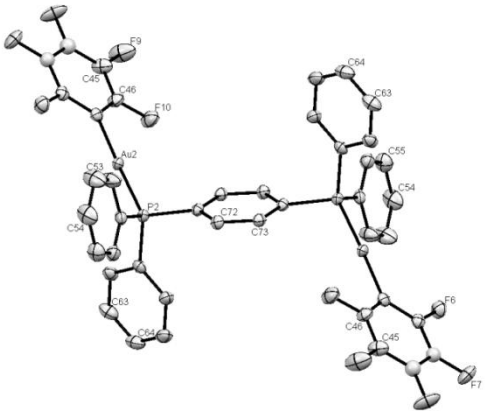


Figure SF1.-Ortep representation of complex **7**. Hydrogen atoms have been omitted for the sake of clarity. The thermal ellipsoids are drawn at 50% of probability.

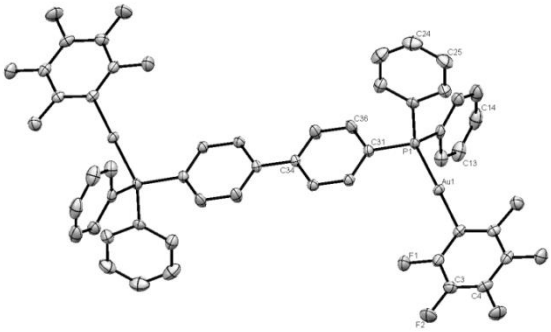


Figure SF2.-Ortep representation of complex **8**. Hydrogen atoms have been omitted for the sake of clarity. The thermal ellipsoids are drawn at 50% of probability.

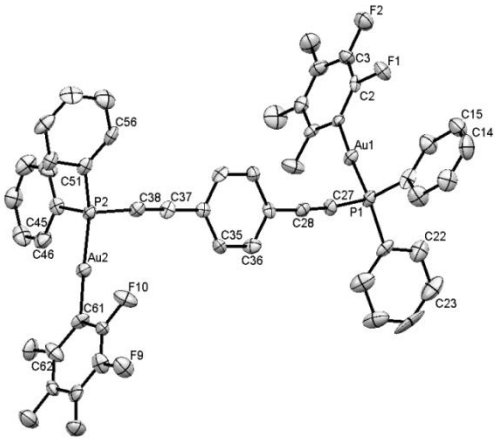


Figure SF3.-Ortep representation of complex **12**. Hydrogen atoms have been omitted for the sake of clarity. The thermal ellipsoids are drawn at 50% of probability.

Description of the π-π interactions

Compound 7: distances between centroids of rings 1 and 2 (see figure 1 in the text) and those between centroids of rings 3 and 4 are the same, 3.914 Å. Distance between centroids of rings 2 and 3 is 3.564 Å. The distances between the centroids of rings 1 and 4 to the planes formed by rings 2 and 3, respectively, are the same, 3.533 Å. That of the centroid of ring 2 to the plane formed by ring 3 is 3.397 Å. Displacement angles are 20.6º, between rings 1 and 2, 3 and 4 and 22.1º between rings 2-3.

Compound 8: distances between centroids of rings 1 and 2 is 3.677 Å, that between centroids of rings 2 and 3 is 4.195 Å. Distance between centroids of rings 1 and 3 and the plane formed by ring 2 are 3.509 and 3.364 Å. The displacement plane between rings 1 and 2 is 17.33º and 36.36º between 2 and 3.

Compound 12: The distances between centroids of rings 1-2 and 2-3 (see figure 3 in the text in which three rings have been numbered) are 3.676 and 4.198 Å respectively, and the distances between the centroid of ring 1 and the plane containing ring 2 is 3.384 Å; that between the centroid of ring 3 and the plane containing ring 2 is 3.318 Å. The displacement angles are 21.03º between rings 1 and 2 and 17.7º between rings 2 and 3.

