New heterometallic Ir(III)$_2$-Eu(III) complexes: white light emission from a single molecule

Andrea Baschieri,*[a] Sara Muzzioli,[a] Elia Matteucci,[a] Stefano Stagni,[a] Massimiliano Massi[b] and Letizia Sambri*[a]

[a]Department of Industrial Chemistry "Toso Montanari", University of Bologna, viale Risorgimento 4, 40136 Bologna, Italy. Fax: +39 051 2093654; Tel: +39 051 2093614;
E-mail: letizia.sambri@unibo.it;

[b]Nanochemistry Research Institute, Department of Chemistry, Curtin University, Kent Street, Bentley 6102 Western Australia, Australia

Electronic Supplementary Information

Contents

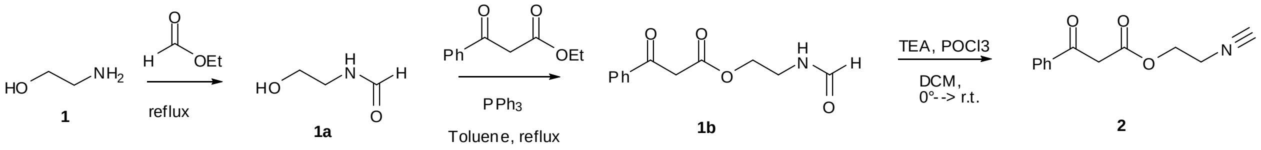
General informations.

The solvents and chemicals were used as received from sellers, unless otherwise mentioned. NMR spectra were recorded by using a Varian Mercury 400 MHz or a Varian Inova 300 MHz spectrometer with tetramethylsilane as the internal standard. Elemental analyses were performed on a ThermoQuest Flash 1112 series EA instrument. ESI-MS analysis were performed by direct injection of acetonitrile solutions of the compounds using a WATERS ZQ 4000 mass spectrometer. UV/Vis absorption spectra were measured on a Varian Cary 4 double-beam UV-Vis spectrometer and baseline corrected. Steady-state emission spectra were recorded on an Edinburgh FLS920P spectrofluorimeter equipped with a 450 W Xenon arc lamp, double excitation and single emission monochromators and a peltier cooled Hamamatsu R928P photomultiplier tube (185–850 nm). Emission and excitation spectra were corrected for source intensity (lamp and grating) and emission spectral response (detector and grating) by calibration curve supplied with the instrument. Emission lifetimes were determined on the same Edinburgh instrument with the Time Correlated Single Photon Counting (TCSPC) technique using pulsed picosecond LEDs (EPLED 295 or EPLED 360, FHWM <800 ps, repetition rates between 10 kHz and 1 MHz) as the excitation source and the above-mentioned R928P PMT as detector. The goodness of fit was assessed by minimizing the reduced χ^2 function and visual inspection of the weighted residuals. The emission quantum yields were determined according to the optically dilute solutions method in ACN solutions with reference to $Ru(bpy)_3Cl_2$ as the standard (r) according to Equation (1),[1] where *I* refers to the area of the emission peaks of the complex and the reference, A to their absorptions and n is the refractive index of the corresponding solvents.

$$\Phi = \Phi_r \, \frac{I}{I_r} \, \frac{A_r}{A} \, \frac{n^2}{n_r^2} \qquad (1)$$

Synthesis of ligand 2.

Ligand **2** was obtained according the following synthetic scheme:

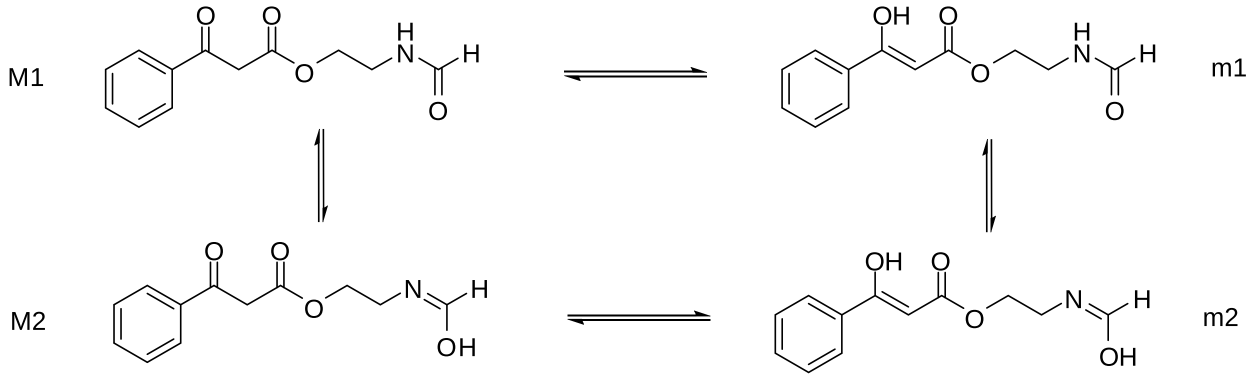


A solution of 2-aminoethanol **1** (2.40 mL, 40.0 mmol) in ethyl formate (4.20 mL) was refluxed for 24 h. The solution was cooled and the solvent was evaporated to give crude **1a** as brown oil that was used in the next step without purification. To a stirred solution of crude **1a** (3.60 g) and ethyl benzoylacetate (7.00 mL, 40.4 mmol) in toluene (200 mL) triphenylphosphine (1.05 g, 4.0 mmol) was added. The resulting reaction mixture was refluxed and the progress of the reaction was monitored by TLC. After complete conversion of

---

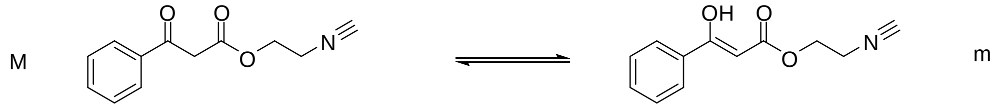
[1] K. Binnemans, Chem. Rev. 2009, 109, 4283-4374

the substrate (6h), the solvent was evaporated and the product was purified by column chromatography on silica gel (DCM/MeOH=97:3) to afford **1b** (3.58 g, 38% yield) as a mixture of keto-enol and amide-imidic acid tautomers at the equilibrium, represented in the following figure as Major (M1, M2) and minor (m1, m2) species. In the ^{1}H NMR description we indicated with M the sum of M1 and M2 species and with m the sum of m1 and m2 species.



^{1}H NMR (300 MHz, CDCl$_3$): δ 12.31 (s, 1H$_{m1}$), 12.27 (s, 1H$_{m2}$), 8.17-7.99 (m, 1H$_{M+m}$), 7.90-7.83 (m, 2H$_M$), 7.79-7.68 (m, 2H$_m$), 7.62-7.53 (m, 3H$_m$), 7.48-7.32 (m, 3H$_M$), 6.42-5.78 (m, 1H$_{M+m}$), 5.62 (s, 1H$_m$), 4.31-4.13 (m, 2H$_{M+m}$), 4.00 (s, 2H$_{M1}$), 3.99 (s, 2H$_{M2}$), 3.60-3.50 (m, 2H$_{M+m}$). ^{13}C NMR (75 MHz, CDCl$_3$): δ 36.8 (CH$_2$), 37.2 (CH$_2$), 40.6 (CH$_2$), 45.6 (CH$_2$), 45.8 (CH$_2$),62.8 (CH$_2$), 63.8 (CH$_2$), 64.6 (CH$_2$), 86.8 (CH), 126.1 (CH), 128.4 (CH), 128.5 (CH), 128.6 (CH), 128.7 (CH), 128.9 (CH), 131.5 (CH), 131.9 (CH), 132.0 (CH), 132.1 (CH), 132.1 (CH), 134.1 (CH), 135.6 (C), 161.6 (CH), 164.8 (CH), 167.5 (C), 172.1 (C), 172.9 (C), 192.7 (CH), 193.2 (CH).

