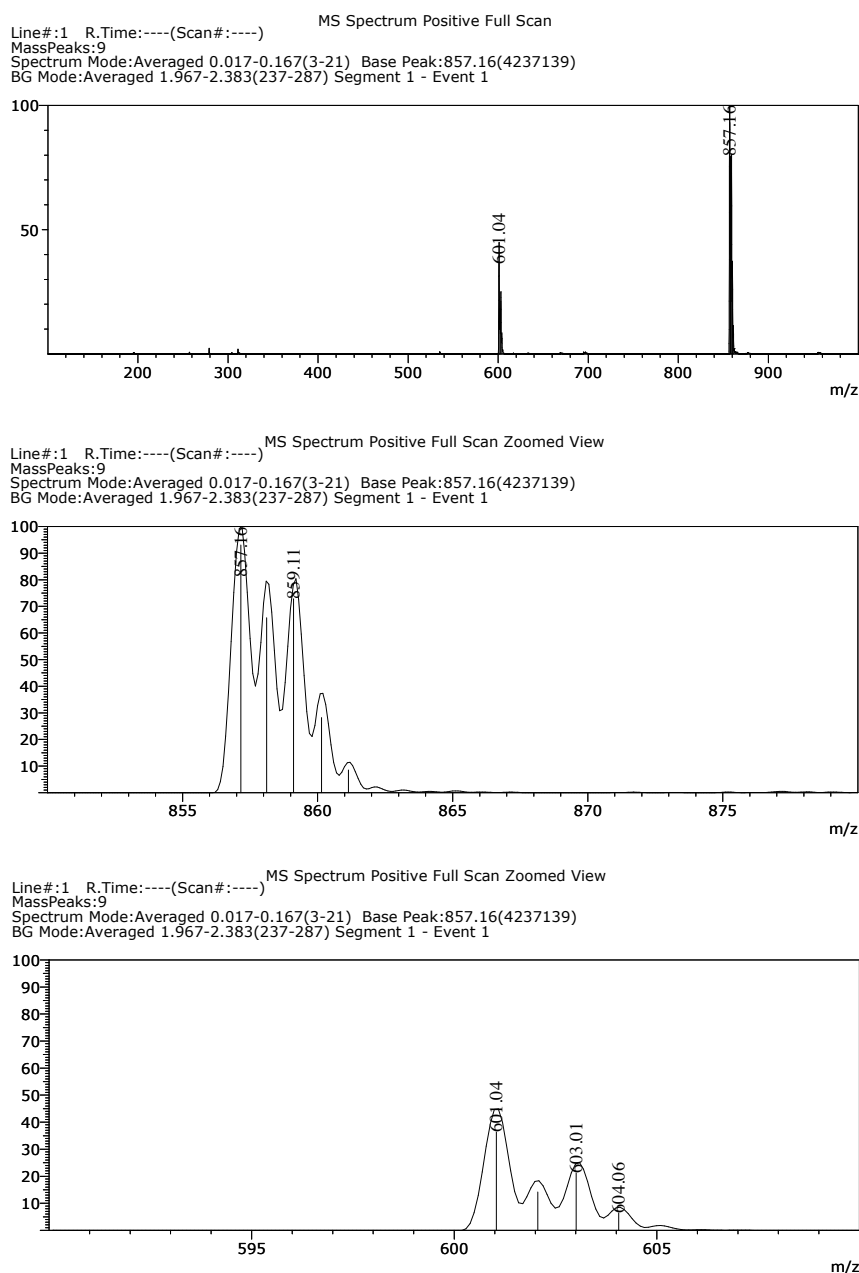


# Heteroleptic [Cu(P<sup>^</sup>P)(N<sup>^</sup>N)][PF<sub>6</sub>] Complexes: Effects of Isomer Switching from 2,2'-biquinoline to 1,1'-biisoquinoline