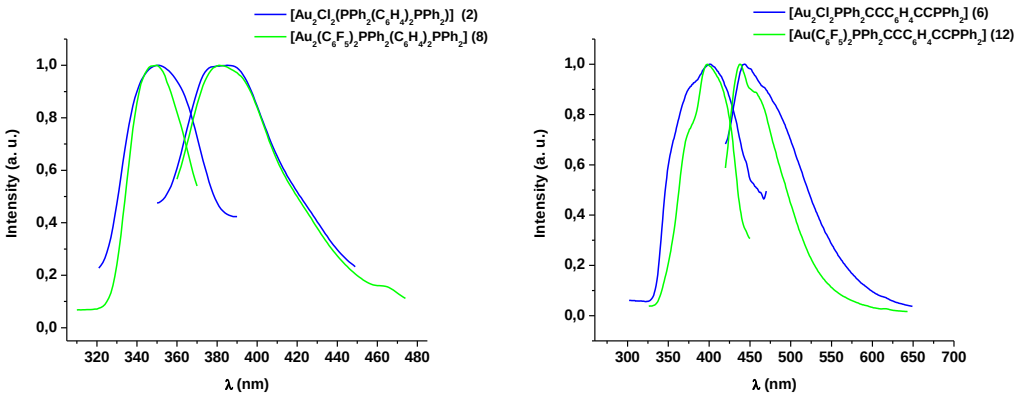


Figure SF4. Left: Normalized excitation (left) and emission (right) for chloro and pentafluorophenyl complexes with the $PPh_2C_6H_4PPh_2$ diphosphine in the solid state at 298 K. Right: Normalized excitation (left) and emission (right) for chloro and pentafluorophenyl complexes with the $PPh_2C{\equiv}CC_6H_4C{\equiv}CPPh_2$ diphosphine in the solid state at 298 K.

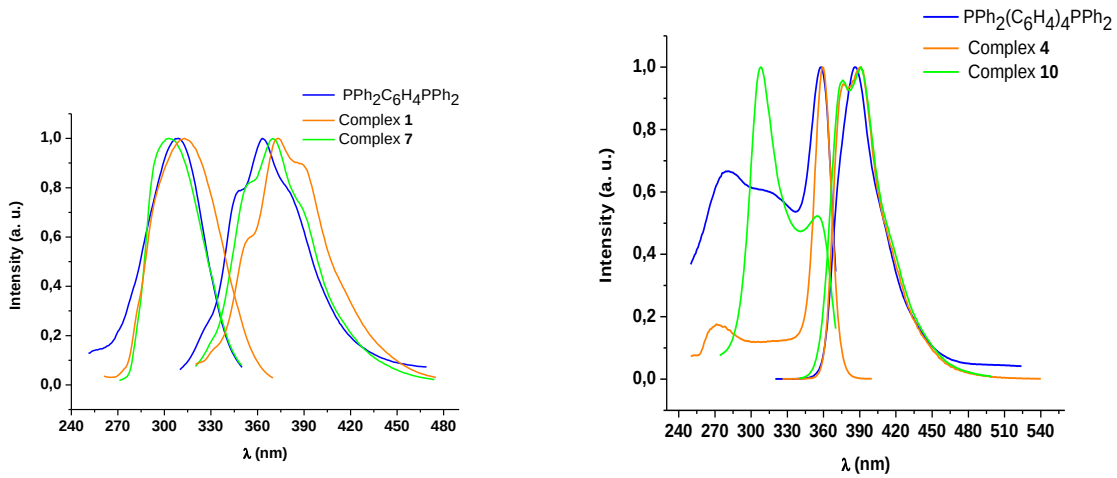


Figure SF6.-Left: Normalized excitation (left) and emission (right) spectra of the diphosphine $PPh_2C_6H_4PPh_2$ and the complexes **1** and **7** in solution at 298 K. Right: Normalized excitation (left) and emission (right) spectra of the diphosphine $PPh_2(C_6H_4)_4PPh_2$ and the complexes **4** and **10** in solution at 298 K