Then a DCM solution (50 mL) of **1b** (3.53 g, 15 mmol) and Et$_3$N (5.2 mL, 37.5 mmol) was cooled at 0°C, and phosphorous oxychloride (1.4 mL, 15.0 mmol) in 20 mL of DCM was added dropwise over a period of 10 min. After the reaction was completed, the reaction was quenched with saturated Na$_2$CO$_3$ aqueous solution at 0°C to and the product was extracted with DCM. The organic phase was washed with aq NH$_4$Cl, then dried over anhydrous MgSO$_4$ and the solvent evaporated. The residue was purified by column chromatography (silica gel, DCM/MeOH=99:1) to give **2** (0.65 g) in 20% yields as a mixture of tautomers M and m as depicted in the following figure:



^{1}H NMR (300 MHz, CDCl$_3$): δ 12.27 (s, 1H$_m$), 7.97-7.91 (m, 2H$_M$), 7.91-7.75 (m, 2H$_m$), 7.66-7.58 (m, 3H$_m$), 7.55-7.41 (m, 3H$_M$), 5.75 (s, 1H$_m$), 4.43-4.26 (m, 2H$_{M+m}$), 4.09 (s, 2H$_M$), 3.77-3.50 (m, 2H$_{M+m}$). ^{13}C NMR (75 MHz, CDCl$_3$): δ 40.6, (t, CH$_2$), 45.5 (CH$_2$), 61.0 (CH$_2$), 62.0 (CH$_2$), 105.0 (CH), 126.2 (CH), 128.4 (CH), 128.6 (CH), 128.8 (CH), 128.9 (CH), 129.2 (CH), 131.7 (CH), 134.0 (CH), 135.7 (C), 167.1 (CO), 191.9 (CO). Anal. Calculated for $C_{12}H_{11}NO_3$ (217.22): C, 66.35; H, 5.10; N, 6.45 %. Found C, 66.58; H, 4.94; N, 6.29 %. ESI-MS: 218 [M$^+$+ 1], 240 [M$^+$+ Na].

Synthesis of Europium complex 3

To a solution of **2** (18.8 mg, 0.08 mmol) in 1.0 mL of DCM and 0.2 mL of ACN, triethylamine (16 µL, 0.117 mmol) was added. After 5 min. $EuCl_3 \cdot 6H_2O$ (7.3 mg, 0.02 mmol) was added and the reaction was vigorously stirred overnight at room temperature. Then the solvent was removed and the crude was dissolved in DCM (1 mL) and then Et_2O (5 mL) was added. The precipitated ammonium salt was filtered off and the solution evaporated to give **3** as a whitish oil (15.7 mg, 70% yield). Anal. Calculated for $C_{54}H_{56}EuN_5O_{12}$ (1119.01): C, 57.96; H, 5.04; N, 6.26 %. Found C, 58.10; H, 4.95; N, 6.42 %.ESI-MS: 1017 [M^-].

Synthesis of the Ir(III)-Eu(III) complexes 7-9

Dimers **4-6** were obtained according to reported procedures.[2]

In a 50 ml round-bottom flask equipped with a stirring bar, Ir(III) dimer **4** (21.4 mg, 0.02mmol) was dissolved in DCM (1mL). Then complex **3** (22 mg, 0.02mmol) was added and the reaction mixture was stirred under N_2 at 30°C overnight. Complex **7** (41.1 mg) was isolated in quantitative yield by precipitation by addition of Et_2O. Anal. Calculated for $C_{92}H_{72}ClEuIr_2N_8O_{12}$ (2053.45): C, 53.81; H, 3.53; N, 5.46 %. Found C, 54.03; H, 3.72; N, 5.40 %. ESI-MS: 2018[M^+].

The same procedure was used for **8** (Anal. Calculated for $C_{92}H_{68}ClEuF_4Ir_2N_8O_{12}$ (2125.41): C, 51.99; H, 3.22; N, 5.27 %. Found C, 52.26; H, 3.15; N, 5.39 %. ESI-MS: 2089[M^+]) and **9** (Anal. Calculated for $C_{92}H_{64}ClEuF_8Ir_2N_8O_{12}$ (2197.38): C, 50.29; H, 2.94; N, 5.10 %. Found C, 49.93; H, 2.72; N, 5.31 %. ESI-MS: 2161[M^+]).

Synthesis of Ir(III) complexes 10-12

In a 50 ml round-bottom flask equipped with a stirring bar, the Ir(III) dimer **4** (10.7 mg, 0.01 mmol) was dissolved in a mixture of DCM/MeOH 1:1 (4 mL). Then AgOTf (7.7 mg, 0.03 mmol) was added and the mixture was stirred for 2h at room temperature. The solution was filtered to remove AgCl and the solvent evaporated. The residual solid was dissolved in 5 mL of DCM and ligand **2** (9.4 mg, 0.04 mmol) was added. After stirring 24 h at room temperature the solvent was removed. The solid was dissolved in the minimum amount of DCM and Et_2O (10 mL) was added. The obtained precipitate was filtered and dried to give pure **10** (10.8 mg) in 50% yield. ^1H NMR (400 MHz, $CDCl_3$): δ 12.18 (s, $1H_m$), 9.25-9.15 (m, 2H), 8.00-7.30 (m, 18H), 7.00-6.80 (m, 4H), 6.20-6.10 (m, 2H), 5.42 (s, $1H_m$), 4.50-4.30 (m, 4H), 4.20-4.00 (m, 4H), 3.90-3.80 (m,

---

[2] (a) E. Baranoff, B. F. E. Curchod, J. Frey, R. Scopelliti, F. Kessler, I. Tavernelli, U. Rothlisberger, M. Grätzel and M. K. Nazeeruddin, *Inorg. Chem.*, 2012, **51**, 215. b) M. Nonoyama, *Bull. Chem. Soc. Jpn.* 1974, **47**, 767. c) S. Lamansky, P. Djurovich, D. Murphy, F. Abdel-Razzaq, R. Kwong, I. Tsyba, M. Bortz, B. Mui, R. Bau, M. E. Thompson, *Inorg. Chem.* 2001, **40**, 1704-1711)

4H). Anal. Calculated for $C_{47}H_{38}F_3IrN_4O_9S$ (1084.10): C, 52.07; H, 3.53; N, 5.17 %. Found C, 51.88; H, 3.64; N, 5.33 %. ESI-MS: 935[M^+], 936 [M^++ 1], ESI-MS^-: 149[M^-].

