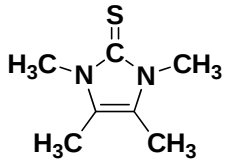
Supporting Information

Design, Synthesis and Study of Main Chain Poly(N-Heterocyclic Carbene) Complexes: Applications in Electrochromic Devices

Adam B. Powell, Christopher W. Bielawski and Alan H. Cowley*

Department of Chemistry and Biochemistry and Center for Nano and Molecular Science and Technology
The University of Texas at Austin, 1 University Station, A5300, Austin, Texas 78712-0165



Kühn Thione

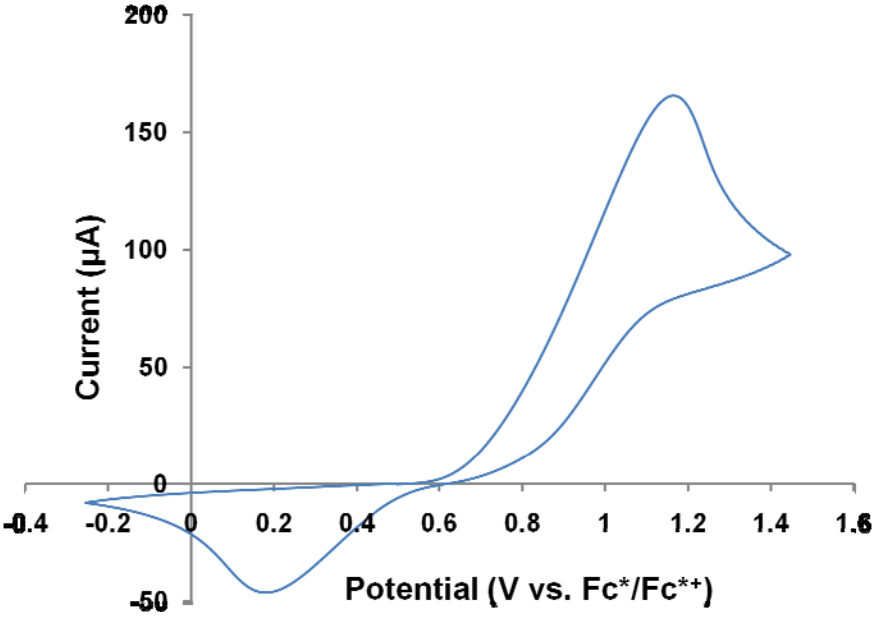
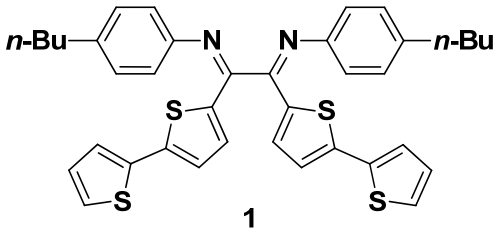


Figure S1. Cyclic Voltammogram of a 1.0 mM solution of the Kuhn thione in CH_2Cl_2.



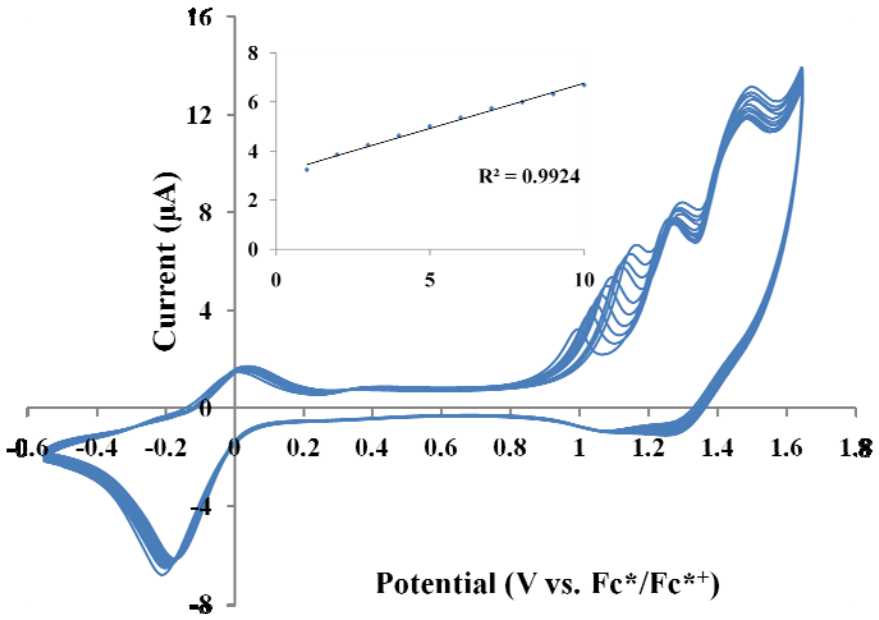
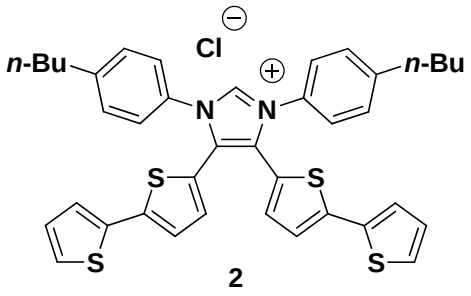


Figure S2.(a) Overlay of continuous cyclic voltammograms of diimine **1** over time. Inset: plot of oxidation current vs. number of cycles. Concentration of **1** was 1.0 mM in 0.1 M $TBAPF_6/CH_2Cl_2$.



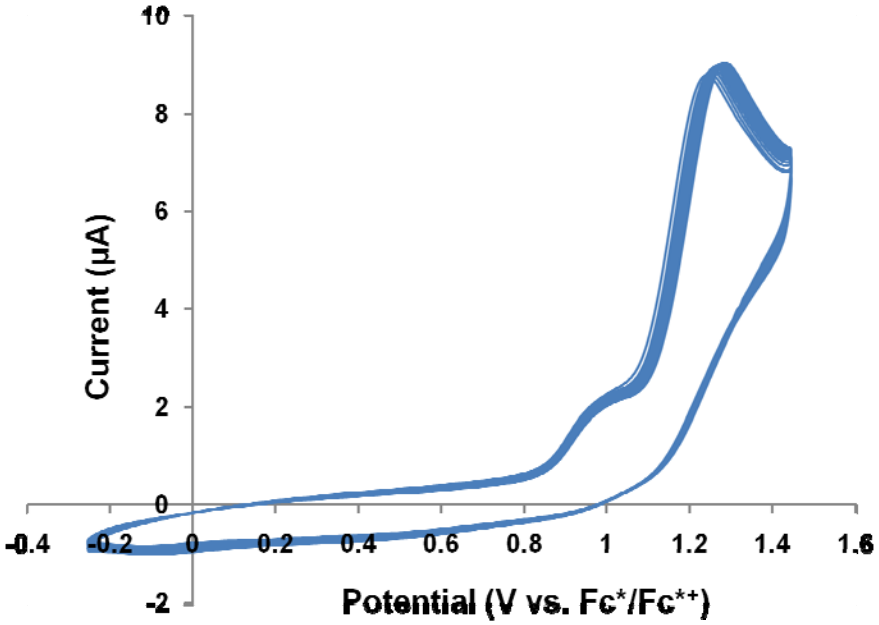
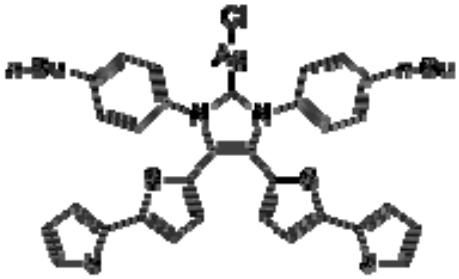


Figure S3. Cyclic voltammogram of bithiophene–substituted imidazolium chloride **2**. Concentration of **2** was 1.0 mM in 0.1 M $TBAPF_6/CH_2Cl_2$.



3

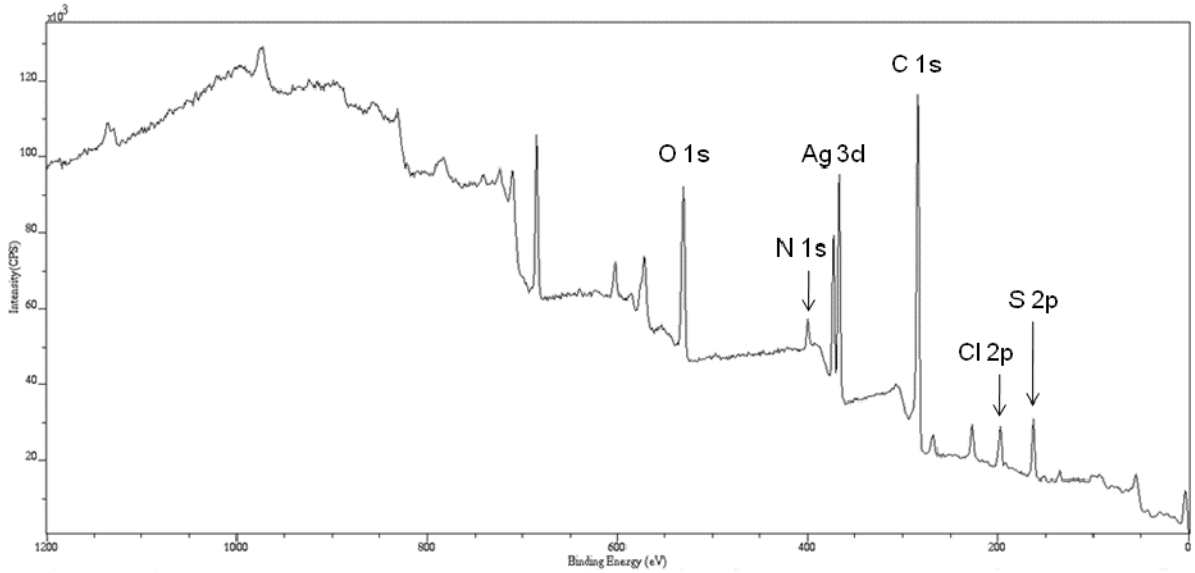
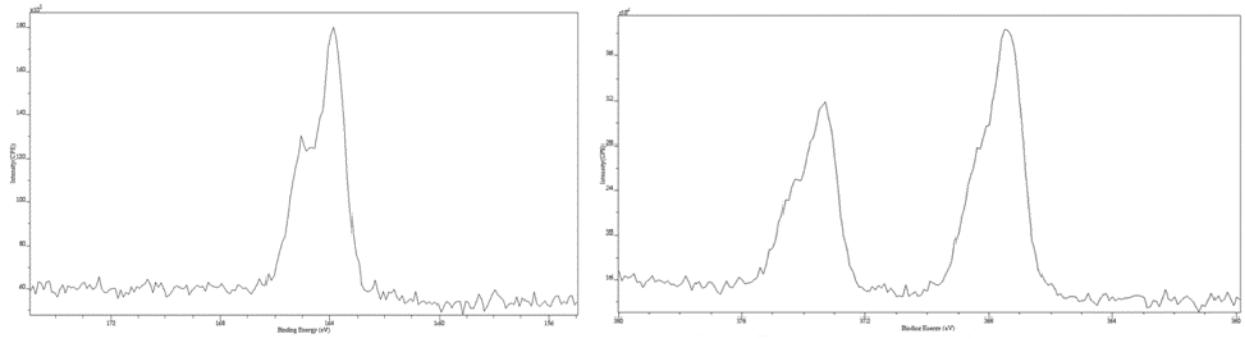


Figure S4. Survey XPS of bithiophene-substituted silver NHC yellow film poly(**3**).