Electronic Supplementary Material (ESI) for Dalton Transactions

Table ST1. UV/vis and RDUV data for complexes **1-12**

Compound	**UV** λ_{max} [a] (ε x 10^{-4}) [b]	**RDUV** λ_{max} [a]
$PPh_2(C_6H_4)PPh_2$	230 (2.5) 275 (2.0)	295
$[(AuCl)_2(PPh_2(C_6H_4)PPh_2)]$ (**1**)	235 (3.8) 260 (2.2)	285
$[\{Au(C_6F_5)\}_2(PPh_2(C_6H_4)PPh_2)]$ (**7**)	235 (5.4) 260 (3.4)	280
$PPh_2(C_6H_4)_2PPh_2$	230 (3.0) 287 (3.0)	308
$[(AuCl)_2(PPh_2(C_6H_4)_2PPh_2)]$ (**2**)	230 (3.7) 285 (4.2)	300
$[\{Au(C_6F_5)\}_2(PPh_2(C_6H_4)_2PPh_2)]$ (**8**)	230 (3.8) 285 (3.4)	300
$PPh_2(C_6H_4)_3PPh_2$	230 (1.2) 285 (2.7)	315
$[(AuCl)_2(PPh_2(C_6H_4)_3PPh_2)]$ (**3**)	230 (4.2) 300 (5.0)	315
$[\{Au(C_6F_5)\}_2(PPh_2(C_6H_4)_3PPh_2)]$ (**9**)	235 (4.4) 300 (3.6)	315
$PPh_2(C_6H_4)_4PPh_2$	229 (1.0) 314 (2.2)	233 330
$[(AuCl)_2(PPh_2(C_6H_4)_4PPh_2)]$ (**4**)	229 (1.6) 314 (2.8)	332
$[\{Au(C_6F_5)\}_2(PPh_2(C_6H_4)_4PPh_2)]$ (**10**)	230 (3.2) 315 (3.4)	330
$PPh_2(C_6H_4)_5PPh_2$	228 (1.3) 320 (3.1)	338
$[(AuCl)_2(PPh_2(C_6H_4)_5PPh_2)]$ (**5**)	229 (1.7) 322 (3.4)	343
$[\{Au(C_6F_5)\}_2(PPh_2(C_6H_4)_5PPh_2)]$ (**11**)	230 (2.7) 322 (3.4)	342
$[(AuCl)_2(PPh_2C{\equiv}CC_6H_4C{\equiv}CPPh_2)]$ (**6**)	232 (1.8) 294 (2.5) 341 (2.9)	315
$[\{Au(C_6F_5)\}_2(PPh_2C{\equiv}CC_6H_4C{\equiv}CPPh_2)]$ (**12**)	233 (1.6) 294 (2.2) 312 (2.5)	311

[a] λ_{max} in nm,. [b] ε in $dm^3 \cdot mol^{-1} \cdot cm^{-1}$ in solution $5 \cdot 10^{-5}$ M

Table TS2. Excitation and emission maxima (λ_{MAX}) in nm of complexes **1-12** in the solid state