The same procedure was used to obtain **11** (11.6 mg, 52% yield): ^1H NMR (400 MHz, $CDCl_3$): δ 12.19 (s, $1H_{m1}$), 12.16 (s, $1H_{m2}$), 9.25-9.10 (m, 2H), 8.30-8.20 (m, 1H), 8.10-7.20 (m, 16H), 7.00-6.80 (m, 2H), 6.45-6.30 (m, 1H), 6.10-6.00 (m, 1H), 5.75 (s, $1H_{m1}$), 5.65-5.55 (m, 1H), 5.40 (s, $1H_{m2}$), 4.60-4.25 (m, 4H), 4.25-4.00 (m, 4H), 4.00-3.90 (m, 4H). ^{19}F NMR (400 MHz, $CDCl_3$): δ −78.19 (s), −106.47 (q, J=9.4Hz), −109.05 (t, J=11.0 Hz). Anal. Calculated for $C_{47}H_{36}F_5IrN_4O_9S$ (1120.08): C, 50.40; H, 3.24; N, 5.00 %. Found C, 50.18; H, 3.43; N, 5.21 %. ESI-MS^+: 971[M^+], 972 [M^++ 1], 149[M^-]; and **12** (11.3 mg, 49% yield): ^1H NMR (400 MHz, $CDCl_3$): δ 12.23 (s, $1H_m$), 9.20-9.15 (m, 2H), 8.35-8.20 (m, 2H), 7.90-7.20 (m, 14H), 6.60-6.40 (m, 2H), 5.74 (s, $1H_m$), 5.55-5.45 (m, 2H), 4.50-4.40 (m, 4H), 4.20-4.10 (m, 4H), 4.00-3.80 (m, 4H). ^{19}F NMR (400 MHz, $CDCl_3$): δ −78.10 (s), −106.03 (q, J=10.2Hz), −108.55 (t, J=12.4 Hz). Anal. Calculated for $C_{47}H_{34}F_7IrN_4O_9S$ (1156.06): C, 48.83; H, 2.96; N, 4.85 %. Found C, 49.07; H, 2.82; N, 4.99 %. ESI-MS^+: 1007[M^+], 1008 [M^++ 1], ESI-MS^-: 149[M^-].

Figure S1: ESI MS spectrum of ligand **2**

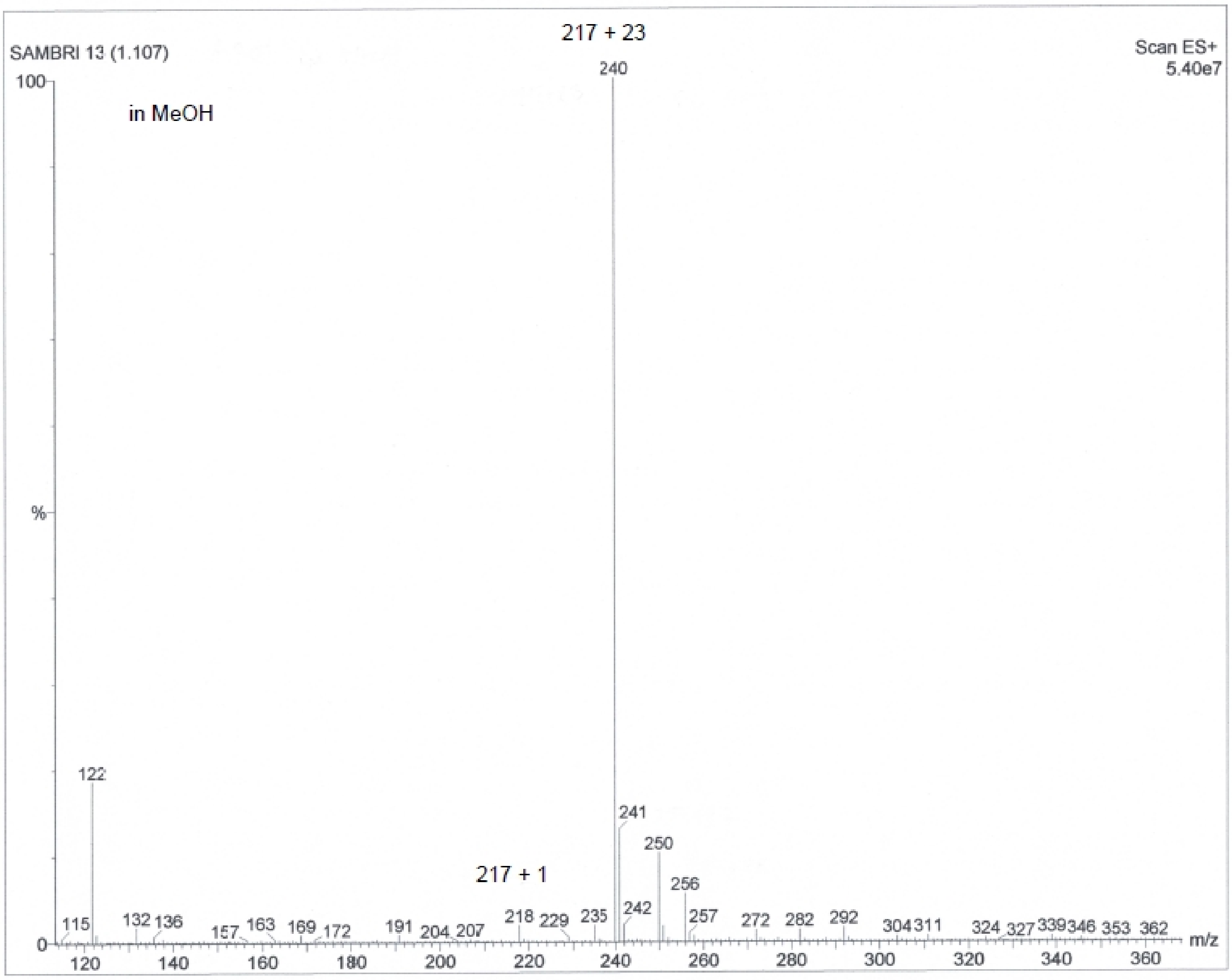
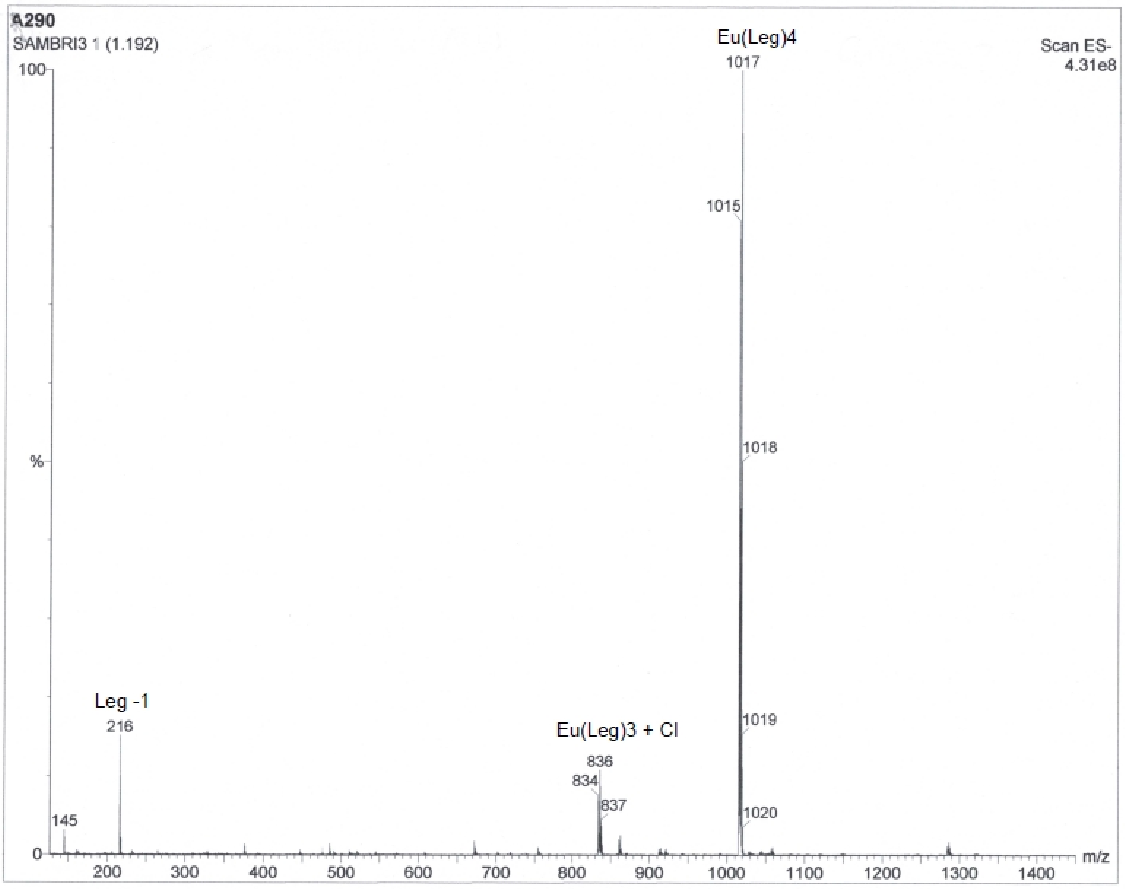
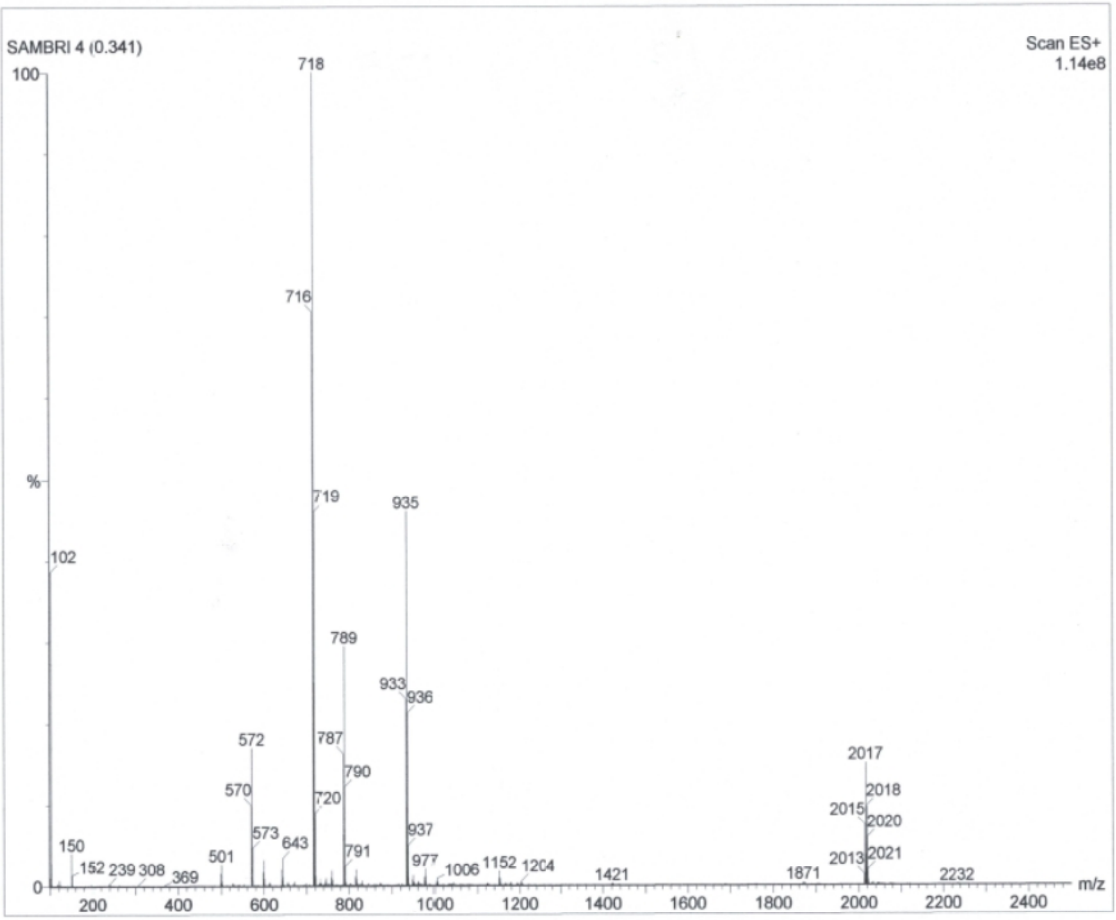


