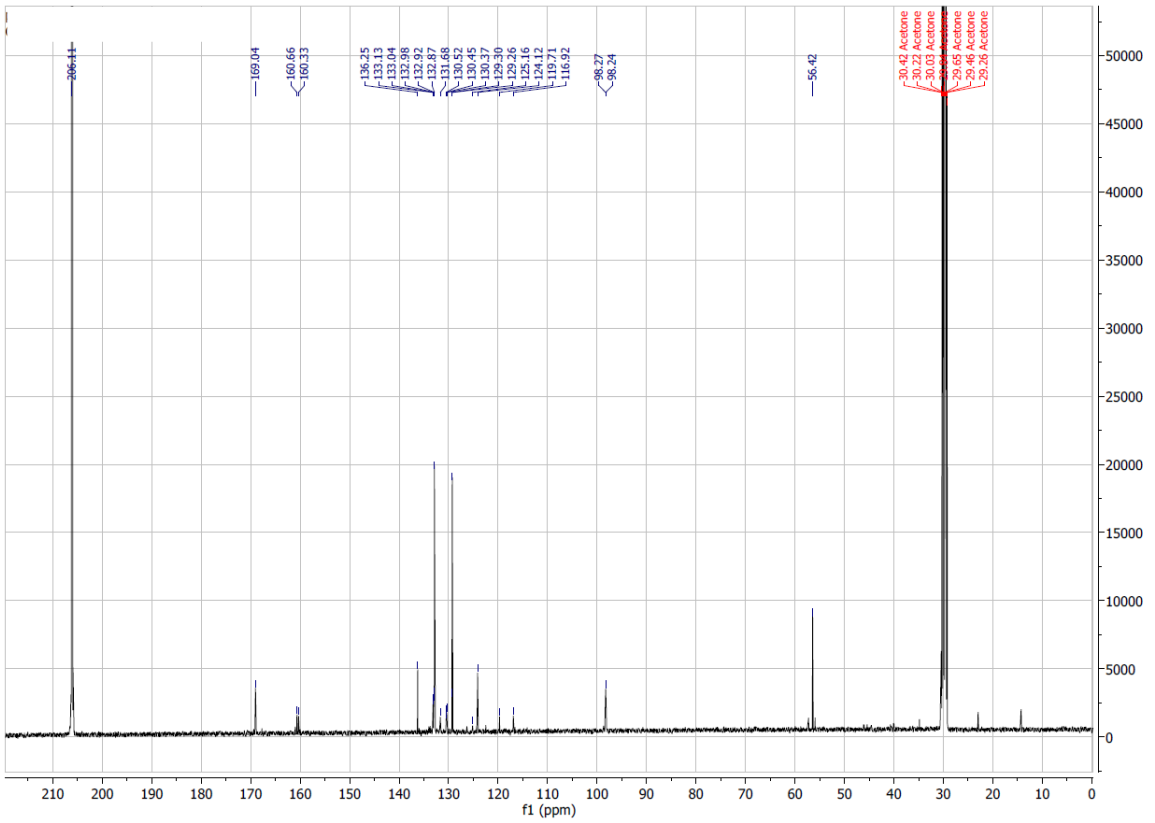

Fig. S7 $^{13}C\{^{1}H\}$ NMR spectrum of the Schiff base complex **3** recorded in $(CD_3)_2CO$ at 298 K.