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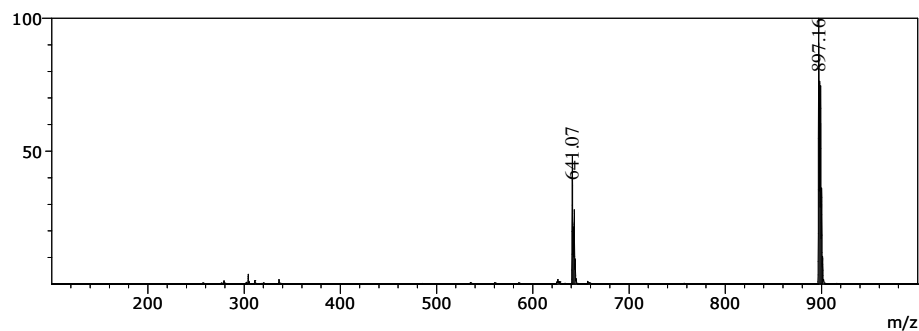
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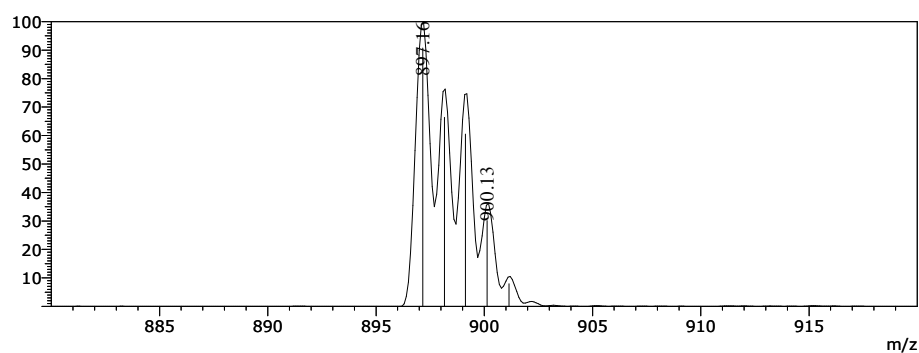


**Figure 1.** Electrospray mass spectrum (positive mode) of [Cu(POP)(biq)][PF<sub>6</sub>].

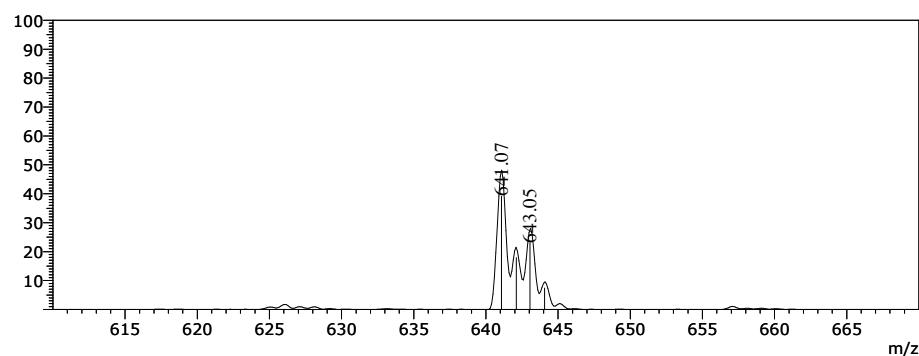
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 BG Mode:Averaged 1.517-1.900(183-229) Segment 1 - Event 1