Theoretical S:Ag Ratio = 4.00:1
Experimental S:Ag Ratio = 3.70:1

(a)



$3d_{5/2}$ = 367.4eV

Theoretical S:N Ratio = 2.00:1
Experimental S:N Ratio = 1.83:1

(b)

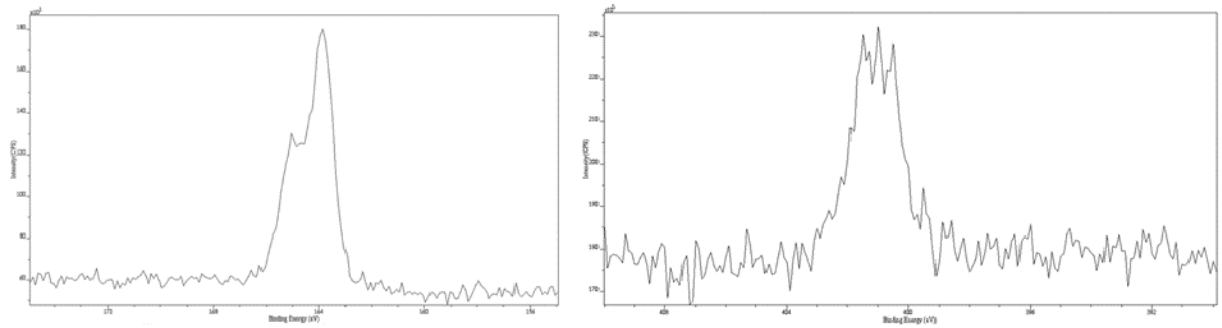


Figure S5. High-resolution XPS of bithiophene-substituted silver NHC yellow film poly(**3**). (a) Ratio of sulfur 2p to silver 3d. (b) Ratio of sulfur 2p to nitrogen 1s.

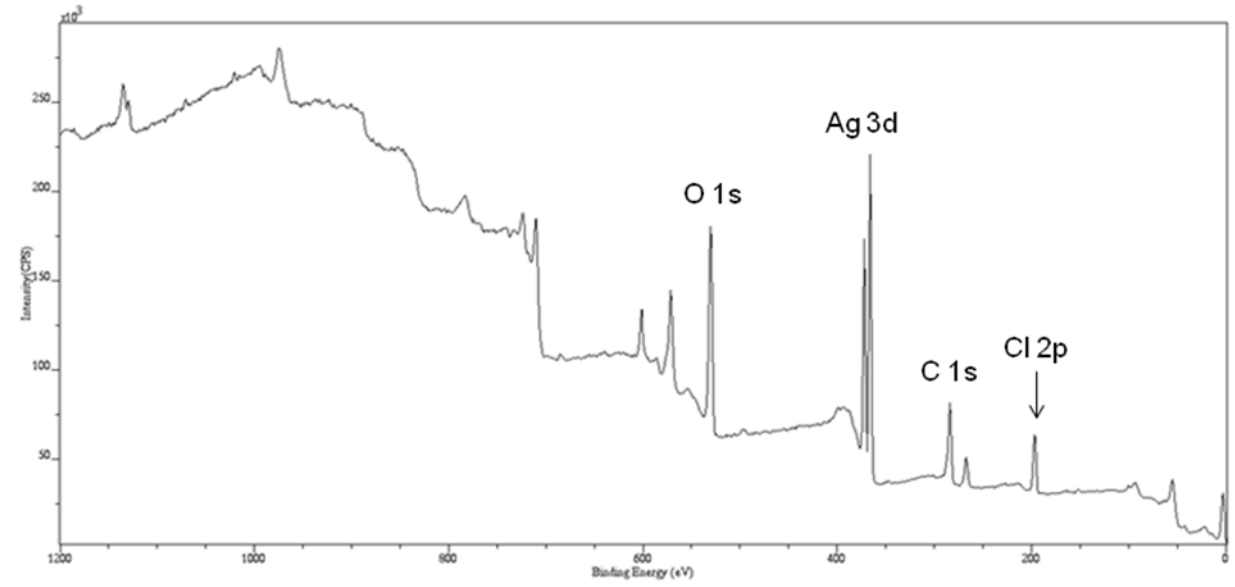


Figure S6. Survey XPS of bithiophene-substituted silver NHC white film poly(**3**).

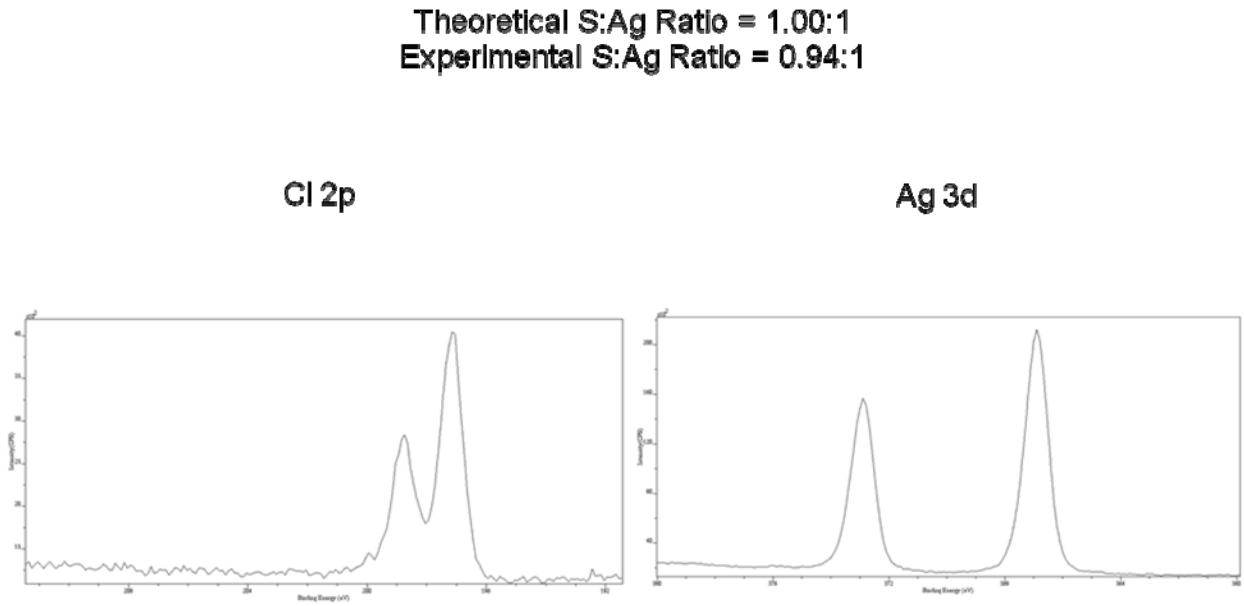
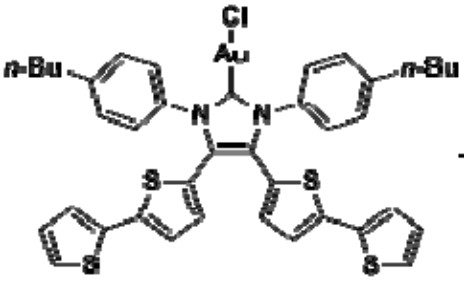


Figure S7. High-resolution XPS of bithiophene-substituted silver NHC white film poly(**3**). Ratio of chlorine 2p to silver 3d.



4

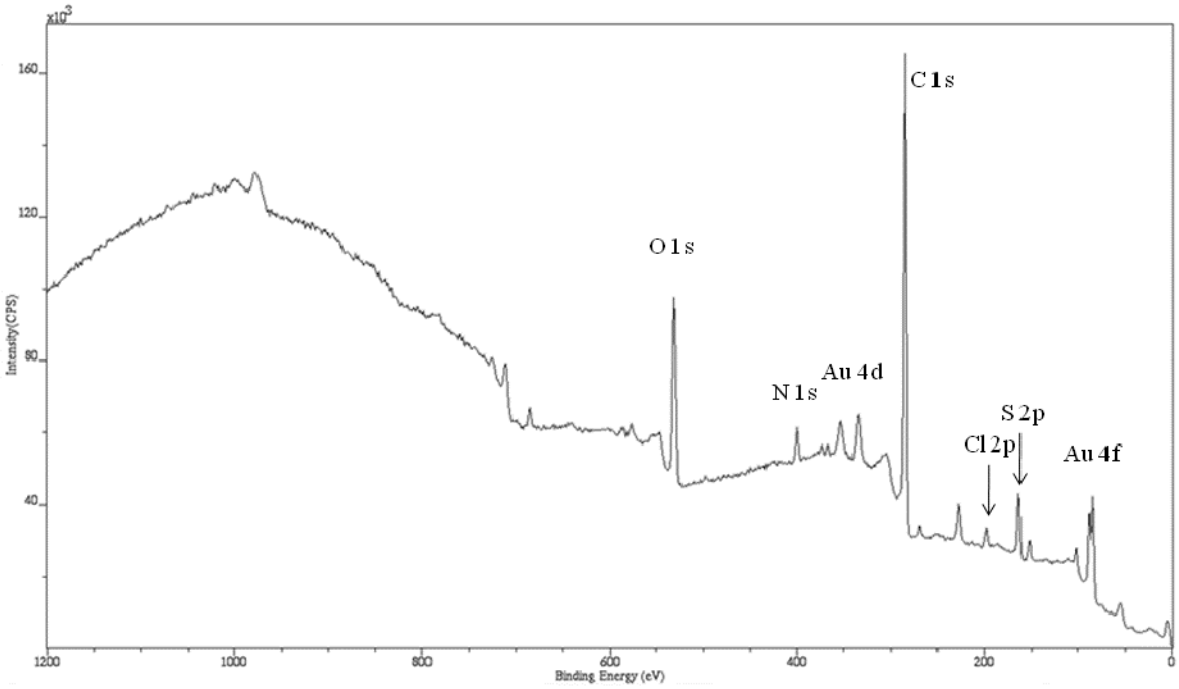
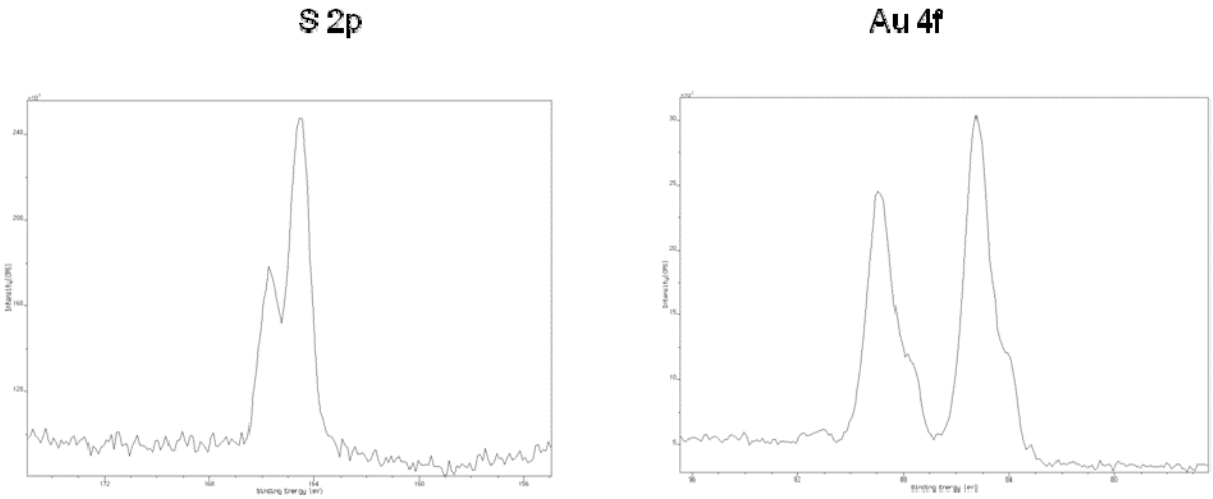


Figure S8. Survey XPS of bithiophene-substituted gold NHC thin film poly(**4**).