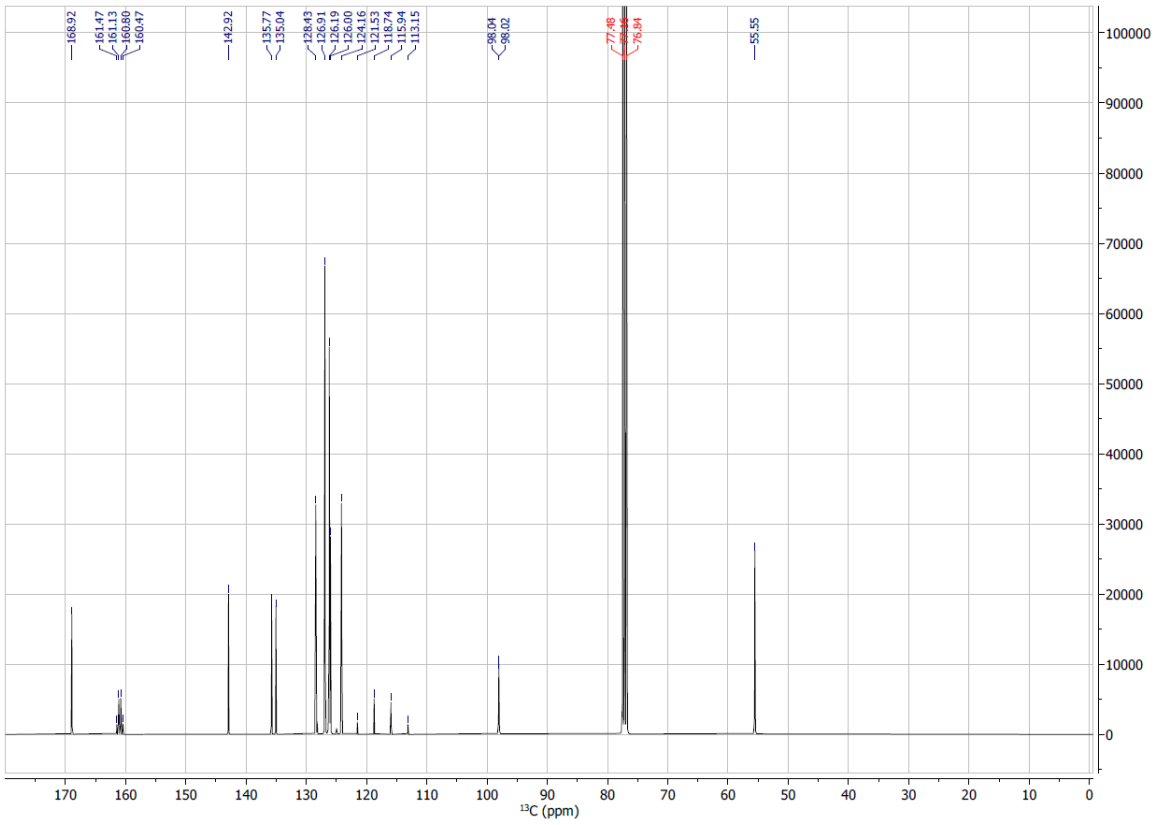

Fig. S8 $^{13}C\{^{1}H\}$ NMR spectrum of the thiophene-appending Schiff base complex **5** recorded in $CDCl_3$ at 298 K.

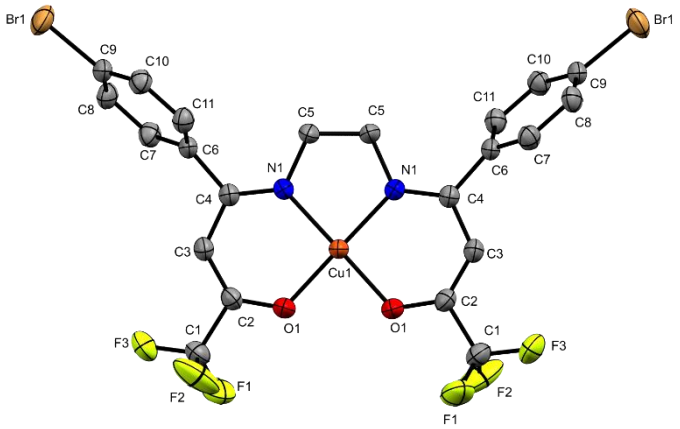

Fig. S9 Molecular structure of the Cu(II) Schiff base complex **4** with its labeling scheme. Hydrogen atoms are omitted for clarity. Thermal ellipsoids are drawn at 50% probability.