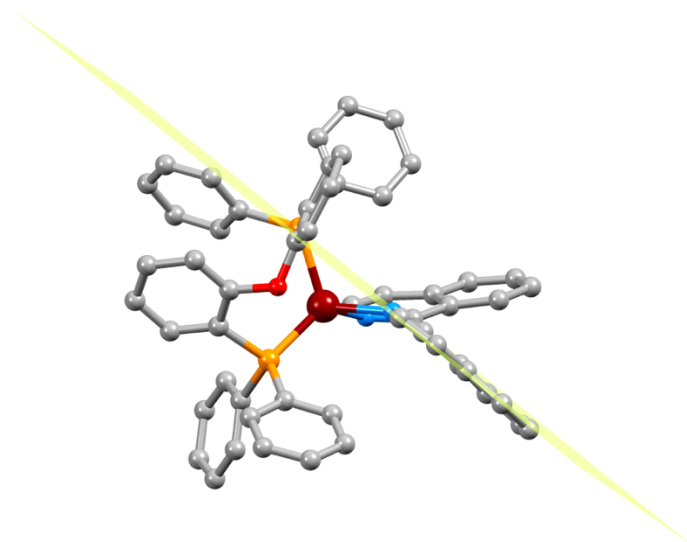
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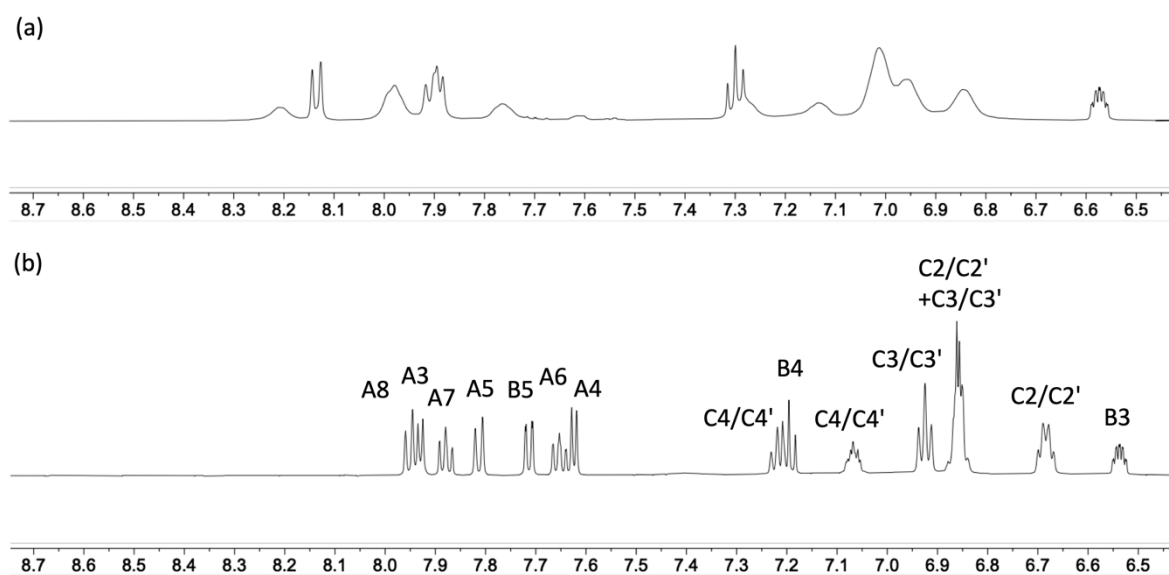
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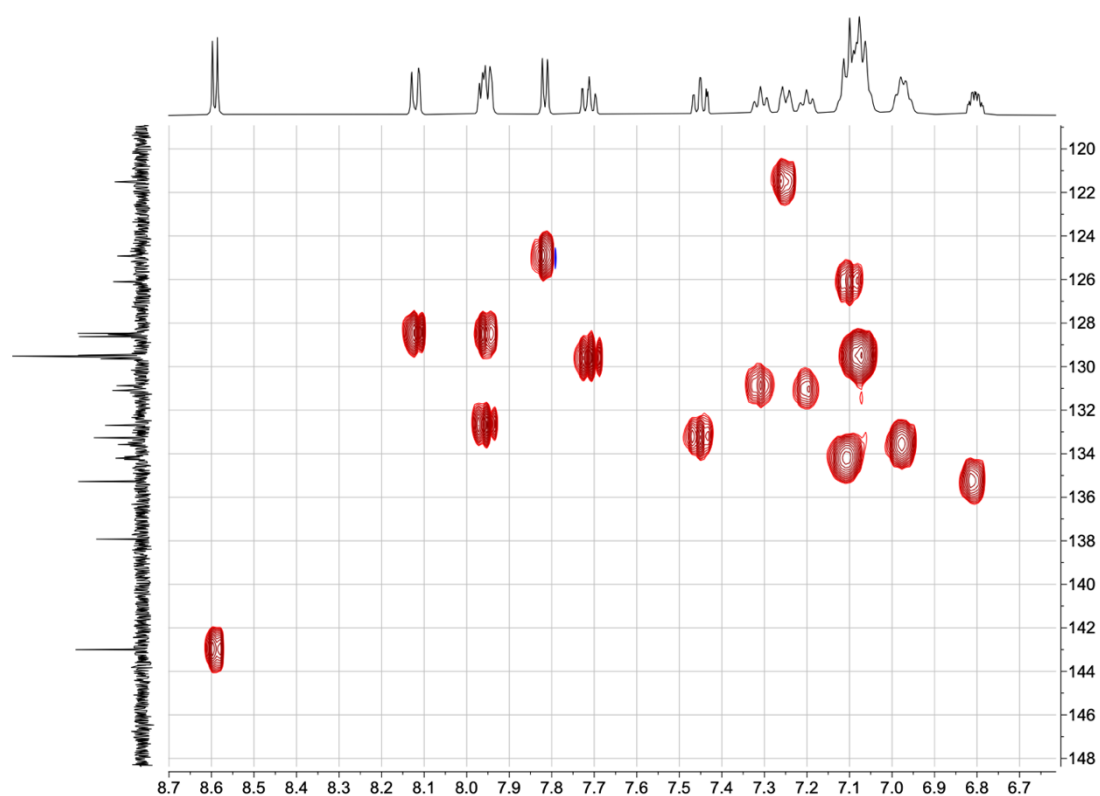
**Figure 2.** Electrospray mass spectrum (positive mode) of [Cu(xantphos)(biq)][PF<sub>6</sub>].