Compound	**298 K**		**77 K**	
	Excitation	Emission	Excitation	Emission
$PPh_2(C_6H_4)PPh_2$	270, 370, 400 360, 400	445 470	330, 405	480
$[(AuCl)_2(PPh_2(C_6H_4)PPh_2)]$ (**1**)	310, 345	385	270, 330	385, 405, 425, 455, 485*
$[\{Au(C_6F_5)\}_2(PPh_2(C_6H_4)PPh_2)]$ (**7**)	330, 350	385	280, 360	380, 400, 420*
$PPh_2(C_6H_4)_2PPh_2$	370	470	335 370	430 500
$[(AuCl)_2(PPh_2(C_6H_4)_2PPh_2)]$ (**2**)	350	385	320 350	390 465, 500, 530*
$[\{Au(C_6F_5)\}_2(PPh_2(C_6H_4)_2PPh_2)]$ (**8**)	350	385	275 340	380 500
$PPh_2(C_6H_4)_3PPh_2$	370, 440 270, 405	450 490	275, 390	480
$[(AuCl)_2(PPh_2(C_6H_4)_3PPh_2)]$ (**3**)	275, 370, 400	385(sh), 425*	275, 355	365, 385, 425* 520, 555, 600*
$[\{Au(C_6F_5)\}_2(PPh_2(C_6H_4)_3PPh_2)]$ (**9**)	280, 360, 400	385(sh), 420*	275, 360	365, 385, 415* 515, 550, 600*
$PPh_2(C_6H_4)_4PPh_2$	275, 375, 410	436, 480*	278, 385	403, 427, 453*
$[(AuCl)_2(PPh_2(C_6H_4)_4PPh_2)]$ (**4**)	345	407	305, 380	410
$[\{Au(C_6F_5)\}_2(PPh_2(C_6H_4)_4PPh_2)]$ (**10**)	280, 370	405	280, 370	400
$PPh_2(C_6H_4)_5PPh_2$	277, 370, 400	423, 445, 478*	277, 375	400, 423, 445, 478*
$[(AuCl)_2(PPh_2(C_6H_4)_5PPh_2)]$ (**5**)	280, 378	427	278, 385	417, 435*
$[\{Au(C_6F_5)\}_2(PPh_2(C_6H_4)_5PPh_2)]$ (**11**)	280, 380	415	280, 370	395, 420, 440*
$[(AuCl)_2(PPh_2C{\equiv}CC_6H_4C{\equiv}CPPh_2)]$ (**6**)	402	459	311, 330, 425	512
$[\{Au(C_6F_5)\}_2(PPh_2C{\equiv}CC_6H_4C{\equiv}CPPh_2)]$ (**12**)	400	450	390 345, 410	460 484, 504, 513, 525, 539*

In the excitation spectra values separated by comma indicate more than one maximum of excitation for the same emission. In the emission spectra values separated by comma indicate a structured band. Values marked with * correspond to the most intense bands. When two emission maxima are observed the corresponding excitation and emission are in the same line.

Table TS3. Excitation and emission maxima (λ_{MAX}) in nm of complexes **1-12** in solution

Compound	**298 K**		**77 K**	
	Excitation	Emission	Excitation	Emission
$PPh_2(C_6H_4)PPh_2$[a]	310	365*	275, 315	450
$[(AuCl)_2(PPh_2(C_6H_4)PPh_2)]$ (**1**)	310	355, 370, 390*	270	385, 405, 425, 455, 485*
$[\{Au(C_6F_5)\}_2(PPh_2(C_6H_4)PPh_2)]$ (**7**)	305	350, 370, 390*	270, 315	410
$PPh_2(C_6H_4)_2PPh_2$[a]	250, 285	340	270, 340	485
$[(AuCl)_2(PPh_2(C_6H_4)_2PPh_2)]$ (**2**)	320	385	280, 320 330	370 465, 495, 525, 570[a]
$[\{Au(C_6F_5)\}_2(PPh_2(C_6H_4)_2PPh_2)]$ (**8**)	320	385	275, 310	460, 490, 525*
$PPh_2(C_6H_4)_3PPh_2$[a]	310, 360	370 420	300, 350	445
$[(AuCl)_2(PPh_2(C_6H_4)_3PPh_2)]$ (**3**)	260, 340	355, 370, 390, 410, 435*	275, 345	355, 375, 390, 410, 435* 510, 545, 590*
$[\{Au(C_6F_5)\}_2(PPh_2(C_6H_4)_3PPh_2)]$ (**9**)	270, 340	355, 370, 390, 410, 435*	275, 355	355, 375, 390, 410, 435* 510, 545, 590*
$PPh_2(C_6H_4)_4PPh_2$	280, 317, 360	387	270, 370	390, 436*
$[(AuCl)_2(PPh_2(C_6H_4)_4PPh_2)]$ (**4**)	308, 355	385	330	385
$[\{Au(C_6F_5)\}_2(PPh_2(C_6H_4)_4PPh_2)]$ (**10**)	270, 360	385	295, 360	390
$PPh_2(C_6H_4)_5PPh_2$	275, 325, 367	393	277, 380	390, 415, 440[a]
$[(AuCl)_2(PPh_2(C_6H_4)_5PPh_2)]$ (**5**)	270, 370	395	303, 375	390, 405, 428*
$[\{Au(C_6F_5)\}_2(PPh_2(C_6H_4)_5PPh_2)]$ (**11**)	275, 367	395	280, 375	390, 410, 430*
$[(AuCl)_2(PPh_2C{\equiv}CC_6H_4C{\equiv}CPPh_2)]$ (**6**)	352	378, 394, 409, 432[a]	273, 335	490, 525*
$[\{Au(C_6F_5)\}_2(PPh_2C{\equiv}CC_6H_4C{\equiv}CPPh_2)]$ (**12**)	353	377, 394, 409, 431*	326	489, 520*