Theoretical S: Au ratio = 4.00: 1
Experimental S: Au ratio = 4.17: 1

(a)



Theoretical N: Au ratio = 2.00: 1
Experimental N: Au ratio = 2.08: 1

(b)

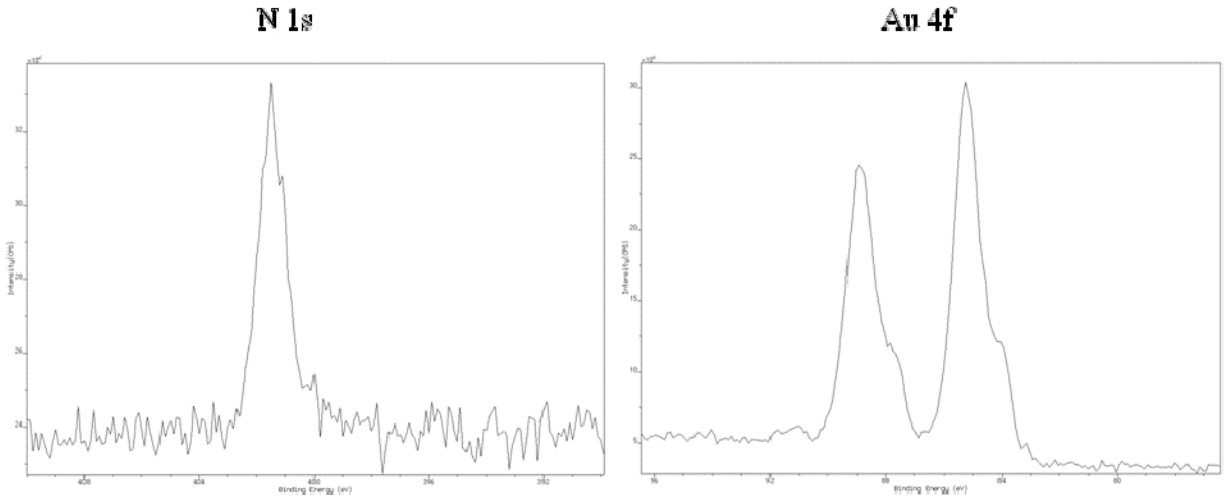
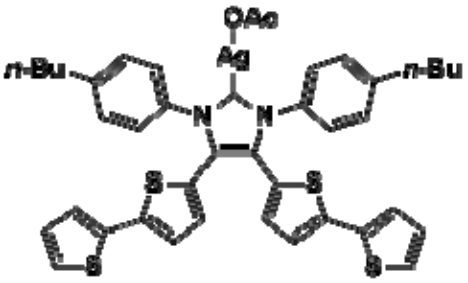


Figure S9. High-resolution XPS of bithiophene-substituted gold NHC thin film poly(**4**). (a) Ratio of sulfur 2p to gold 4f. (b) Ratio of nitrogen 1s to gold 4f.



5

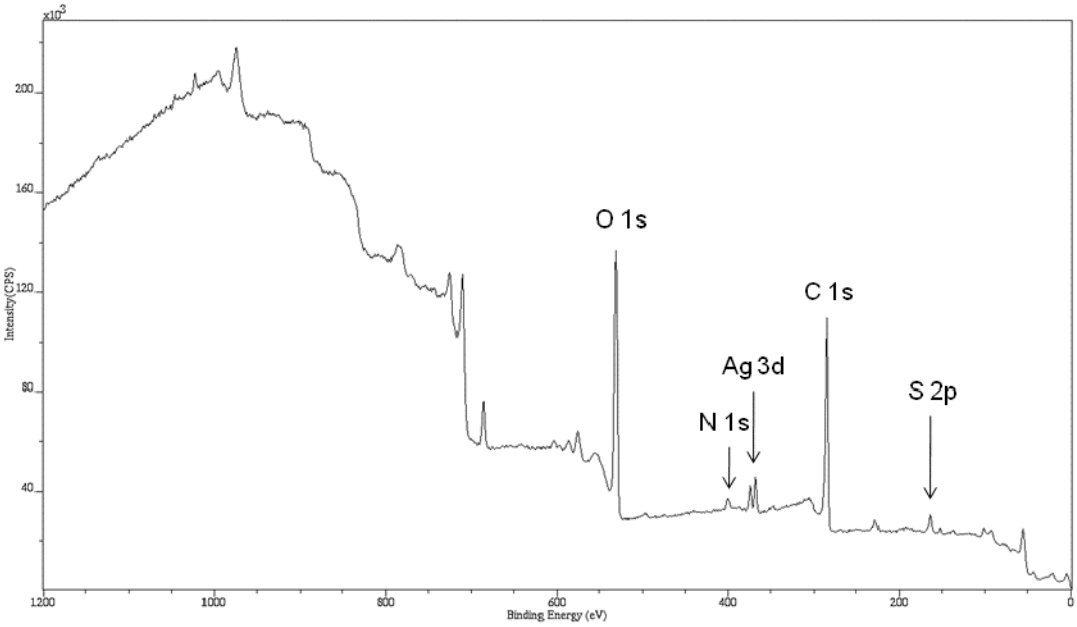
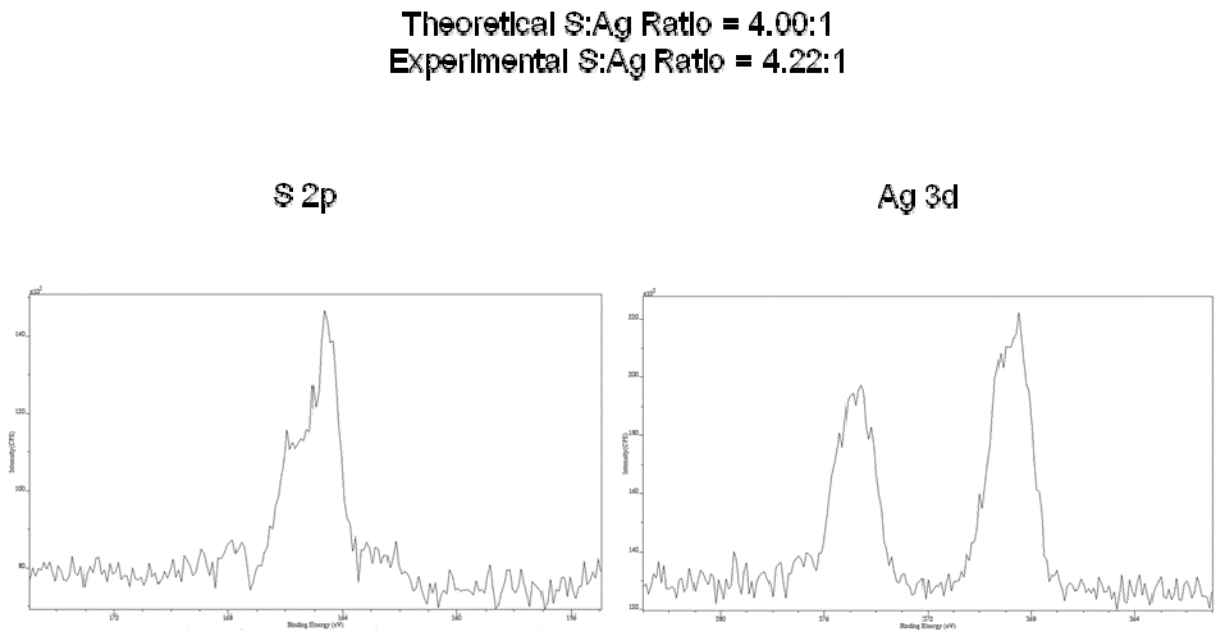


Figure S10. Survey XPS of bithiophene-substituted silver NHC thin film poly(**5**).

(a)



(b)

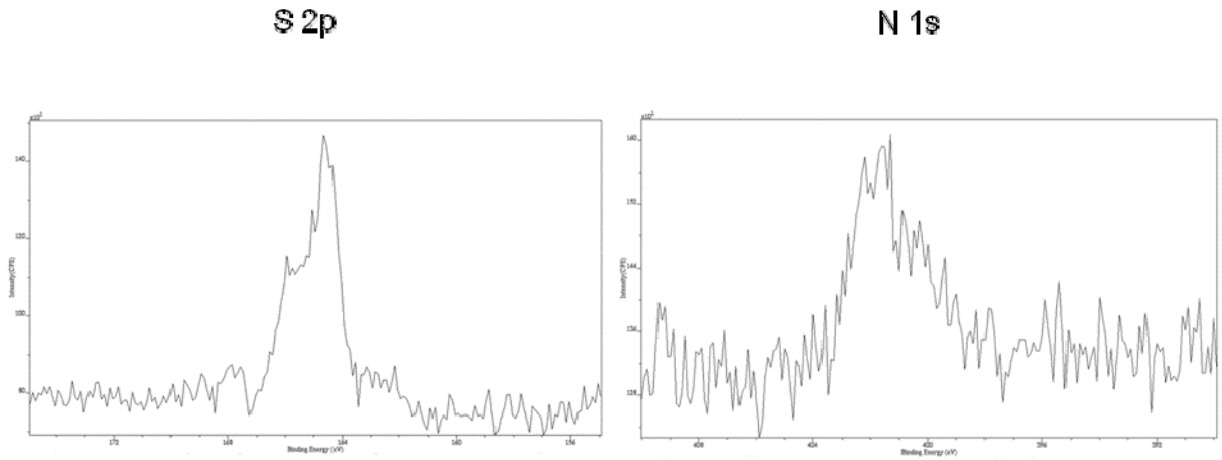
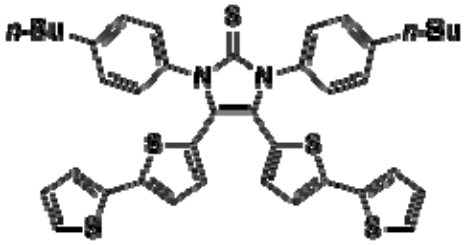


Figure S11. High-resolution XPS of bithiophene-substituted silver NHC thin film poly(**5**). (a) Ratio of sulfur 2p to silver 3d. (b) Ratio of sulfur 2p to nitrogen 1s.



6

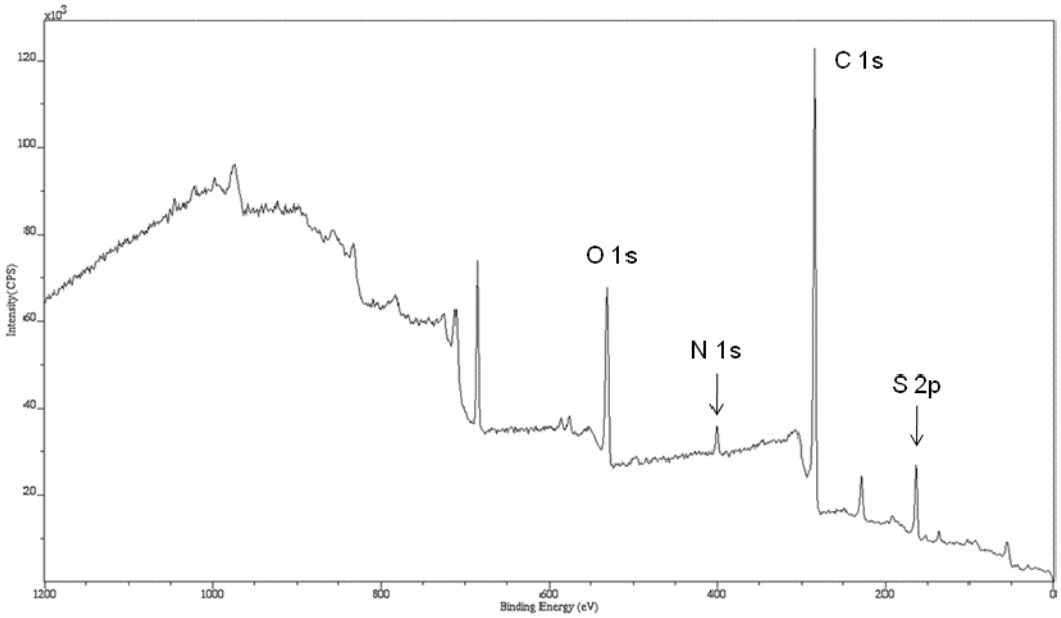


Figure S12. Survey XPS of bithiophene-substituted thione thin film poly(**6**).