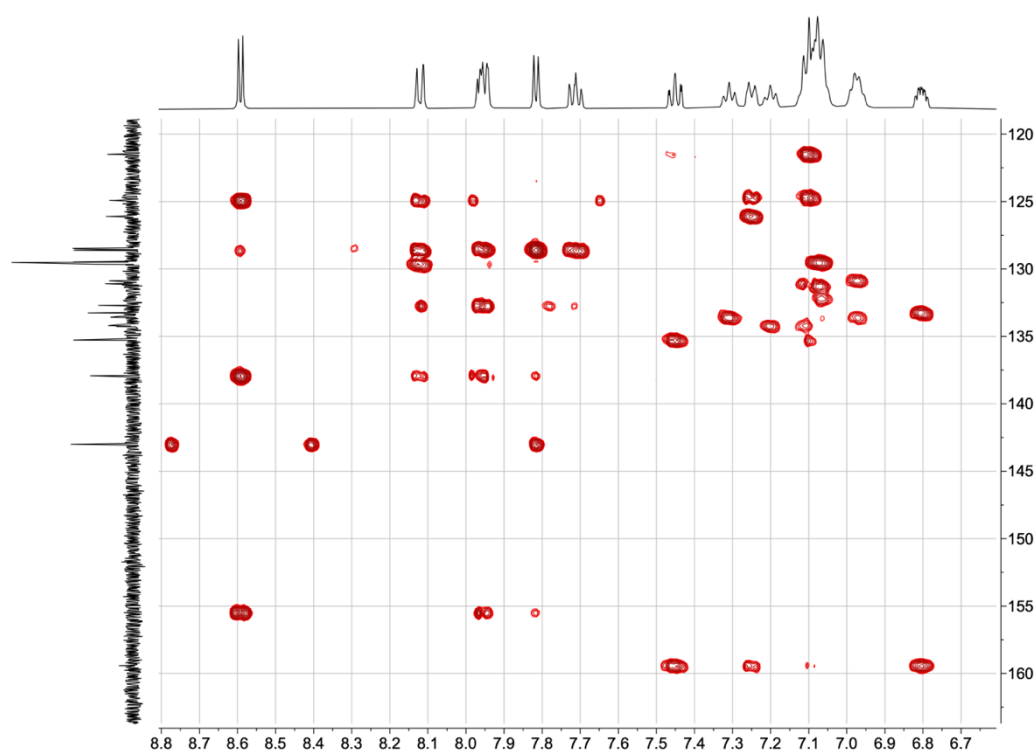
**Figure 3.** Structure of the  $[\text{Cu}(\text{POP})(\text{biq})]^+$  cation highlighting the relationship between one of the Cu–N bond vectors and the plane of the corresponding NC<sub>5</sub>-ring in one isoquinoline unit. H atoms are omitted.