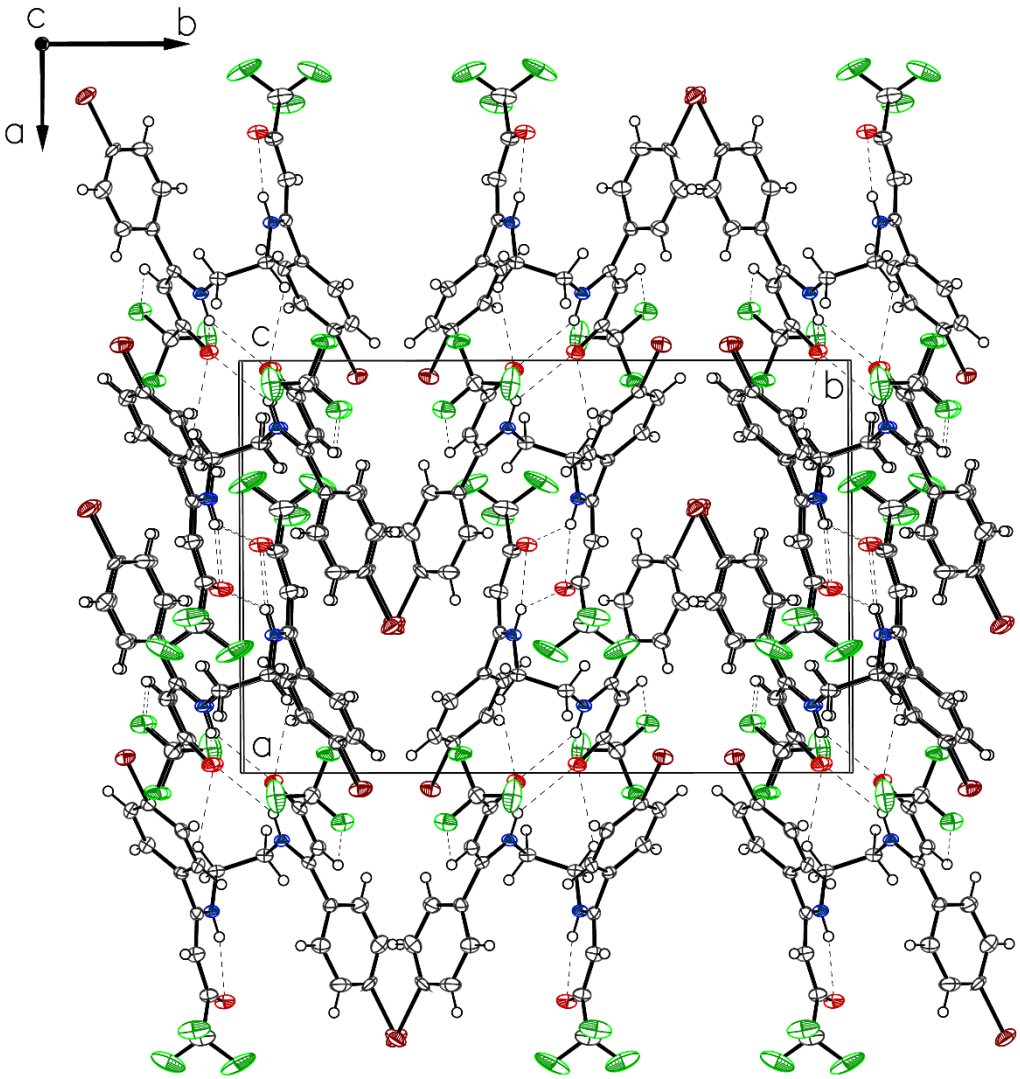

Fig. S10 Intermolecular hydrogen bond interactions observed in the solid-state structures of Schiff base proligand **2**.

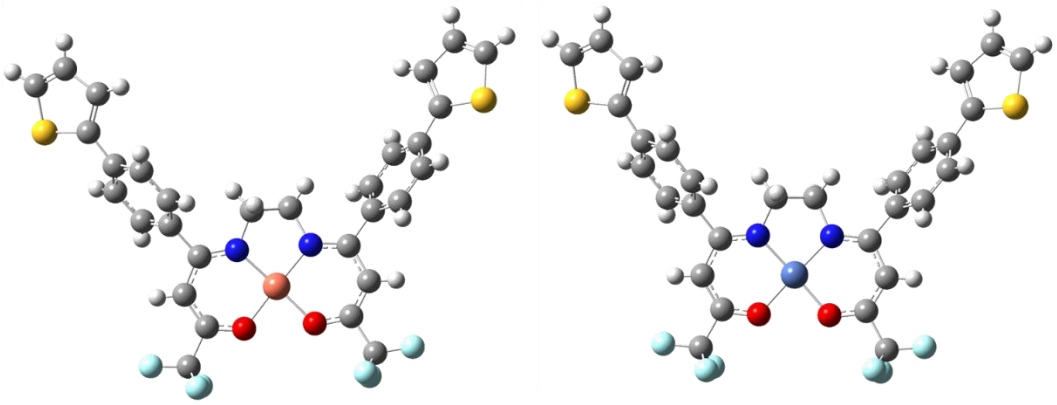

Fig. S11 Optimized geometries of **5** (left) and **6** (right).