In the excitation spectra values separated by comma indicate more than one maximum of excitation for the same emission. In the emission spectra values separated by comma indicate a structured band. Values marked with * correspond to the most intense bands. When two emission maxima are observed the corresponding excitation and emission are in the same line. [a] From reference 9d cited in the manuscript.

THEORETICAL STUDIES

Figure SF9. Selection of frontier molecular orbitals incomplex 7.

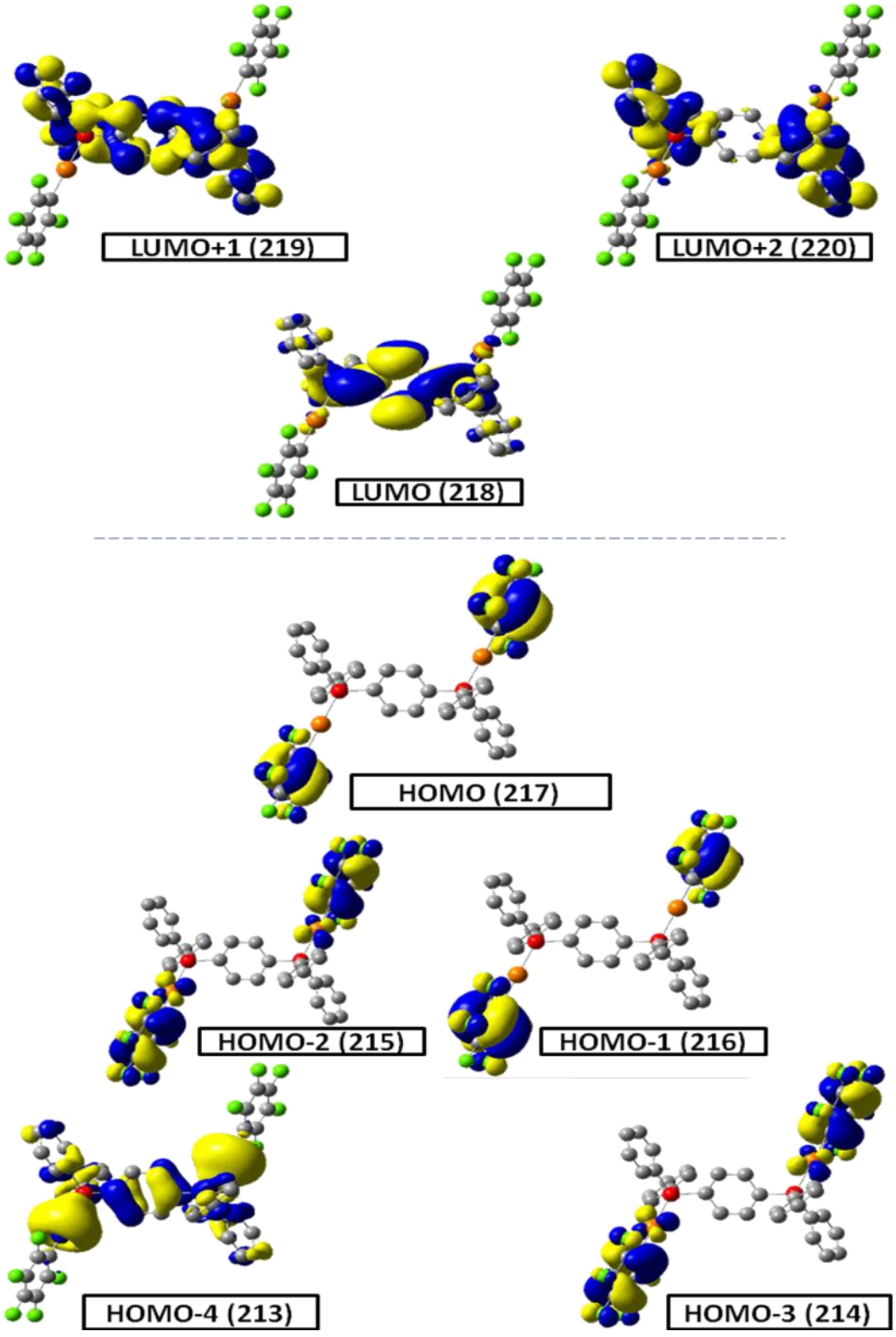
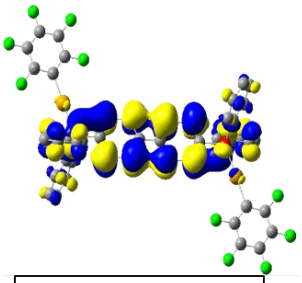