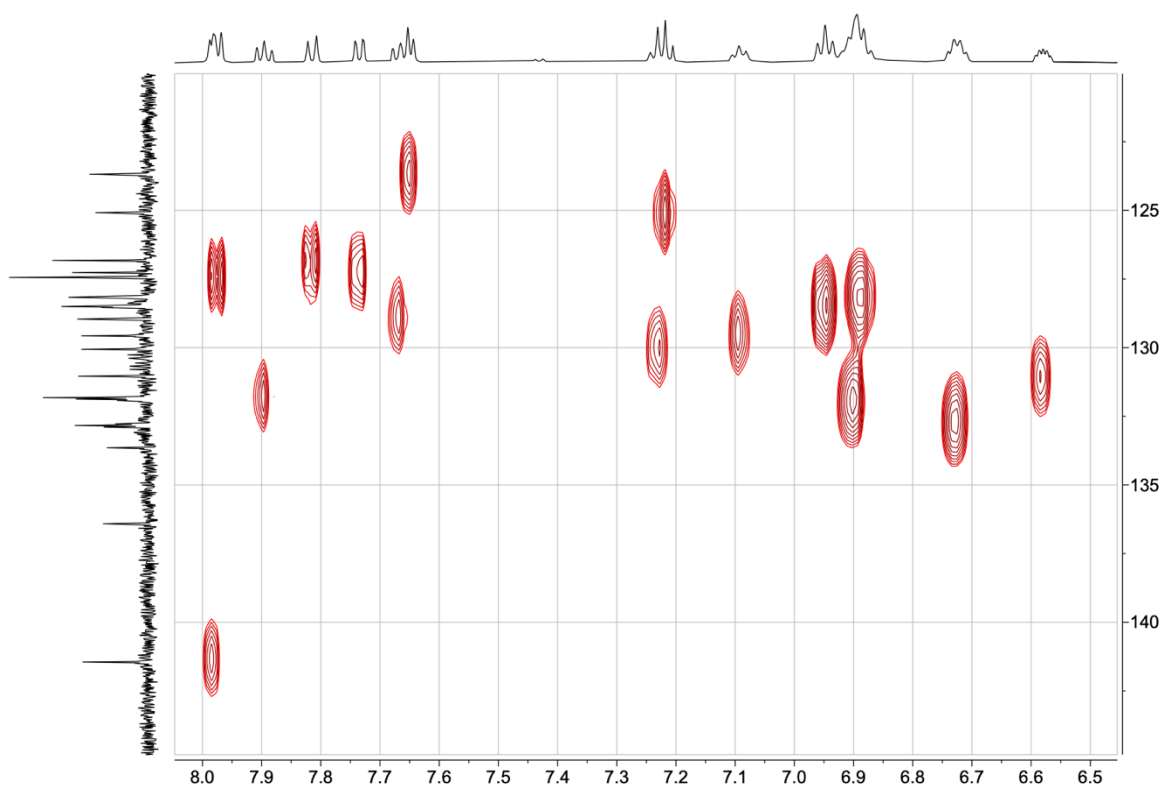
**Figure 4.**  $^1\text{H}$  NMR spectra (aromatic region) of  $[\text{Cu}(\text{xantphos})(\text{biq})][\text{PF}_6]$  in (a) acetone- $\text{d}_6$  (500 MHz, 298 K) and (b)  $\text{C}_2\text{D}_2\text{Cl}_4$  (600 MHz, 298 K). See Scheme 2 for atom labels.