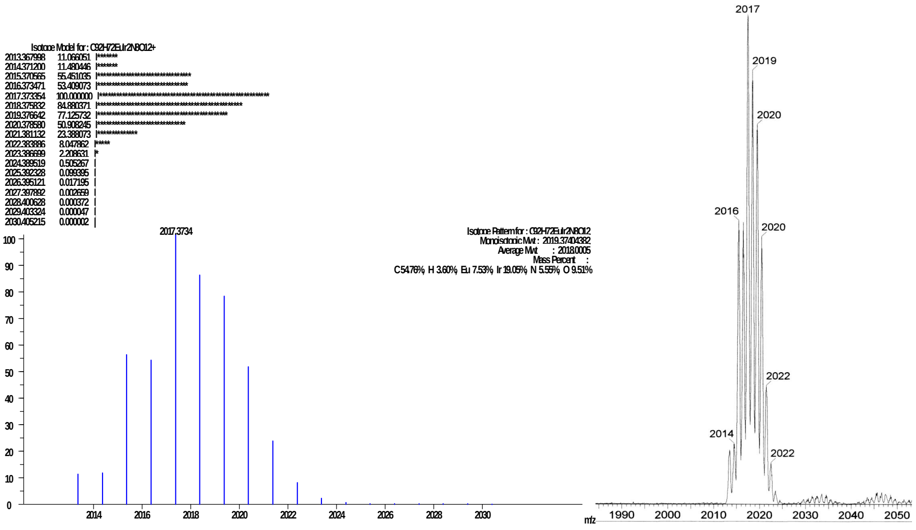
Figure S2: ESI MS spectrum of complex **3**



....

Figure S3: ESI MS spectrum of complex **7** and measured and simulated isotopic patterns