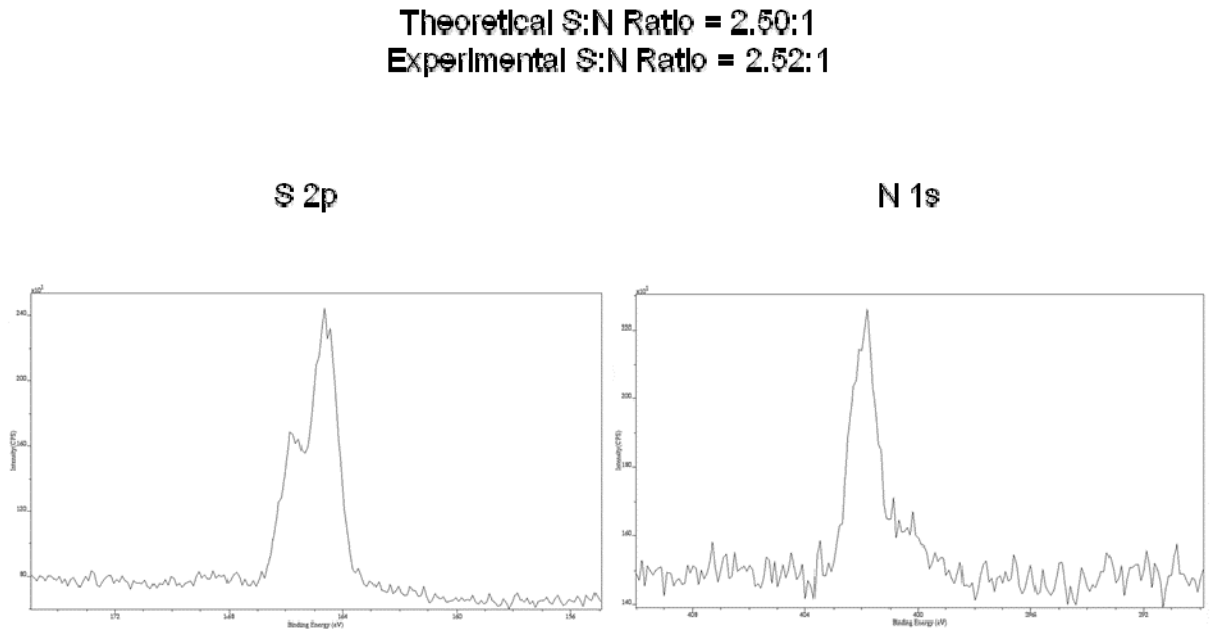
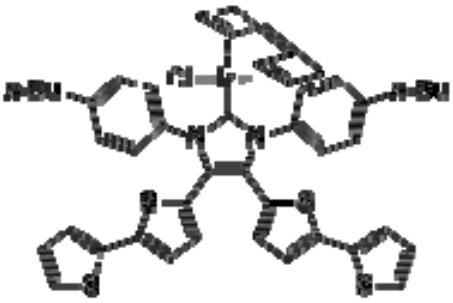


Figure S13. High-resolution XPS of bithiophene-substituted thione thin film poly(**6**). Ratio of sulfur 2p to nitrogen 1s.



7

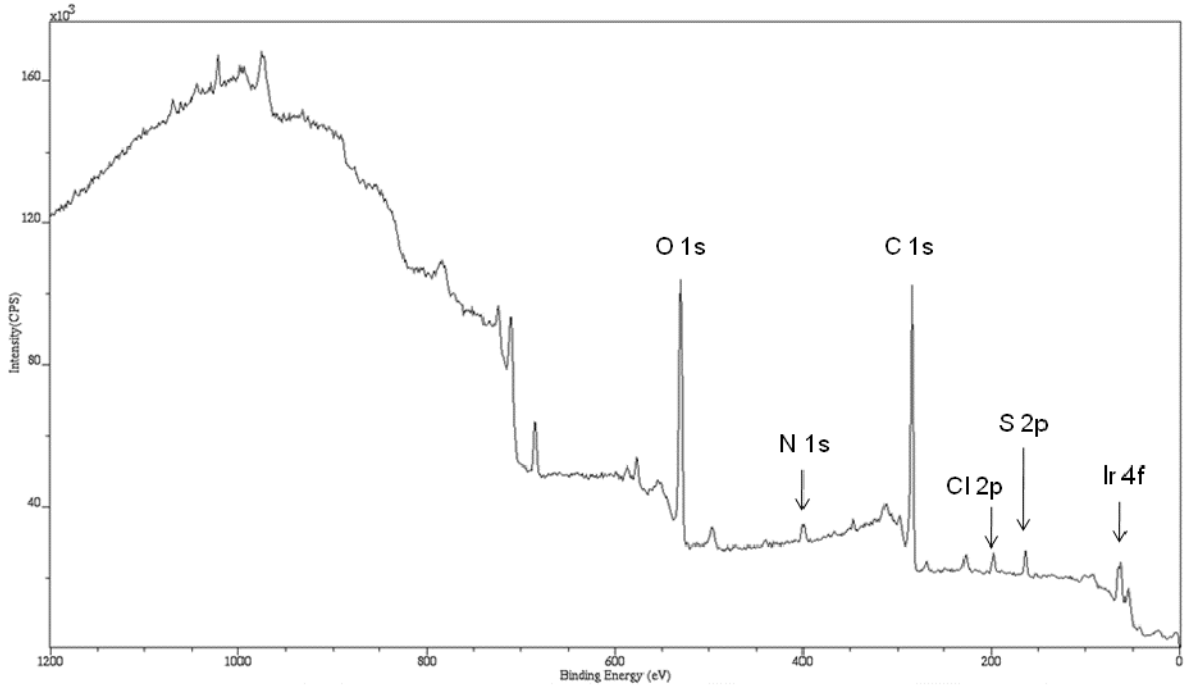
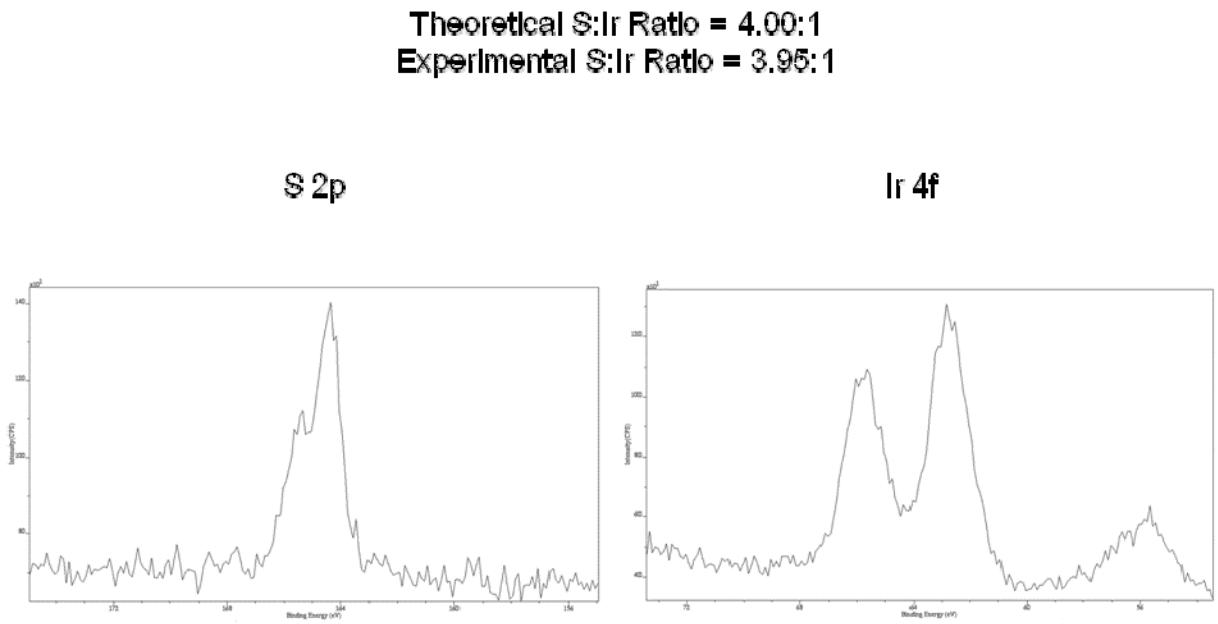


Figure S14. Survey XPS of bithiophene-substituted iridium NHC thin film poly(**7**).

(a)



(b)

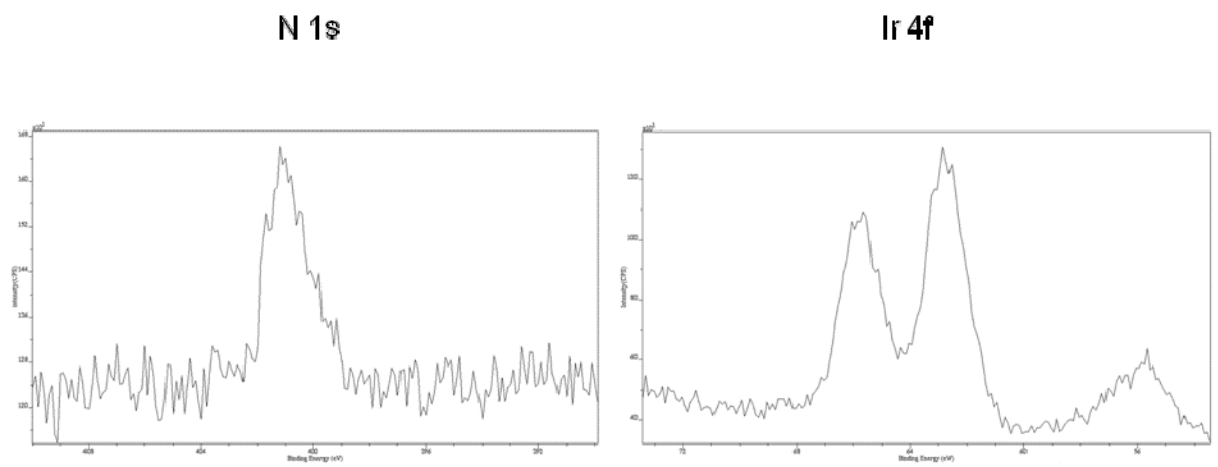
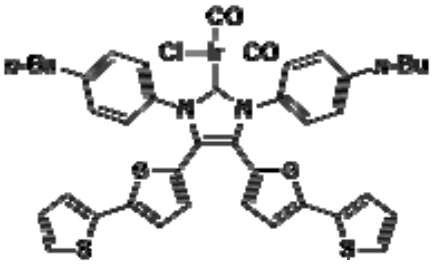


Figure S15. High-resolution XPS of bithiophene-substituted iridium NHC thin film poly(**7**). (a) Ratio of sulfur 2p to iridium 4f. (b) Ratio of nitrogen 1s to iridium 4f.