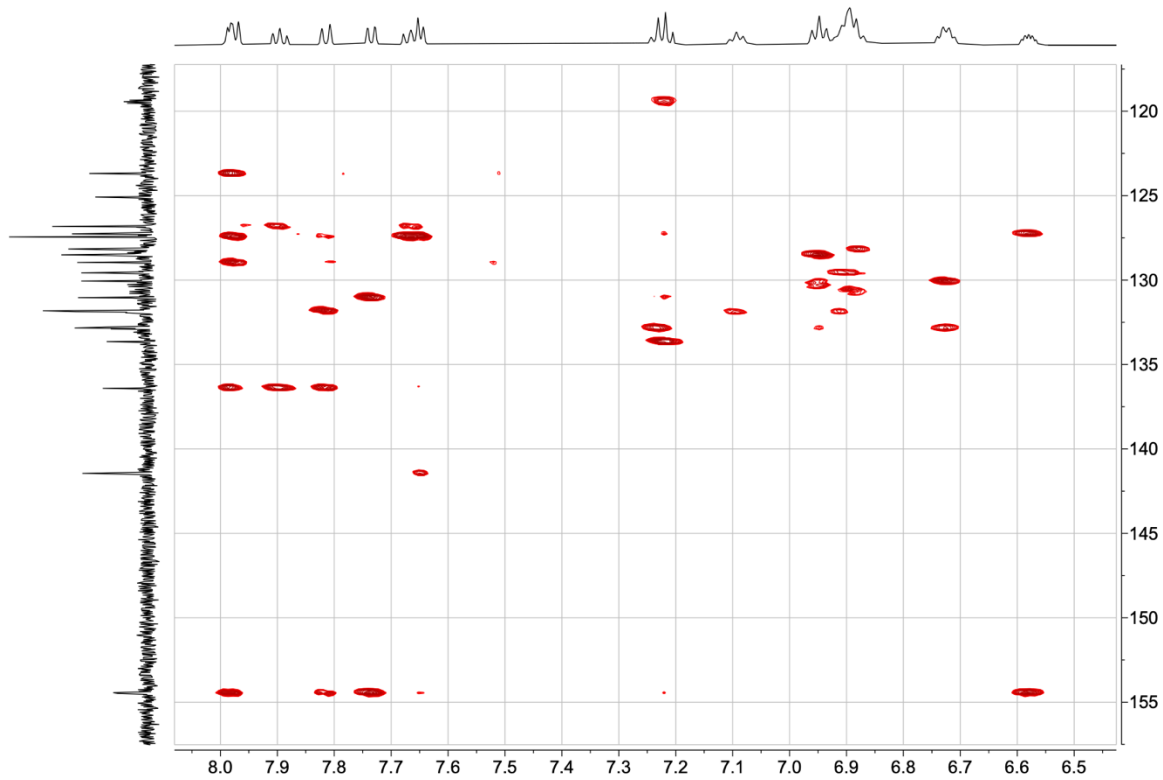
**Figure 5.** HMQC spectrum of  $[\text{Cu}(\text{POP})(\text{biq})][\text{PF}_6]$  (acetone- $\text{d}_6$ , 500 MHz for  $^1\text{H}$ , 126 MHz for  $^{13}\text{C}$ , 298 K).