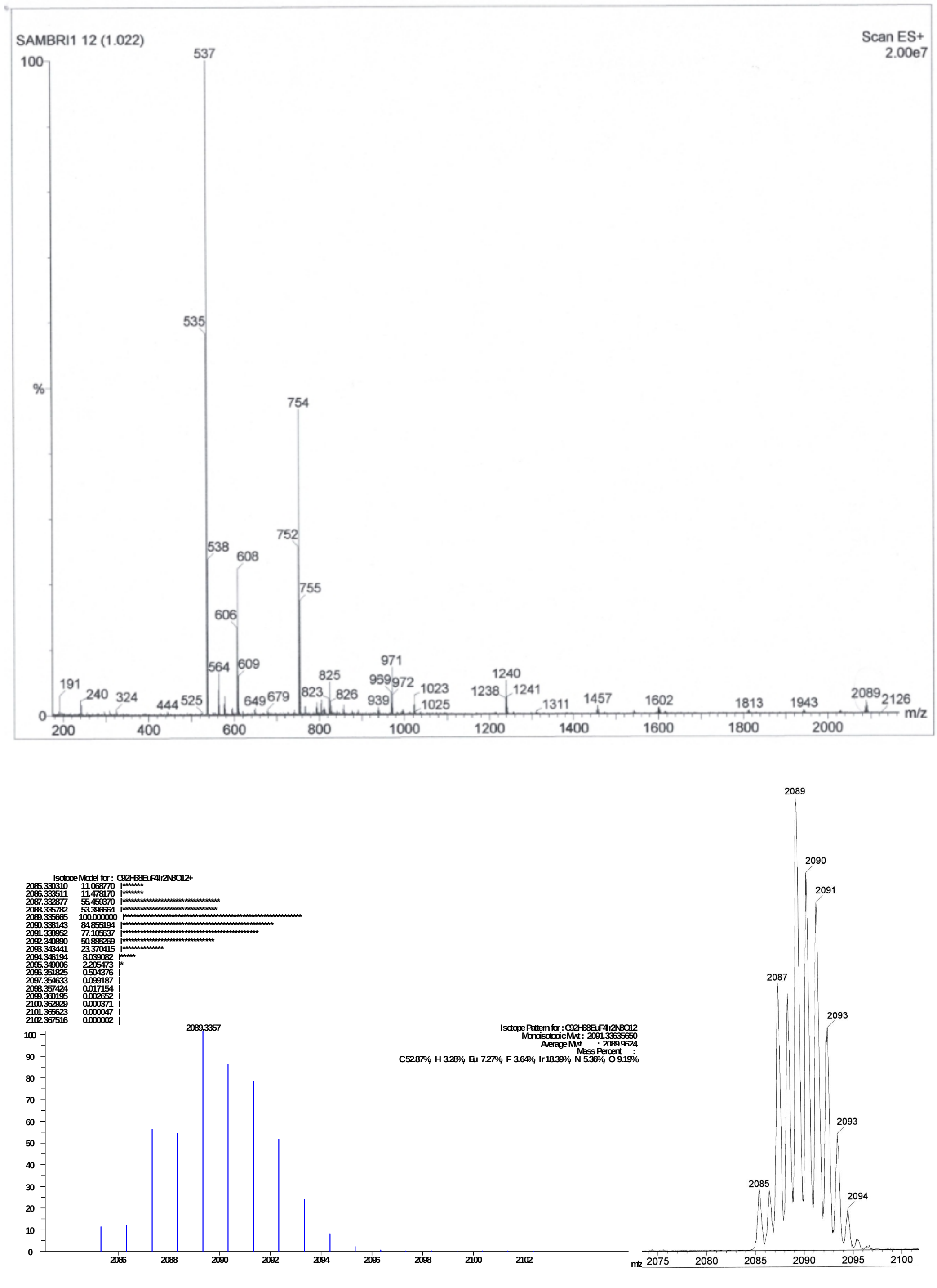




```
            Isotope Model for : C92H72EuIr2N8O12+
2013.367998    11.066051  |*******
2014.371200    11.480446  |*******
2015.370565    55.451035  |********************************
2016.373471    53.409073  |*******************************
2017.373354   100.000000  |***********************************************************
2018.375832    84.880371  |**************************************************
2019.376642    77.125732  |*********************************************
2020.378580    50.908245  |******************************
2021.381132    23.388073  |**************
2022.383886     8.047862  |*****
2023.386699     2.208631  |*
2024.389519     0.505267  |
2025.392328     0.099395  |
2026.395121     0.017195  |
2027.397892     0.002659  |
2028.400628     0.000372  |
2029.403324     0.000047  |
2030.405215     0.000002  |
```

```
                Isotope Pattern for : C92H72EuIr2N8O12
                 Monoisotopic Mwt :  2019.37404382
                    Average Mwt       :  2018.0005
                          Mass Percent     :
C 54.76%,  H 3.60%,  Eu 7.53%,  Ir 19.05%,  N 5.55%,  O 9.51%
```

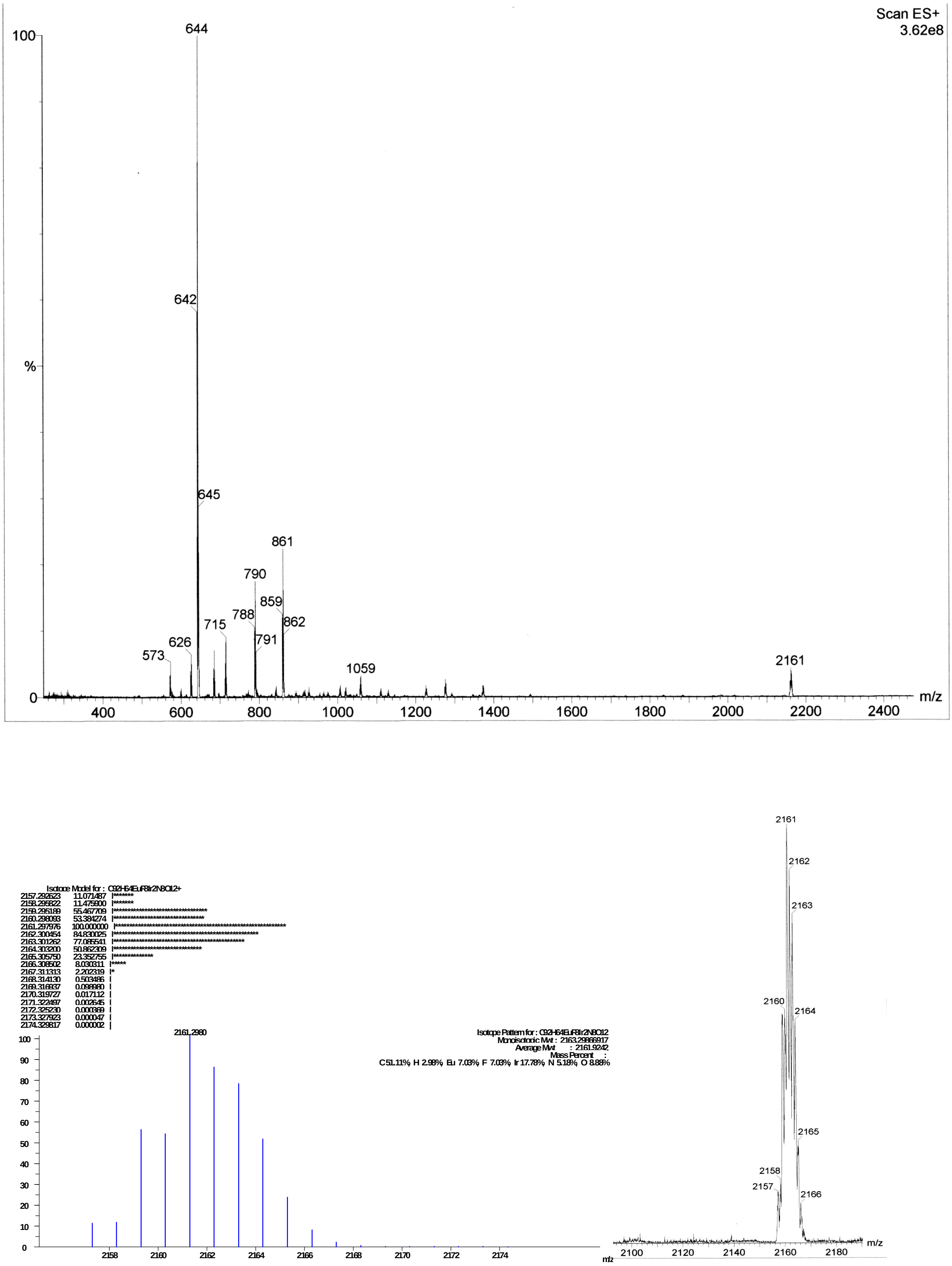
Figure S4: ESI MS spectrum of complex **8** and measured and simulated isotopic patterns



```
              Isotope Model for :  C92H68EuF4Ir2N8O12+
 2085.330310     11.068770  |*******
 2086.333511     11.478170  |*******
 2087.332877     55.459370  |************************************
 2088.335782     53.396664  |***********************************
 2089.335665    100.000000  |*****************************************************************
 2090.338143     84.855194  |*******************************************************
 2091.338952     77.105637  |**************************************************
 2092.340890     50.885269  |*********************************
 2093.343441     23.370415  |***************
 2094.346194      8.039082  |*****
 2095.349006      2.205473  |*
 2096.351825      0.504376  |
 2097.354633      0.099187  |
 2098.357424      0.017154  |
 2099.360195      0.002652  |
 2100.362929      0.000371  |
 2101.365623      0.000047  |
 2102.367516      0.000002  |
```

```
                        Isotope Pattern for : C92H68EuF4Ir2N8O12
                              Monoisotopic Mwt :  2091.33635650
                                 Average Mwt      :  2089.9624
                                       Mass Percent      :
C52.87%,  H 3.28%,  Eu  7.27%,  F 3.64%,  Ir 18.39%,  N 5.36%,  O 9.19%
```