8

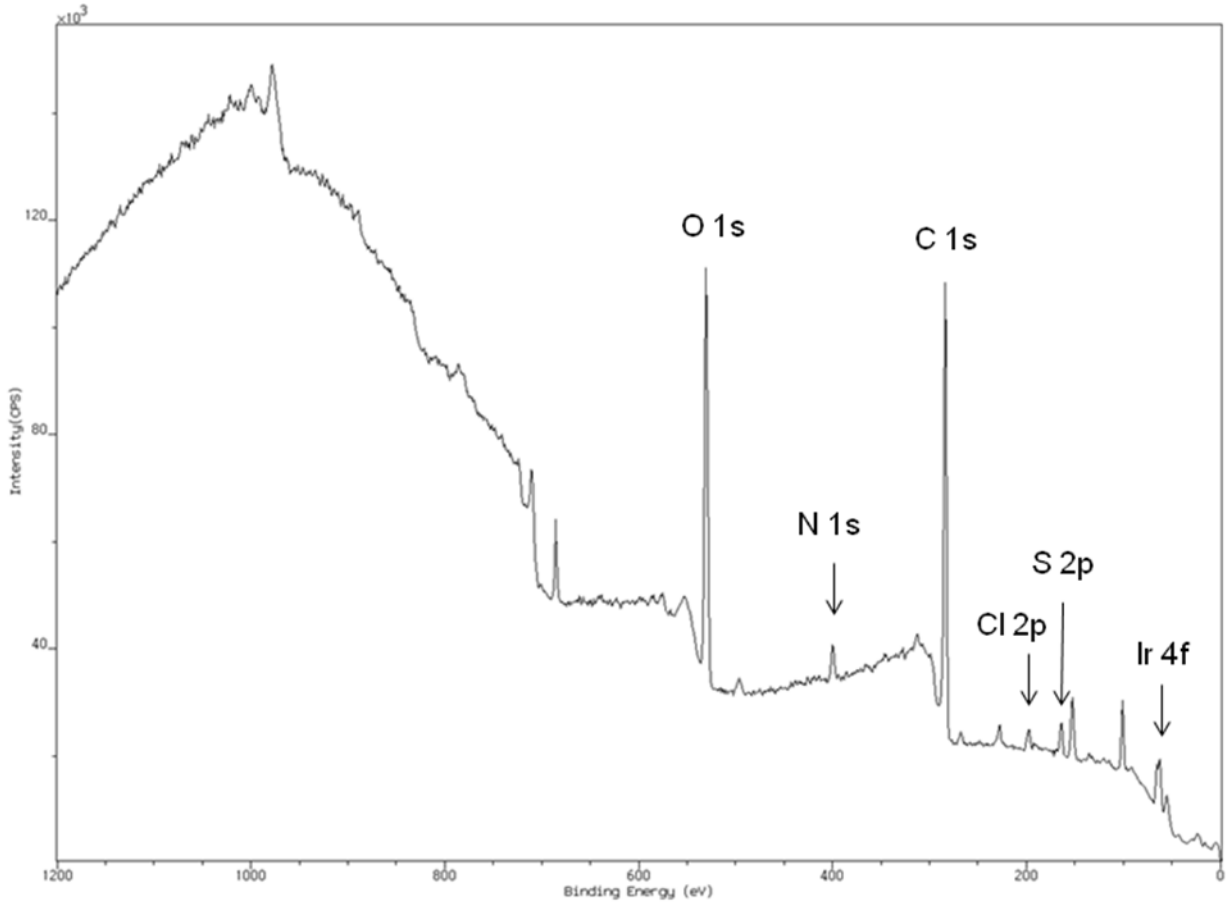


Figure S16. Survey XPS of bithiophene-substituted iridium NHC thin film poly(**8**).

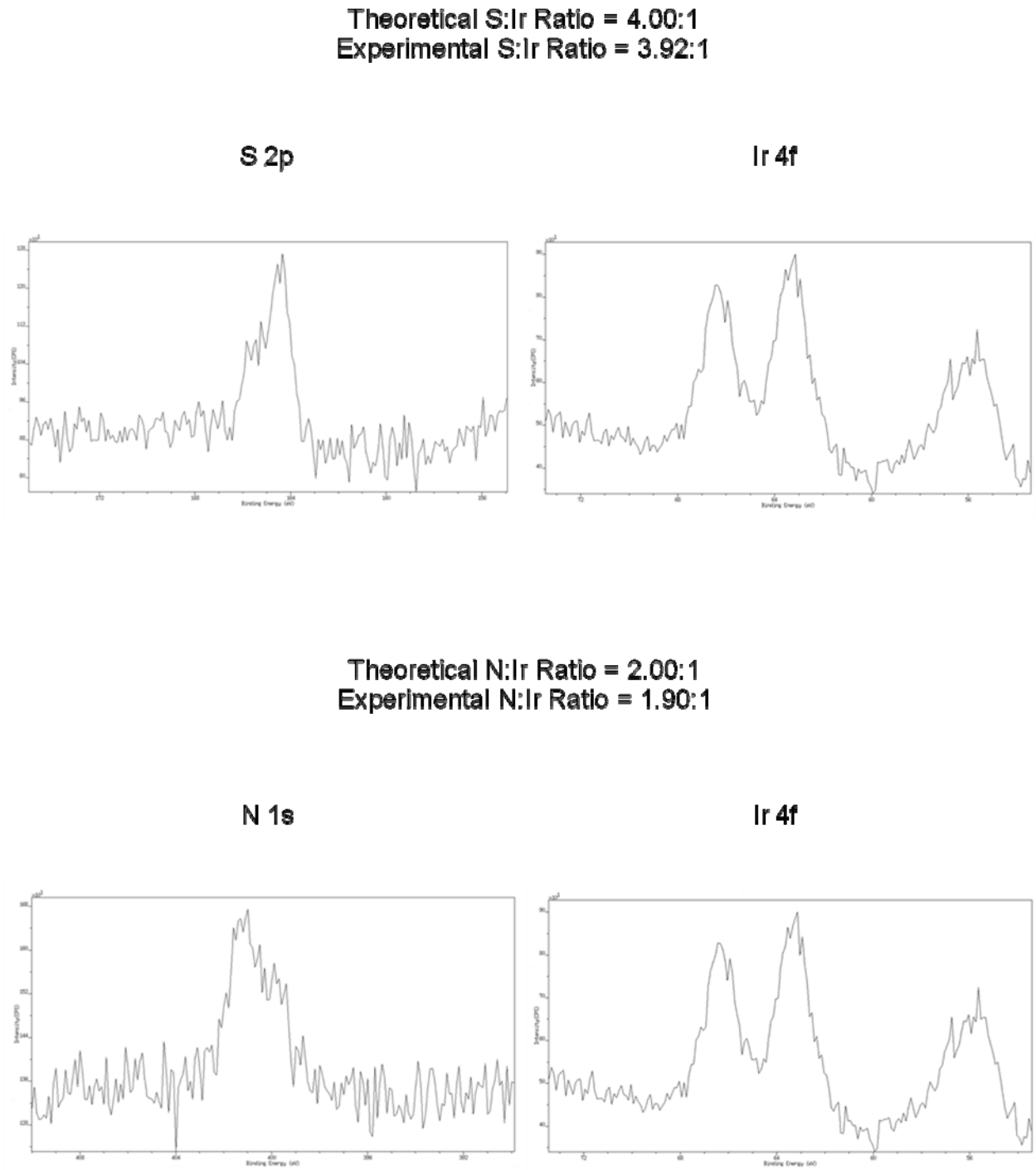
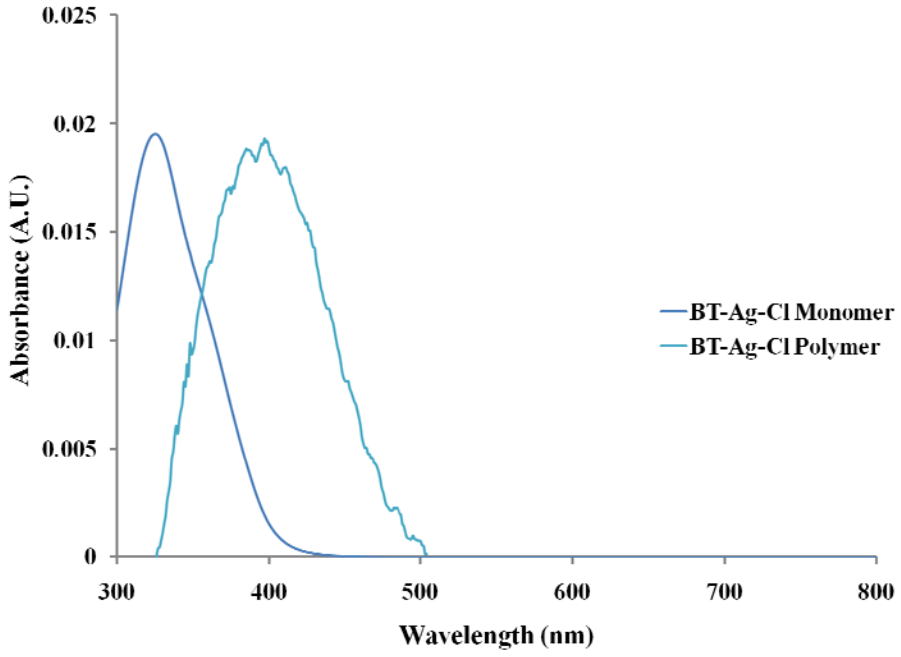


Figure S17. High-resolution XPS of bithiophene-substituted iridium NHC thin film poly(**8**). (a) Ratio of sulfur 2p to iridium 4f. (b) Ratio of nitrogen 1s to iridium 4f.

(a)



(b)

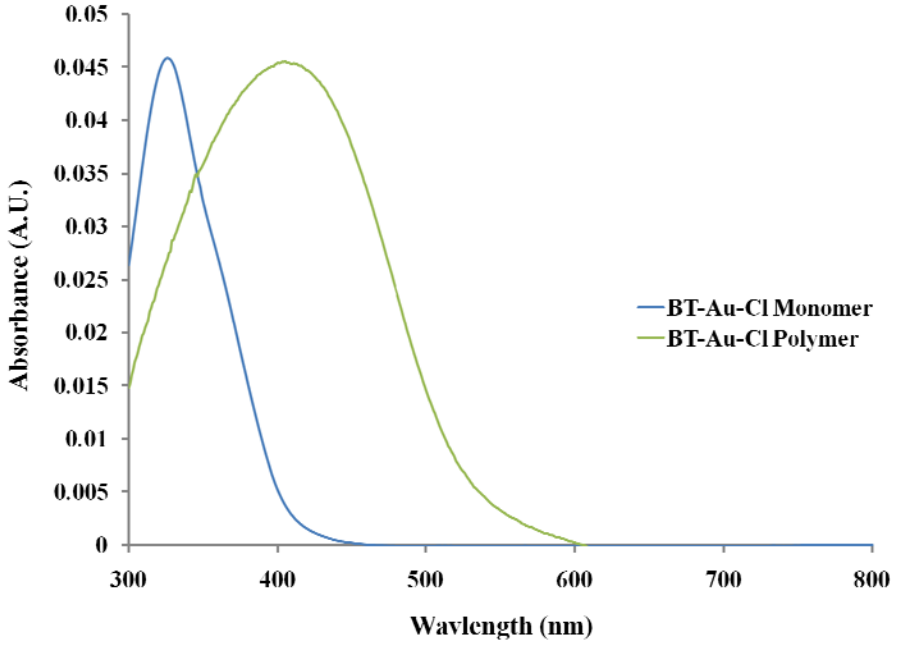
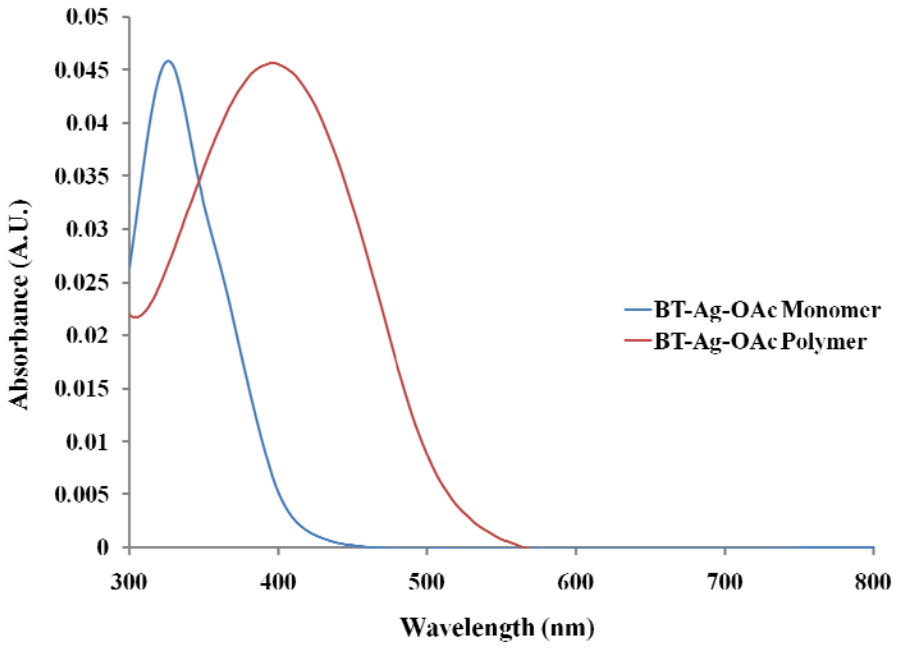


Figure S18. UV-vis profiles for compounds (a) **3** and poly(**3**). (b) **4** and poly(**4**). The concentration for both monomers was 2 x 10^{-6} M in CH_2Cl_2 and the absorbance maxima were adjusted to the same absorbance of their corresponding thin film.