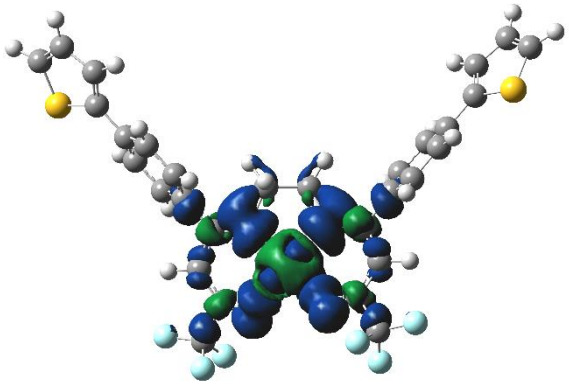

Fig. S12 Computed spin density of the ground state of the Cu(II) complex **6**.

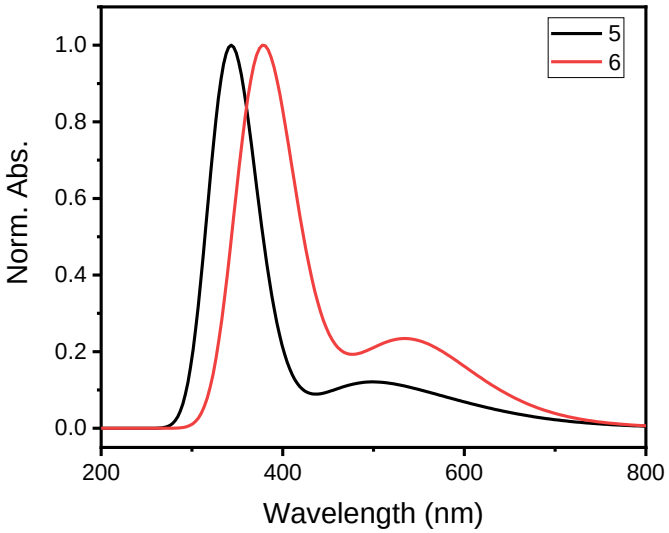

Fig. S13 TD-DFT simulated UV-vis spectra of compounds **5** and **6**.

Table S1 Selected bond distances (Å) and angles (°) of the fluorinated Schiff base proligand **2**.

Bond distances			
O(1)-C(2)	1.248(4)	O(2)-C(22)	1.239(4)
N(1)-C(4)	1.323(4)	N(2)-C(24)	1.328(4)
N(1)-C(5)	1.459(4)	N(2)-C(25)	1.464(4)
C(1)-C(2)	1.533(5)	C(21)-C(22)	1.537(4)
C(2)-C(3)	1.393(4)	C(22)-C(23)	1.408(4)
C(3)-C(4)	1.398(4)	C(23)-C(24)	1.389(4)
C(4)-C(6)	1.492(4)	C(24)-C(26)	1.493(4)
C(1)-F(1)	1.327(5)	C(21)-F(4)	1.331(4)
C(1)-F(2)	1.337(5)	C(21)-F(5)	1.336(4)
C(1)-F(3)	1.331(4)	C(21)-F(6)	1.331(4)
C(9)-Br(1)	1.900(3)	C(29)-Br(2)	1.903(3)
C(5)-C(25)	1.515(5)		
Bond angles			
O(1)-C(2)-C(1)	115.40(3)	O(2)-C(22)-C(21)	115.50(3)
O(1)-C(2)-C(3)	127.10(3)	O(2)-C(22)-C(23)	127.10(3)
N(1)-C(4)-C(3)	121.50(3)	N(2)-C(24)-C(23)	122.10(3)
N(1)-C(4)-C(6)	121.70(3)	N(2)-C(24)-C(26)	119.30(3)
C(4)-N(1)-C(5)	127.60(3)	C(24)-N(2)-C(25)	127.10(3)
C(2)-C(3)-C(4)	123.70(3)	C(22)-C(23)-C(24)	122.50(3)
N(1)-C(5)-C(25)	112.80(3)	N(2)-C(25)-C(5)	111.20(3)
C(8)-C(9)-Br(1)	118.70(2)	C(28)-C(29)-Br(2)	118.80(3)
C(10)-C(9)-Br(1)	119.60(3)	C(30)-C(29)-Br(2)	119.50(3)