Figure S5: ESI MS spectrum of complex **9** and measured and simulated isotopic patterns



```
          Isotope Model for :  C92H64EuF8Ir2N8O12+
2157.292623      11.071487   |*******
2158.295822      11.475900   |*******
2159.295189      55.467709   |********************************
2160.298093      53.384274   |*******************************
2161.297976     100.000000   |**********************************************************
2162.300454      84.830025   |*************************************************
2163.301262      77.085541   |*********************************************
2164.303200      50.862309   |******************************
2165.305750      23.352755   |**************
2166.308502       8.030311   |*****
2167.311313       2.202319   |*
2168.314130       0.503486   |
2169.316937       0.098980   |
2170.319727       0.017112   |
2171.322497       0.002645   |
2172.325230       0.000369   |
2173.327923       0.000047   |
2174.329817       0.000002   |
```

```
                         Isotope Pattern for : C92H64EuF8Ir2N8O12
                                  Monoisotopic Mwt :  2163.29866917
                                       Average Mwt     :  2161.9242
                                               Mass Percent     :
C 51.11%, H 2.98%, Eu 7.03%, F 7.03%, Ir 17.78%, N 5.18%, O 8.88%
```

Figure S6: ESI MS spectrum of complex **10**

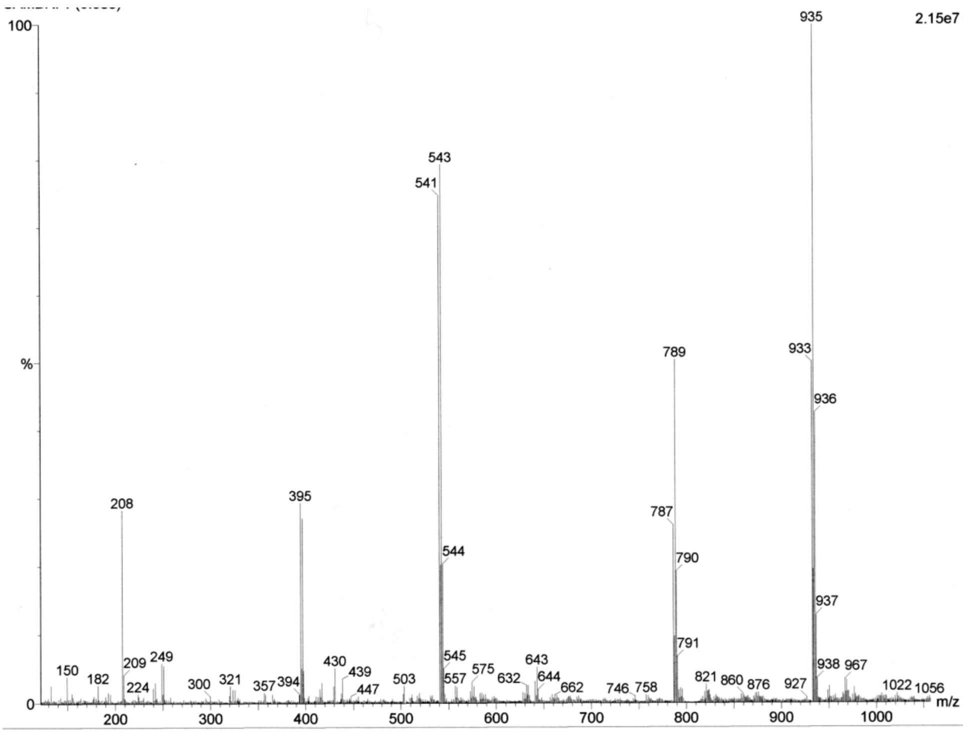


Figure S7: ESI MS spectrum of complex **11**

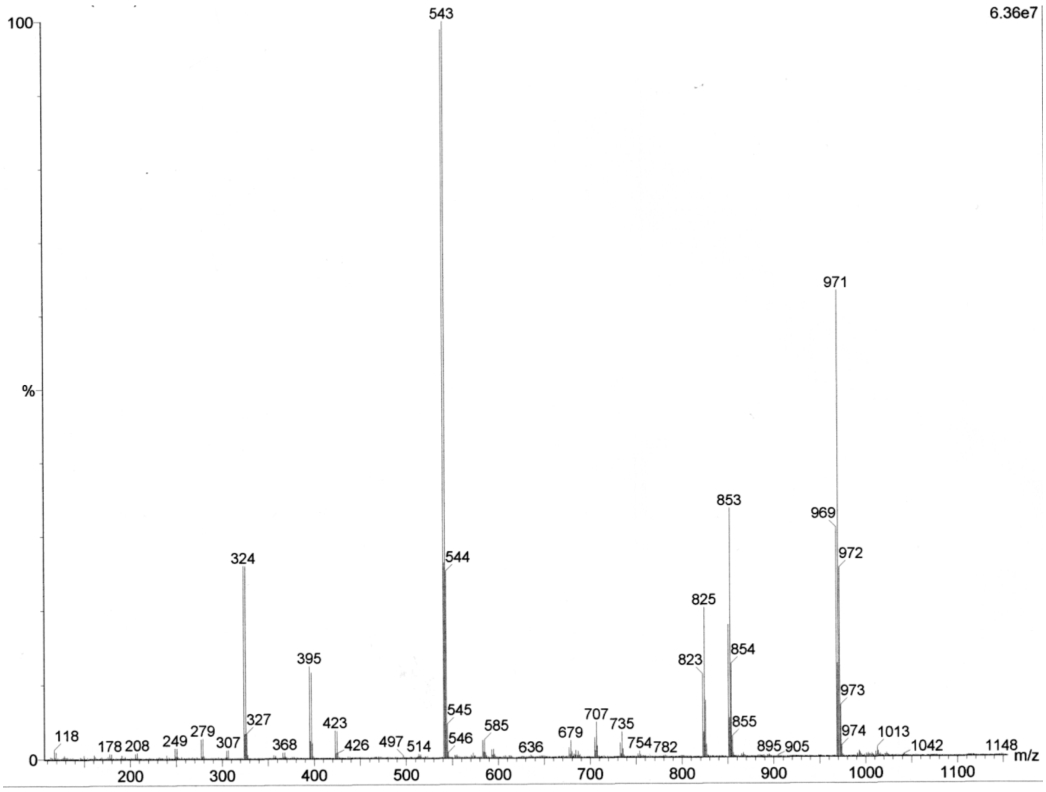


Figure S8: ESI MS spectrum of complex **12**

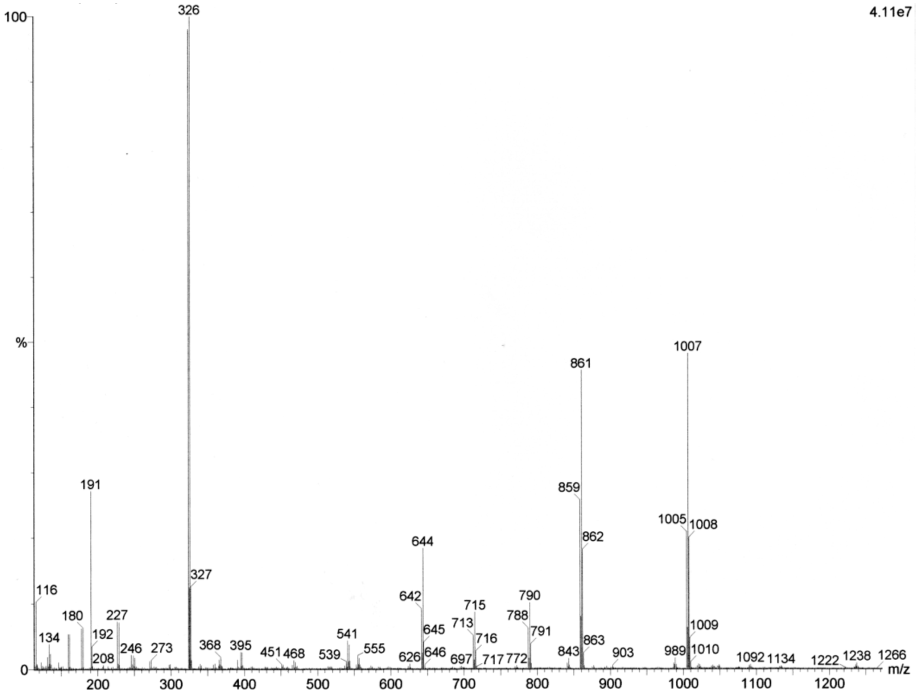