(a)



(b)

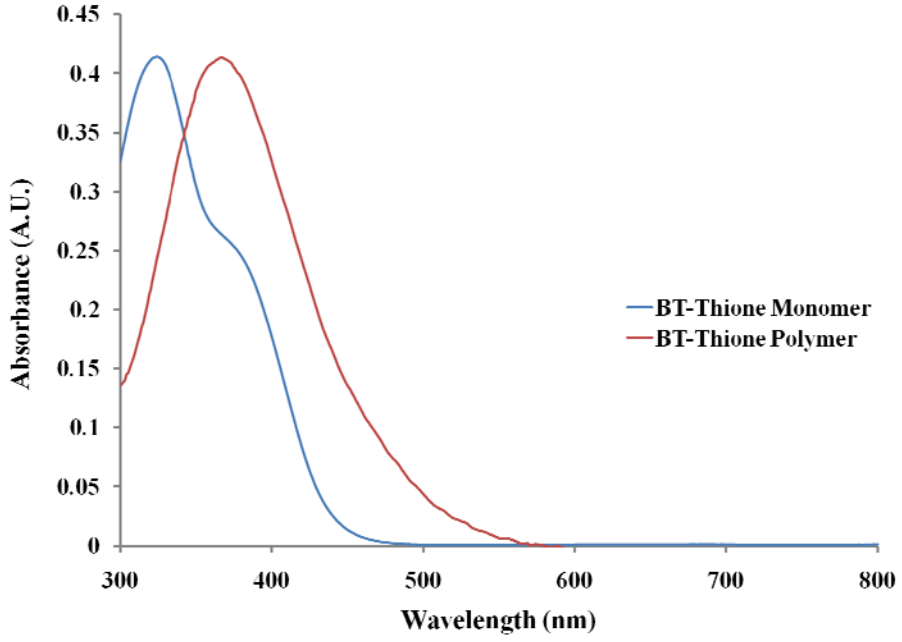
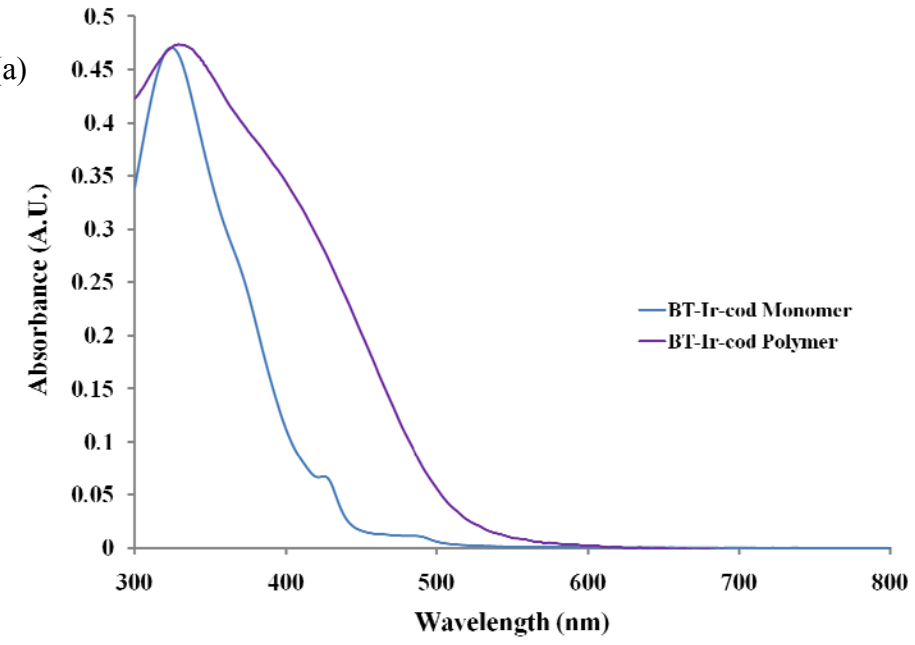


Figure S19. UV-vis profiles for compounds (a) **5** and poly(**5**). (b) **6** and poly(**6**). The concentration for both monomers was 2 x 10^{-6} M in CH_2Cl_2 and the absorbance maxima were adjusted to the same absorbance of their corresponding thin film.

(a)



(b)

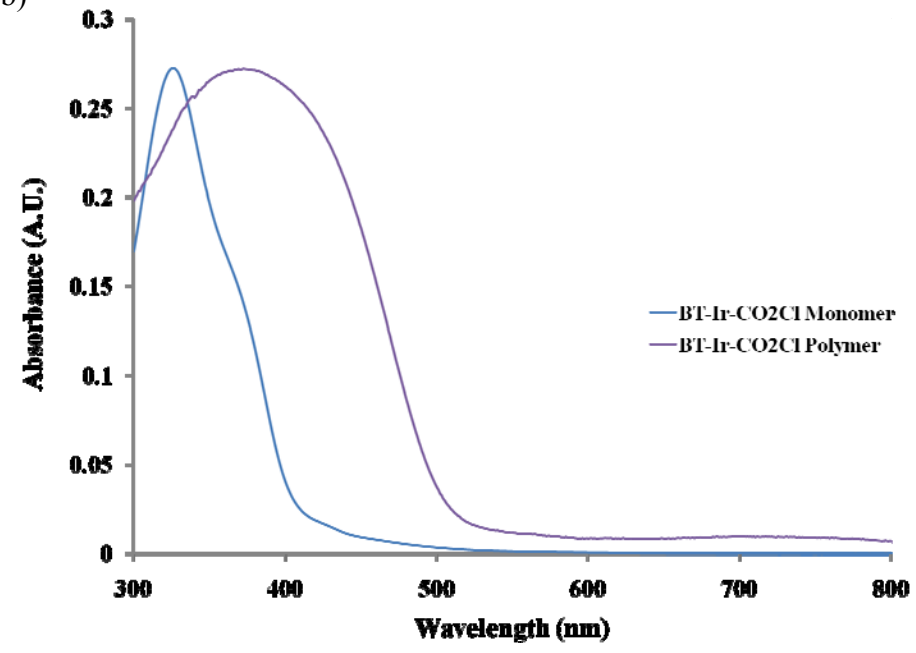
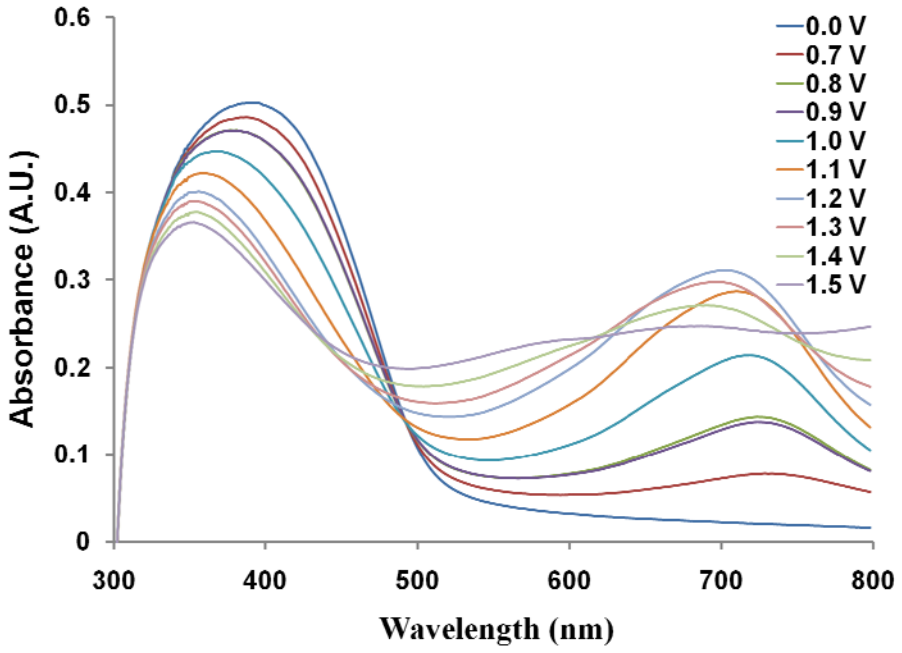


Figure S20. UV-vis profiles for compounds **7** and poly(**7**). (b) **8** and poly(**8**). The concentration for both monomers was 2 x 10^{-6} M in CH_2Cl_2 and the absorbance maxima were adjusted to the same absorbance of their corresponding thin film.

(a)



(b)