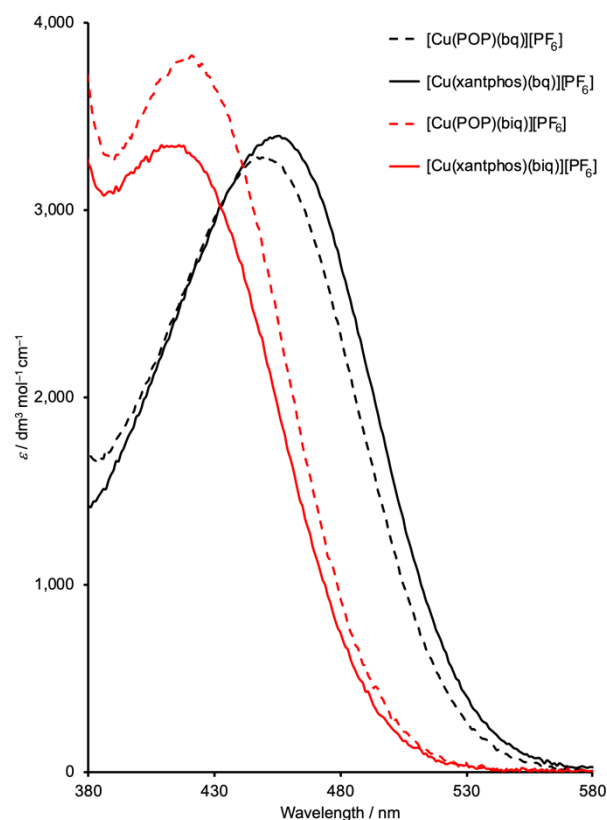
**Figure 6.** HMBC spectrum of  $[\text{Cu}(\text{POP})(\text{biq})][\text{PF}_6]$  (acetone- $\text{d}_6$ , 500 MHz for  $^1\text{H}$ , 126 MHz for  $^{13}\text{C}$ , 298 K).



**Figure 7.** HMQC spectrum (aromatic region) of  $[\text{Cu}(\text{xantphos})(\text{biq})][\text{PF}_6]$  ( $\text{C}_2\text{D}_2\text{Cl}_4$ , 600 MHz, 328 K).



**Figure 8.** HMBC spectrum (aromatic region) of  $[\text{Cu}(\text{xantphos})(\text{biq})][\text{PF}_6]$  ( $\text{C}_2\text{D}_2\text{Cl}_4$ , 600 MHz for  $^1\text{H}$  and 151 MHz for  $^{13}\text{C}$ , 328 K).



**Figure 9.** Expansion of the MLCT region in the solution absorption spectra of  $[\text{Cu}(\text{POP})(\text{bq})][\text{PF}_6]$  and  $[\text{Cu}(\text{xantphos})(\text{bq})][\text{PF}_6]$  compared to their biq analogs ( $\text{CH}_2\text{Cl}_2$ ,  $2.5 \times 10^{-5} \text{ mol dm}^{-3}$ ).

**Table 1.** Cartesian coordinates for the DFT modelled structure of  $[\text{Cu}(\text{xantphos})(\text{bq})]^+$ .

Cu	-1.242000	-1.002000	1.221000
N	-2.138000	-2.572000	2.331000
C	-1.473000	-2.858000	3.395000
C	-3.603000	-4.340000	2.565000
C	-1.670000	-4.169000	3.960000
C	-3.186000	-3.172000	1.954000
C	-2.803000	-4.893000	3.552000
C	-0.793000	-4.828000	4.863000
H	-3.714000	-2.769000	1.097000
H	-3.992000	-6.693000	3.792000
H	-4.493000	-4.843000	2.205000
C	-1.080000	-6.087000	5.398000
H	0.151000	-4.365000	5.140000
H	-0.385000	-6.551000	6.093000
C	-2.246000	-6.743000	5.031000
H	-2.477000	-7.722000	5.442000
C	-3.101000	-6.153000	4.104000
N	-0.005000	-1.024000	2.995000
C	-0.472000	-1.836000	3.875000