Table S1: Photophysical data of the obtained complexes

Complex	**Absorption**	**Emission 298 K**			**Emission 77K**		**Solid state**	
	λ_{max}(nm) $10^4\varepsilon$ (M^{-1} cm^{-1})	λ (nm)	τ (μs) deair	τ (μs) air	λ (nm)	τ (μs)	λ (nm)	τ (μs)
3	246(7.86) 287(3.41)	612	/	86.44(25%) 447.42(75%) (612nm)	592,612 700	267 (25%) 573 (75%) (612nm)	612	251(612nm)
7	240(9.52) 284(5.18) 375(0.42)	471, 504 573(sh) 612	0.26(470nm) 603 (612nm)	0.12(470nm) 608 (612nm)	464, 498 612	6,0 (464nm) 680 (612nm)	611	365.61(42%) 702.81(58%) (611nm)
8	249(12.10) 280(6.88) 370(0.81)	465,497 530,612	1.23(466nm) 599 (612nm)	0.30(466nm) 597 (612)	465, 495 524, 612	6.2 (466nm) 591 (612nm)	611	311.2(20%) 629.65(80%) (611nm)
9	247(10.69) 285(5.04)(sh) 362(0.87)	452, 482 612	1.20(482nm) 613 (612nm)	0.30(482nm) 613 (612nm)	447, 479 506,613	5.8 (479nm) 506(60%) 943 (40%) (612nm)	612	392.27(35%) 679.45(65%) (612nm)
10	245(8.00) 283(3.67) 347(0.77)	455,485 511	2.63(485nm)	0.81(485nm)	449,481 508	24,2 (481nm)	457 489 520	0.24(16%) 2.46(84%) (489nm)
11	247 (10.33) 282 (4.38) 346 (1.06)	452,484 510	16.71(484m)	0.95(484nm)	448,480 508	12 (480nm)	453 484 514	1.50(484nm)
12	242(9.18) 301(2.57)	442,470 496	8.64(470nm)	1.04(470nm)	434,466 502	24 (466nm)	444 474 499	0.14(16%) 1.31(84%) (472nm)

Figure S9: Absorption spectra of complexes **3**, **7** and **10**

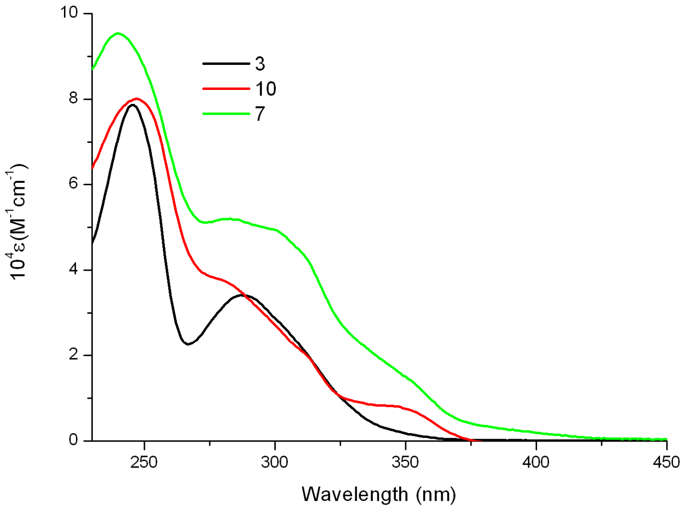


Figure S10: Absorption spectra of complexes **3**, **9** and **12**

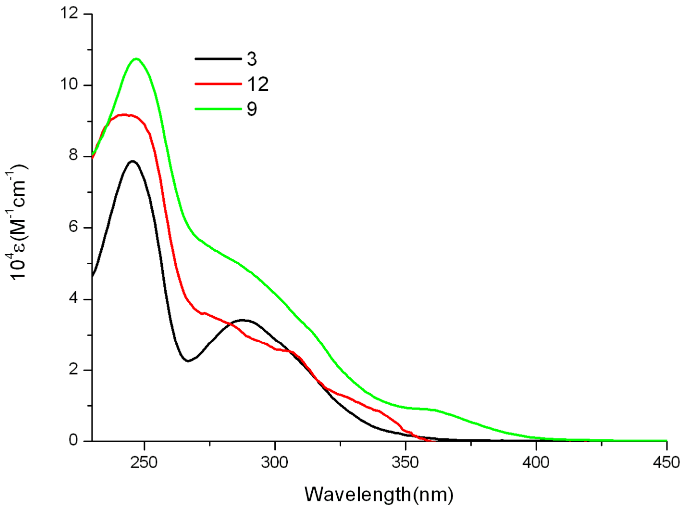
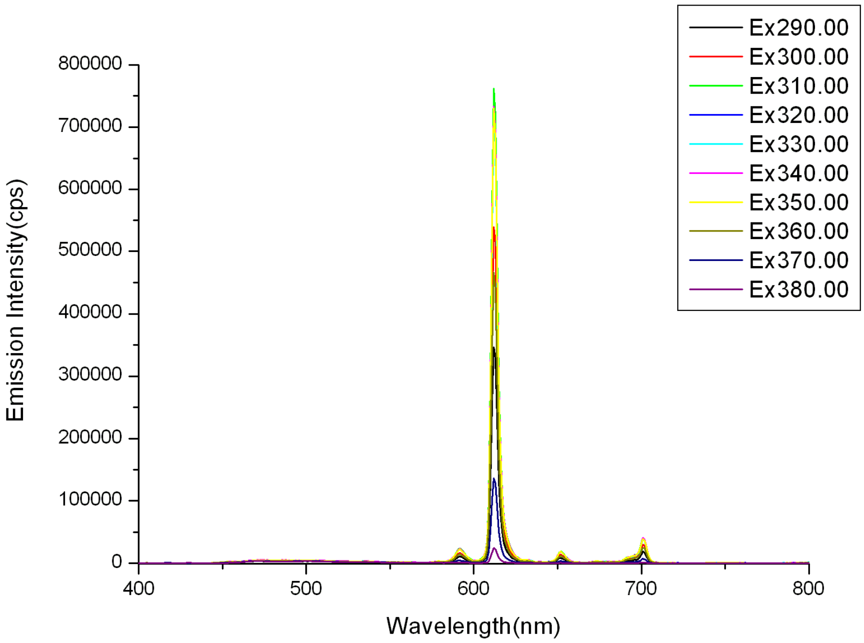
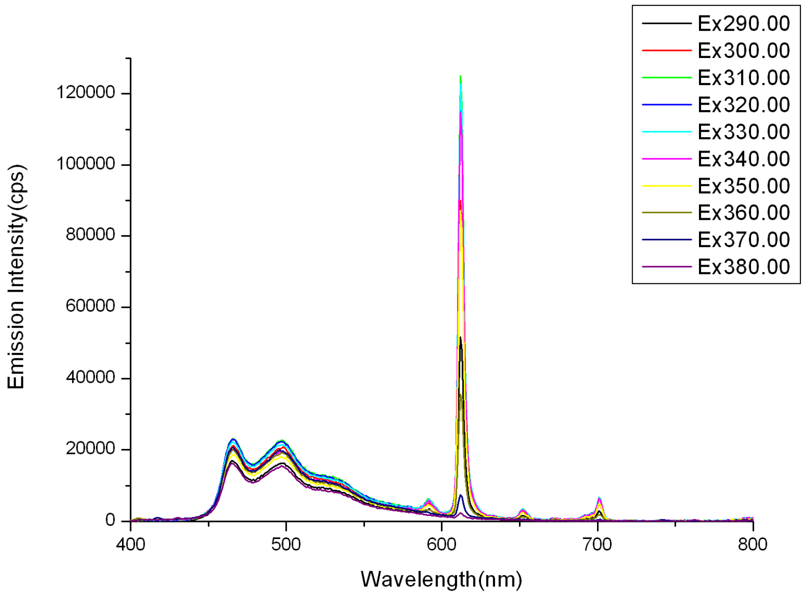