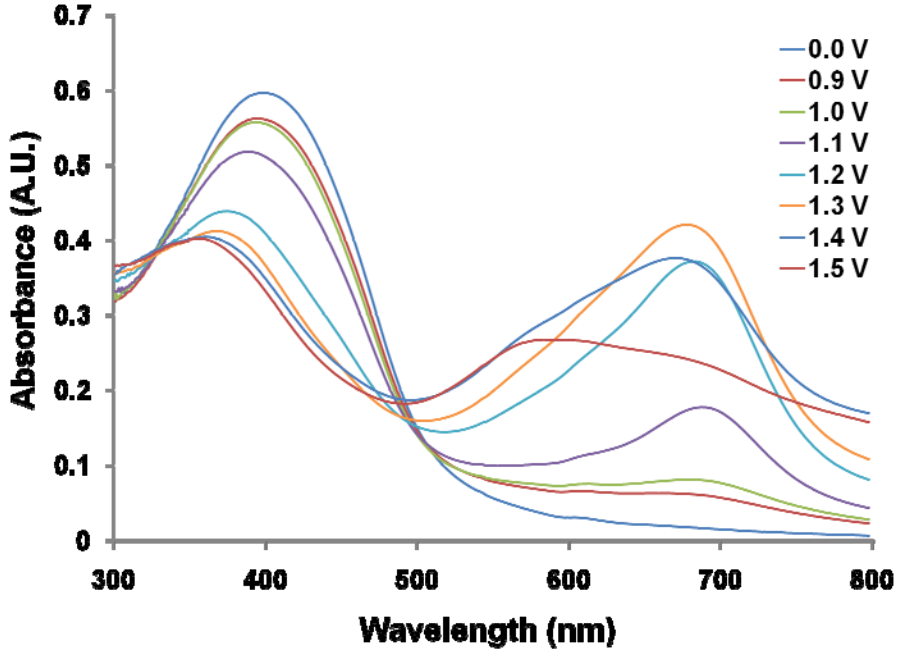
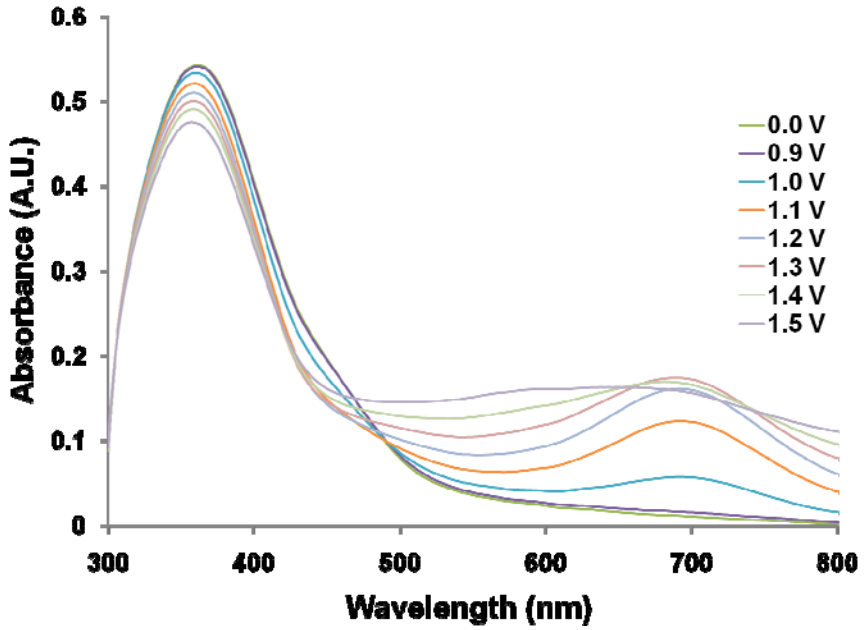


Figure S21. UV-vis overlay at different potentials of (a) Bithiophene-substituted gold NHC thin film poly(**4**). (b) Bithiophene-substituted silver NHC thin film poly(**5**). The spectra were acquired by depositing the thin film on an ITO slide, then assembling a three-electrode cell (0.1 M $TBAPF_6/CH_2Cl_2$) with the ITO slide as the working electrode and varying the potential from 0.0 to 1.5 V.

(a)



(b)

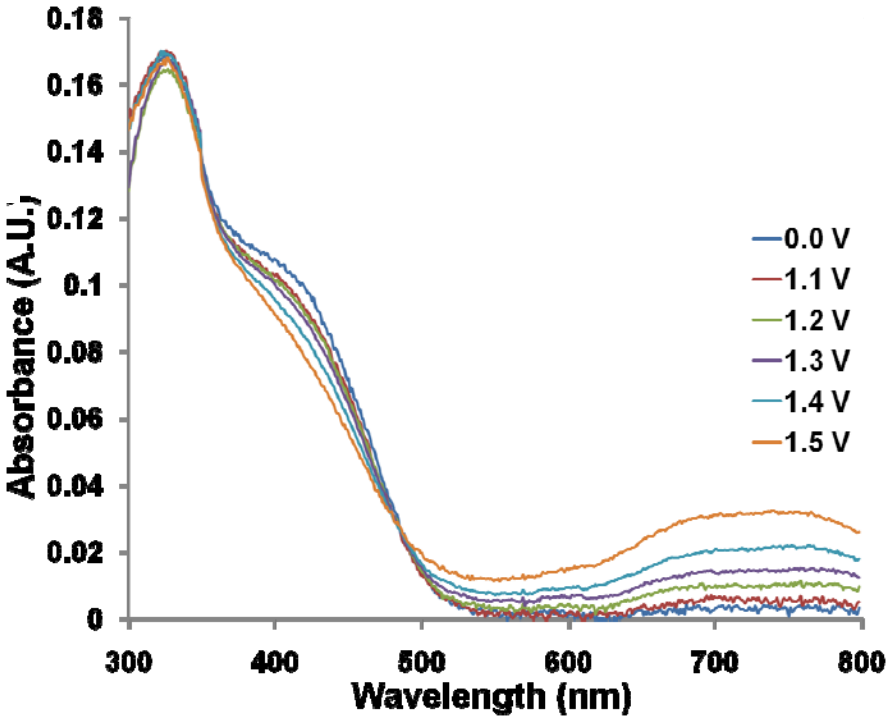


Figure S22. UV-vis overlay at different potentials of (a) Bithiophene-substituted thione poly(**6**). (b) Bithiophene-substituted iridium NHC thin film poly(**7**). The spectra were acquired by depositing the thin film on an ITO slide, then assembling a three-electrode cell (0.1 M $TBAPF_6/CH_2Cl_2$) with the ITO slide as the working electrode and varying the potential from 0.0 to 1.5 V.

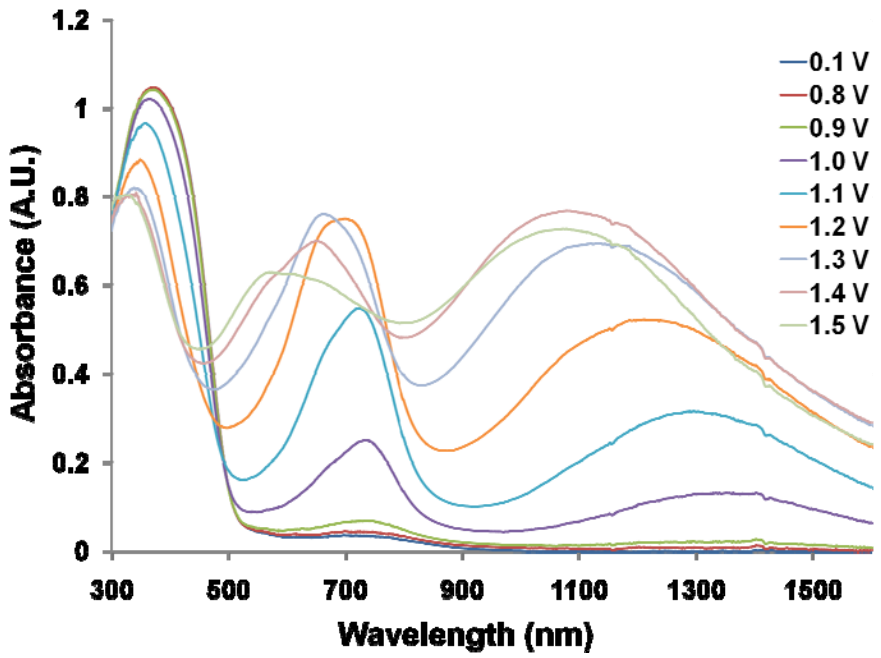


Figure S23. UV-vis overlay at different potentials of bithiophene-substituted iridium NHC thin film poly(**8**). The spectra were acquired by depositing the thin film on an ITO slide, then assembling a three-electrode cell (0.1 M $TBAPF_6/CH_2Cl_2$) with the ITO slide as the working electrode and varying the potential from 0.0 to 1.5 V.

Table S1. Crystal data and structure refinement of **3**.

Empirical formula	C39 H36 Ag Cl N2 S4	
Formula weight	804.26	
Temperature	153(2) K	
Wavelength	0.71069 Å	
Crystal system	Monoclinic	
Space group	I2/a	
Unit cell dimensions	a = 32.472(2) Å	□= 90°.
	b = 6.2695(7) Å	□= 95.889(2)°.
	c = 36.429(2) Å	□ = 90°.
Volume	7377.2(10) $Å^3$	
Z	8	
Density (calculated)	1.448 Mg/m^3	
Absorption coefficient	0.876 mm^{-1}	
F(000)	3296	
Crystal size	0.32 x 0.16 x 0.04 mm	
Theta range for data collection	1.8 to 27.5°.	
Index ranges	-37<=h<=42, -8<=k<=6, -47<=l<=47	
Reflections collected	23951	
Independent reflections	8425 [R(int) = 0.0734]	
Completeness to theta = 27.49°	99.5 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.966 and 0.806	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	8425 / 282 / 426	
Goodness-of-fit on F^2	1.226	
Final R indices [I>2sigma(I)]	R1 = 0.0593, wR2 = 0.1258	
R indices (all data)	R1 = 0.1067, wR2 = 0.1431	
Largest diff. peak and hole	1.362 and -1.060 $e.Å^{-3}$	

Table S2. Selected bond lengths (Å) and angles (°) of **3**.

Bond Lengths (Å)	
Ag(1)-C(1)	2.087(3)
Ag(1)-Cl(1)	2.3470(10)
N(1)-C(2)	1.402(5)
N(1)-C(1)	1.351(5)
N(2)-C(3)	1.390(5)
N(2)-C(1)	1.357(5)
C(2)-C(3)	1.334(6)
Bond angles (°)	
C(1)-Ag(1)-Cl(1)	175.26(10)
N(1)-C(1)-Ag(1)	128.7(3)
N(2)-C(1)-Ag(1)	126.9(3)
C(1)-N(1)-C(2)	111.0(3)
C(2)-N(2)-C(3)	111.3(3)
N(1)-C(1)-N(2)	104.3(3)
C(3)-C(2)-N(1)	106.6(3)
C(2)-C(3)-N(2)	106.9(3)

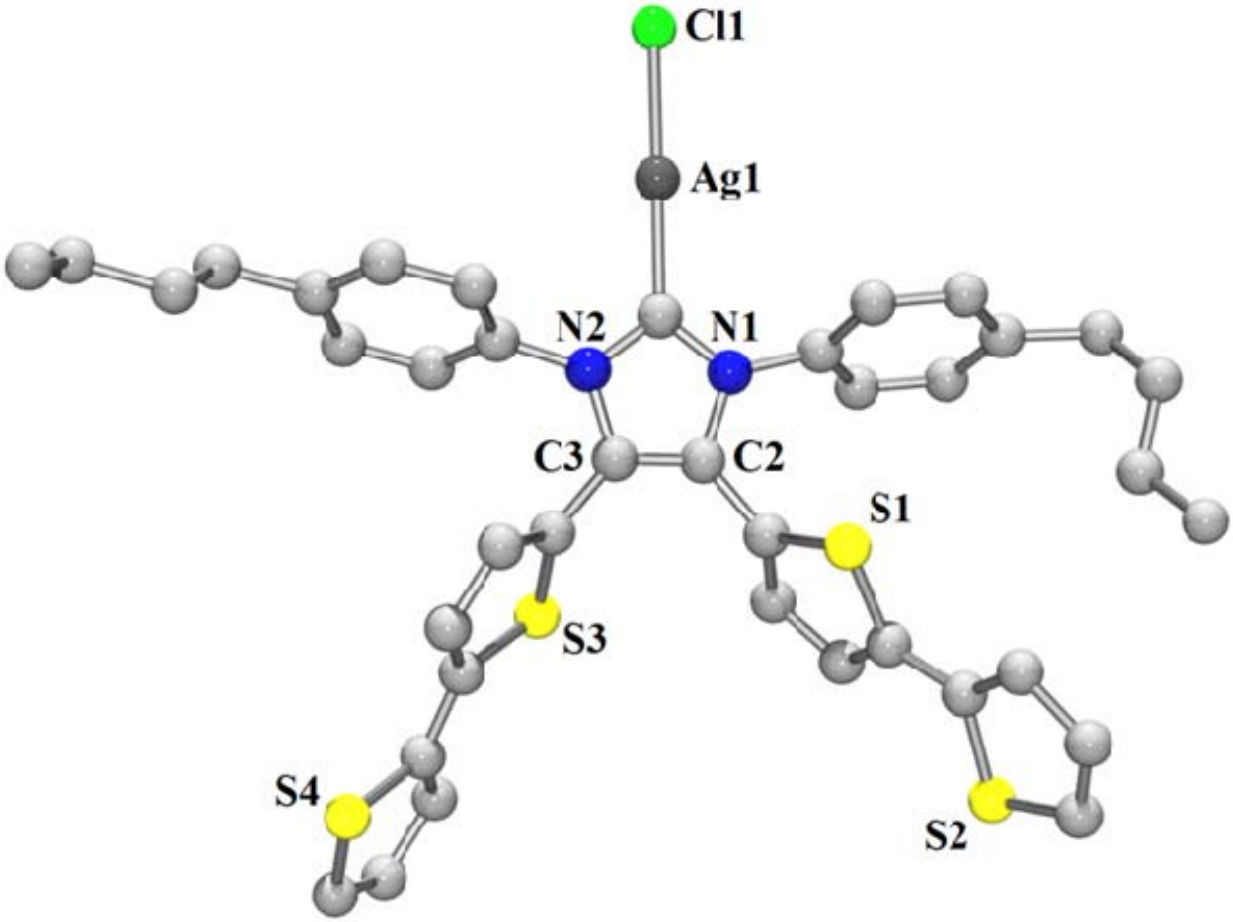


Figure S24. POV-Ray diagram drawn at 50% probability of bithiophene-substituted silver NHC **3**. Hydrogen atoms have been omitted for clarity.