Table S2 Selected bond distances (Å) and angles (°) of Schiff base ligands in compounds **3**, **4** and **5**·CH_2Cl_2.[a]

	3	**4**	**5**·CH_2Cl_2
Bond distances			
O(1)-C(2)	1.297(10)	1.283(3)	1.288(5)
N(1)-C(4)	1.315(10)	1.310(3)	1.314(5)
N(1)-C(5)	1.470(9)	1.478(3)	1.477(5)
C(2)-C(3)	1.355(11)	1.360(4)	1.353(6)
C(3)-C(4)	1.437(10)	1.430(4)	1.420(5)
C(5)-C(5)[#]	1.526(15)	1.532(5)	1.495(9)
C(1)-C(2)	1.521(11)	1.520(4)	1.517(6)
C(4)-C(6)	1.499(10)	1.498(4)	1.492(6)
C(1)-F(1)	1.321(11)	1.326(4)	1.308(8)
C(1)-F(2)	1.339(10)	1.308(4)	1.315(7)
C(1)-F(3)	1.325(10)	1.333(4)	1.307(8)
C(9)-X[b]	1.902(8)	1.898(3)	1.464(6)
S(1)-C(12)	-	-	1.703(5)
S(1)-C(15)	-	-	1.682(7)
Bond angles			
M(1)-O(1)-C(2)	123.70(5)	122.77(18)	124.50(3)
M(1)-N(1)-C(4)	126.00(5)	126.17(19)	127.60(3)
M(1)-N(1)-C(5)	113.40(5)	112.21(16)	112.00(2)
O(1)-C(2)-C(3)	128.40(7)	129.30(3)	127.80(4)
O(1)-C(2)-C(1)	111.70(7)	111.80(2)	111.90(4)
N(1)-C(4)-C(3)	122.80(7)	121.80(2)	121.40(4)
C(4)-N(1)-C(5)	120.40(6)	121.50(2)	120.40(3)
N(1)-C(5)-C(5)[#]	106.80(5)	108.67(17)	106.90(3)
N(1)-C(4)-C(6)	122.60(7)	123.30(2)	122.40(3)
C(2)-C(3)-C(4)	122.00(7)	124.40(2)	123.20(4)
C(8)-C(9)-X[b]	118.60(6)	120.00(2)	119.80(4)
C(10-C(9)-X[b]	119.10(6)	118.50(2)	122.00(4)
C(12)-S(1)-C(15)	-	-	93.10(3)

[a]M = Ni, **3** and **5**·CH_2Cl_2; Cu, **4**. [b]X = Br, **3** and **4**; C(12), **5**. Symmetry transformations used to generate equivalent atoms: # -x, y, -z+1/2

Table S3 Intramolecular hydrogen bonding parameters for the fluorinated Schiff base proligand **2**.

D-H···A (Å)	D-H (Å)	H···A (Å)	D···A (Å)	D—H···A (°)
N(1)-H(1)···O(1)	0.88	2.04	2.734(3)	135.4
N(2)-H(2)···O(2)	0.88	2.03	2.712(3)	133.4
N(1)-H(1)···O(1)$^{\#1}$	0.88	2.32	3.007(3)	134.9
N(2)-H(1)···O(2)$^{\#2}$	0.88	2.39	3.055(4)	132.2
C(8)-H(7)···F(4)	0.95	2.95	3.202(4)	120.5
C(10)-H(9)···Br(1)$^{\#3}$	0.95	3.10	3.924(3)	145.7
C(5)-H11A)···O(2)$^{\#2}$	0.99	2.51	3.254(4)	131.4
C(5)-H11A)···F(5)$^{\#2}$	0.99	2.63	3.185(4)	115.9
C(25)-H(12A)···O(1)$^{\#1}$	0.99	2.52	3.268(4)	132.3

Symmetry transformations used to generate equivalent atoms:

#1 -x, -y, -z T = [1, 0, 0];

#2 -x, -y, -z T = [2, 0, 0];

#3 x, -y-1/2, z-1/2 T = [0, 0, 0].