Figure S11: Emission map of complex **7** and corresponding CIE coordinates



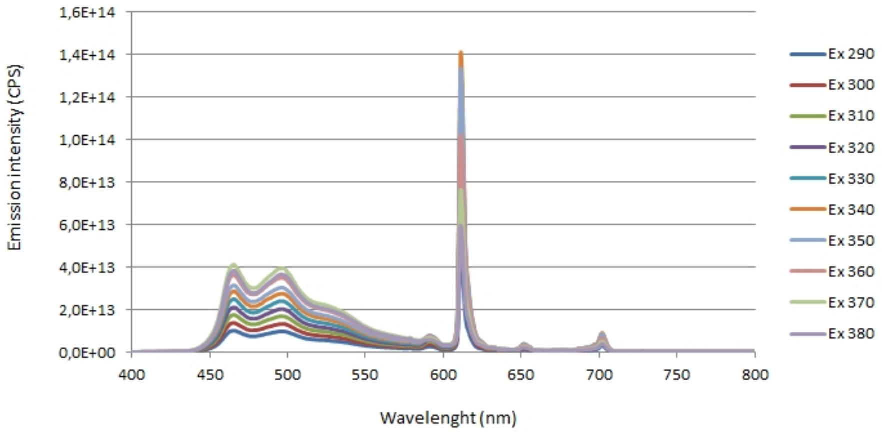
Ex	**Complex 7**		
λ	X	Y	Z
290	*0,611*	*0,337*	*0,053*
300	*0,621*	*0,335*	*0,044*
310	*0,63*	*0,335*	*0,035*
320	*0,629*	*0,335*	*0,035*
330	*0,628*	*0,335*	*0,037*
340	*0,626*	*0,335*	*0,04*
350	*0,629*	*0,333*	*0,038*
360	*0,617*	*0,335*	*0,049*
370	*0,539*	*0,342*	*0,119*
380	*0,356*	*0,358*	*0,287*

Figure S12: Emission map of complex **8** and corresponding CIE coordinates



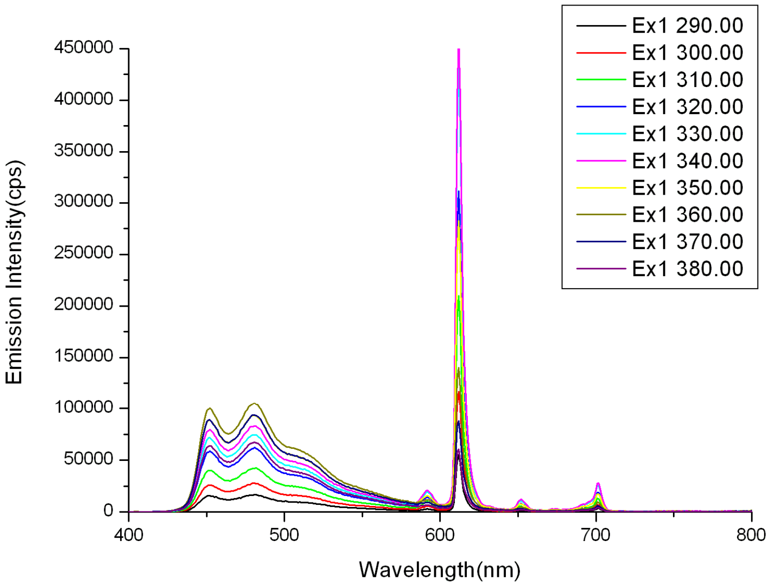
Ex	**Complex 8**		
λ	X	Y	Z
290	*0,285*	*0,364*	*0,351*
300	*0,313*	*0,362*	*0,325*
310	*0,336*	*0,36*	*0,304*
320	*0,333*	*0,359*	*0,308*
330	*0,338*	*0,358*	*0,304*
340	*0,341*	*0,356*	*0,303*
350	*0,32*	*0,356*	*0,323*
360	*0,25*	*0,361*	*0,389*
370	*0,202*	*0,365*	*0,433*
380	*0,193*	*0,362*	*0,444*

Figure S13: Solid state emission map of complex **8** (20%) in PMMA and corresponding CIE coordinates



Ex	**Complex 8 (20%) in PMMA**		
λ	X	Y	Z
290	*0,316*	*0,353*	*0,332*
300	*0,324*	*0,352*	*0,324*
310	*0,331*	*0,351*	*0,318*
320	*0,331*	*0,350*	*0,319*
330	*0,329*	*0,350*	*0,321*
340	*0,322*	*0,351*	*0,328*
350	*0,307*	*0,351*	*0,343*
360	*0,273*	*0,353*	*0,374*
370	*0,247*	*0,355*	*0,398*
380	*0,238*	*0,357*	*0,405*

Figure S14: Emission map of complex **9** and corresponding CIE coordinates



Ex	**Complex 9**		
λ	X	Y	Z
290	*0,278*	*0,276*	*0,445*
300	*0,301*	*0,278*	*0,421*
310	*0,316*	*0,279*	*0,404*
320	*0,318*	*0,279*	*0,403*
330	*0,333*	*0,281*	*0,387*
340	*0,328*	*0,28*	*0,392*
350	*0,27*	*0,271*	*0,459*
360	*0,218*	*0,263*	*0,519*
370	*0,204*	*0,262*	*0,534*
380	*0,202*	*0,262*	*0,536*

Table 2: CIE data of complexes **3**, **10-12**

Complex	X	Y	Z
3	*0,644*	*0,356*	*0*
10	*0,191*	*0,320*	*0,489*
11	*0,188*	*0,318*	*0,494*
12	*0,172*	*0,228*	*0,600*