Table S3. Crystal data and structure refinement of **5**.

Empirical formula	C45 H47 Ag N2 O3 S4	
Formula weight	899.96	
Temperature	233(2) K	
Wavelength	0.71069 Å	
Crystal system	Triclinic	
Space group	P-1	
Unit cell dimensions	a = 11.495(3) Å	□= 103.717(5)°.
	b = 13.381(3) Å	□= 92.327(6)°.
	c = 14.703(4) Å	□ = 101.007°.
Volume	2147.9(9) $Å^3$	
Z	2	
Density (calculated)	1.392 Mg/m^3	
Absorption coefficient	0.705 mm^{-1}	
F(000)	932	
Crystal size	0.24 x 0.13 x 0.09 mm	
Theta range for data collection	3.02 to 25.00°.	
Index ranges	-16<=h<=16, -31<=k<=31, -11<=l<=11	
Reflections collected	13683	
Independent reflections	7422 [R(int) = 0.0412]	
Completeness to theta = 25.00°	98.1 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.940 and 0.600	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	7422 / 0 / 454	
Goodness-of-fit on F^2	1.160	
Final R indices [I>2sigma(I)]	R1 = 0.0756, wR2 = 0.0983	
R indices (all data)	R1 = 0.1838, wR2 = 0.1986	
Largest diff. peak and hole	1.182 and -0.568 e.$Å^{-3}$	

Table S4. Selected bond lengths (Å) and angles (°) of **5**.

Bond Lengths (Å)	
Ag(1)-C(1)	2.085(6)
Ag(1)-O1(1)	2.196(5)
N(1)-C(2)	1.413(8)
N(1)-C(1)	1.366(7)
N(2)-C(3)	1.404(7)
N(2)-C(1)	1.350(8)
C(2)-C(3)	1.381(9)
Bond angles (°)	
C(1)-Ag(1)-O(1)	170.8(2)
N(1)-C(1)-Ag(1)	125.6(5)
N(2)-C(1)-Ag(1)	129.8(4)
C(1)-N(1)-C(2)	111.4(5)
C(1)-N(2)-C(3)	112.3(5)
N(1)-C(1)-N(2)	104.6(5)
C(3)-C(2)-N(1)	105.8(5)
C(2)-C(3)-N(2)	105.9(5)

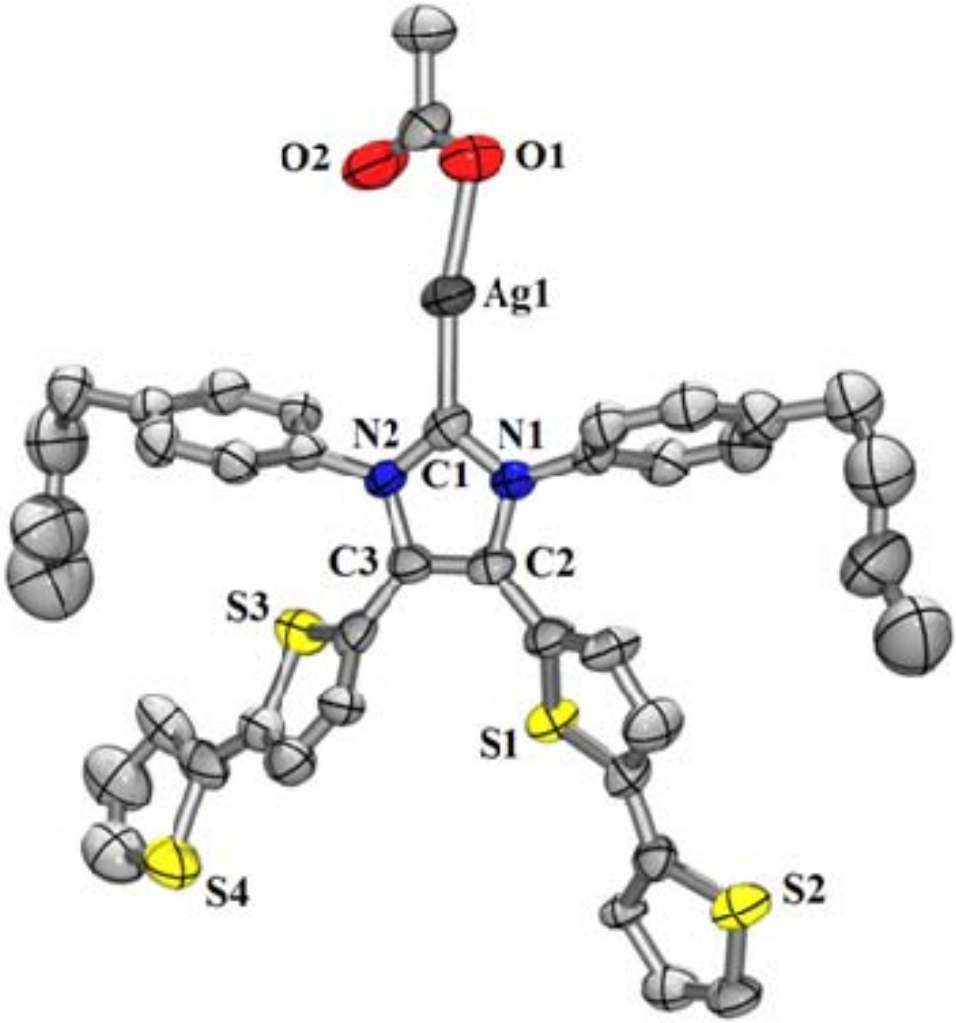


Figure S25. POV-Ray diagram drawn at 50% probability of bithiophene-substituted silver NHC **5**. One THF molecule was removed using SQUEEZE and hydrogen atoms have been omitted for clarity.

Table S5. Crystal data and structure refinement of **6**.

Empirical formula	C39 H36 N2 S5	
Formula weight	693.00	
Temperature	233(2) K	
Wavelength	0.71069 Å	
Crystal system	Monoclinic	
Space group	P21/c	
Unit cell dimensions	a = 14.114(3) Å	□= 90°.
	b = 26.755(6) Å	□= 107.286(6)°.
	c = 10.005(2) Å	□ = 90°.
Volume	3607.4(13) $Å^3$	
Z	4	
Density (calculated)	1.276 Mg/m^3	
Absorption coefficient	0.352 mm^{-1}	
F(000)	1456	
Crystal size	0.46 x 0.06 x 0.02 mm	
Theta range for data collection	3.02 to 25.00°.	
Index ranges	-16<=h<=16, -31<=k<=31, -11<=l<=11	
Reflections collected	27560	
Independent reflections	6338 [R(int) = 0.1108]	
Completeness to theta = 25.00°	99.9 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.990 and 0.531	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	6338 / 492 / 487	
Goodness-of-fit on F^2	1.098	
Final R indices [I>2sigma(I)]	R1 = 0.0678, wR2 = 0.1364	
R indices (all data)	R1 = 0.1361, wR2 = 0.1622	
Largest diff. peak and hole	0.340 and -0.362 $e.Å^{-3}$	

Table S6. Selected bond lengths (Å) and angles (°) of **6**.

Bond Lengths (Å)	
S(1)-C(1)	1.665(4)
N(1)-C(3)	1.405(5)
N(1)-C(1)	1.374(5)
N(2)-C(2)	1.411(5)
N(2)-C(1)	1.379(5)
C(2)-C(3)	1.376(5)
Bond angles (°)	
N(1)-C(1)-(S)1	128.7(3)
N(2)-C(1)-(S)1	126.7(3)
N(1)-C(1)-N(2)	104.6(3)
C(1)-N(2)-C(2)	111.1(3)
C(1)-N(1)-C(3)	111.2(3)
C(3)-C(2)-N(2)	106.2(3)
C(2)-C(3)-N(1)	106.9(3)

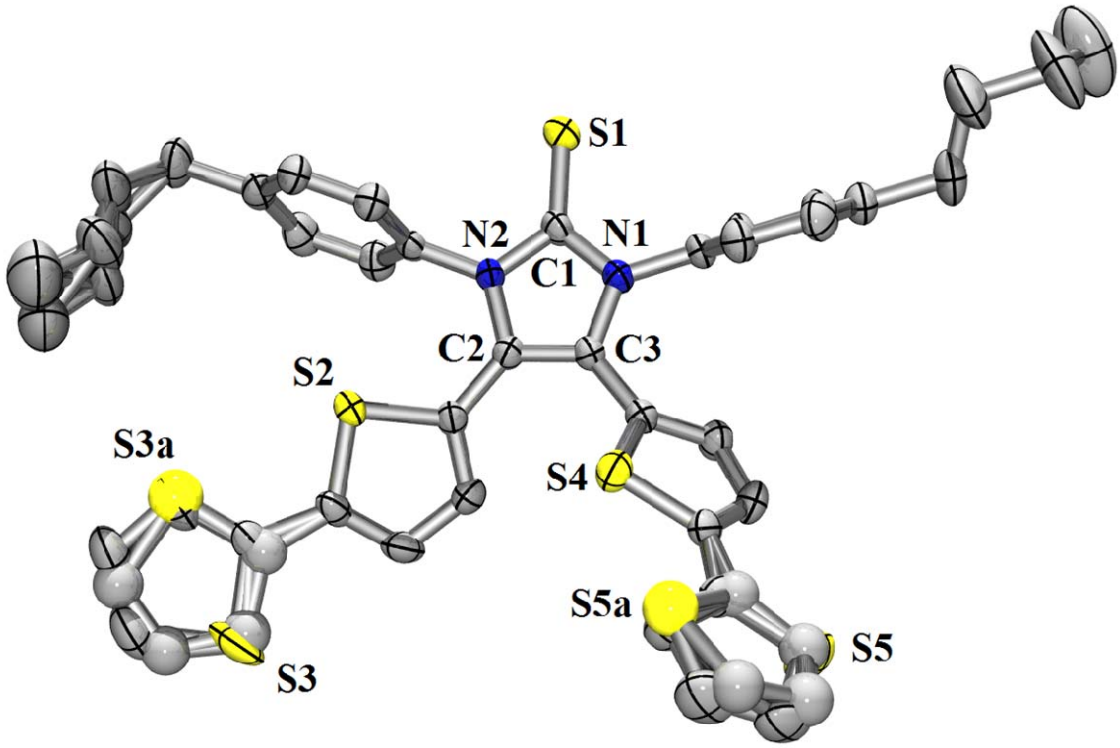


Figure S26. POV-Ray diagram drawn at 50% probability of bithiophene-substituted thione **6**. Hydrogen atoms have been omitted for clarity.