Figure SF8. Selection of frontier molecular orbitals incomplex 8.



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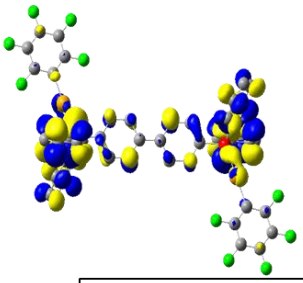

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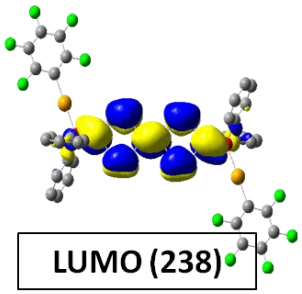

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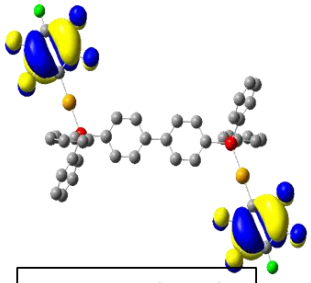

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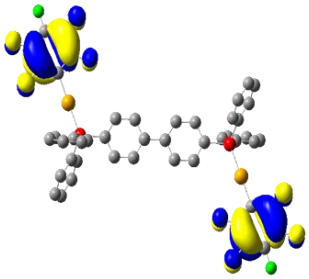

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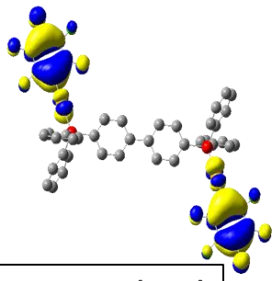

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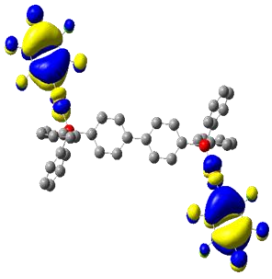

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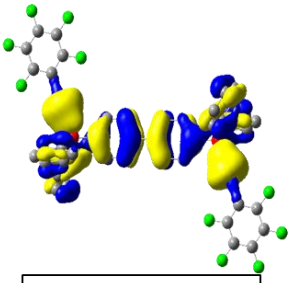

HOMO-4 (233)