C	1.628000	-0.175000	4.381000
C	-0.075000	-1.618000	5.242000
C	1.021000	-0.299000	3.146000
C	1.042000	-0.795000	5.474000
C	-0.740000	-2.117000	6.392000
H	1.371000	0.262000	2.285000
H	2.407000	0.041000	6.939000
H	2.493000	0.471000	4.488000
C	-0.265000	-1.891000	7.687000
H	-1.668000	-2.676000	6.285000
H	-0.800000	-2.300000	8.540000
C	0.884000	-1.136000	7.878000
H	1.261000	-0.956000	8.880000
C	1.530000	-0.582000	6.776000
P	-2.486000	1.052000	1.019000
P	-0.046000	-1.711000	-0.747000
C	-3.541000	1.314000	2.574000
C	-5.055000	1.730000	4.885000
C	-3.008000	1.008000	3.827000
C	-4.829000	1.850000	2.482000
C	-5.585000	2.053000	3.637000
C	-3.765000	1.209000	4.980000
H	-2.000000	0.614000	3.913000
H	-5.249000	2.117000	1.517000
H	-6.588000	2.464000	3.563000
H	-3.345000	0.958000	5.950000
H	-5.644000	1.885000	5.785000
C	-3.619000	0.926000	-0.484000
C	-5.347000	0.721000	-2.667000
C	-3.452000	1.764000	-1.588000
C	-4.650000	-0.017000	-0.478000
C	-5.514000	-0.118000	-1.567000
C	-4.316000	1.659000	-2.678000
H	-2.654000	2.499000	-1.613000
H	-4.788000	-0.667000	0.382000
H	-6.315000	-0.852000	-1.559000
H	-4.182000	2.308000	-3.539000
H	-6.016000	0.638000	-3.519000
C	0.637000	-3.461000	-0.485000
C	1.660000	-6.030000	-0.095000
C	0.706000	-4.359000	-1.555000
C	1.099000	-3.847000	0.773000
C	1.603000	-5.132000	0.970000

C	1.215000	-5.642000	-1.358000
H	0.364000	-4.066000	-2.544000
H	1.062000	-3.155000	1.609000
H	1.944000	-5.432000	1.958000
H	1.261000	-6.342000	-2.188000
H	2.050000	-7.032000	0.062000
C	-1.254000	-1.746000	-2.195000
C	-3.054000	-1.878000	-4.323000
C	-1.074000	-0.929000	-3.311000
C	-2.338000	-2.628000	-2.144000
C	-3.235000	-2.695000	-3.208000
C	-1.975000	-0.996000	-4.374000
H	-0.239000	-0.237000	-3.366000
H	-2.478000	-3.269000	-1.277000
H	-4.077000	-3.380000	-3.166000
H	-1.838000	-0.355000	-5.241000
H	-3.756000	-1.925000	-5.151000
C	-1.321000	2.535000	0.850000
C	0.453000	4.667000	0.576000
C	-1.604000	3.750000	1.468000
C	-0.155000	2.402000	0.092000
C	0.769000	3.442000	-0.037000
C	-0.720000	4.817000	1.322000
H	-2.506000	3.877000	2.060000
H	-0.943000	5.770000	1.796000
H	1.112000	5.526000	0.482000
C	1.405000	-0.554000	-1.111000
C	3.499000	1.216000	-1.606000
C	1.242000	0.819000	-0.914000
C	2.626000	-1.043000	-1.567000
C	3.668000	-0.156000	-1.823000
C	2.283000	1.728000	-1.123000
H	2.774000	-2.107000	-1.729000
H	4.621000	-0.533000	-2.189000
H	4.336000	1.874000	-1.825000
O	-0.010000	1.203000	-0.538000
C	2.055000	3.219000	-0.843000
C	3.263000	3.785000	-0.055000
H	4.206000	3.677000	-0.600000
H	3.379000	3.276000	0.910000
H	3.163000	4.857000	0.148000
C	1.928000	3.959000	-2.189000
H	2.828000	3.838000	-2.803000



H	1.773000	5.035000	-2.046000
H	1.080000	3.582000	-2.775000