

ELECTRONIC SUPPLEMENTARY INFORMATION

Cyclometalated Pt(IV) trans-diiodo adducts: experimental and computational studies within an homologous series of compounds

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PHOTOPHYSICS

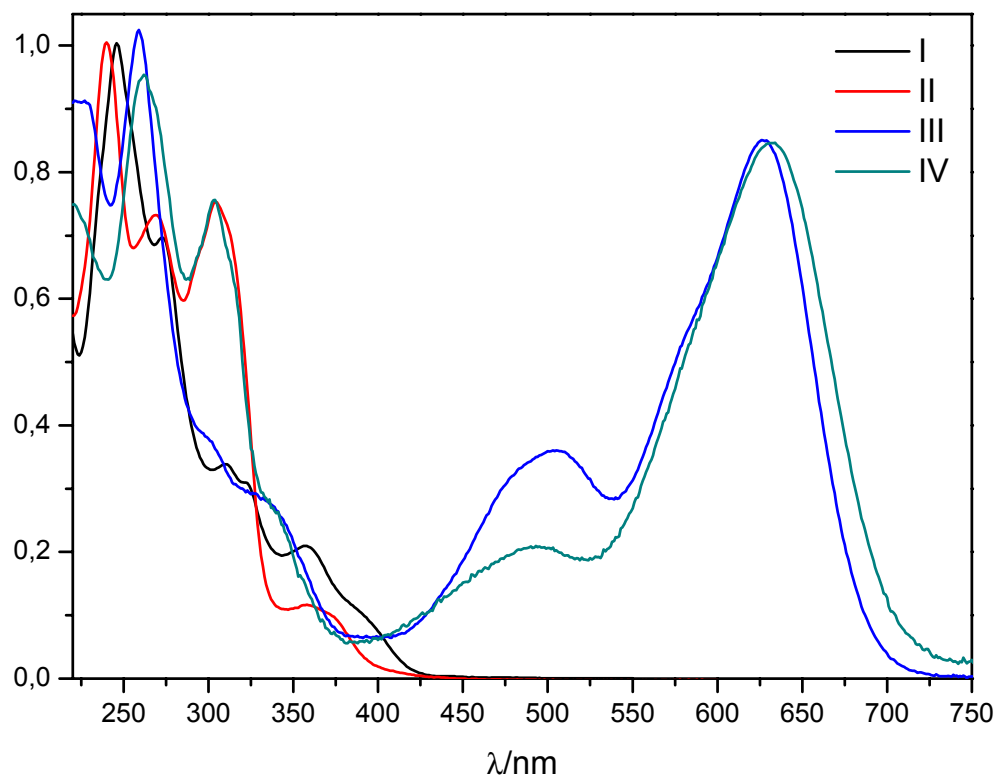


Fig. S1. Absorption spectra of Pt(II) compounds **I-IV** in acetonitrile solution.

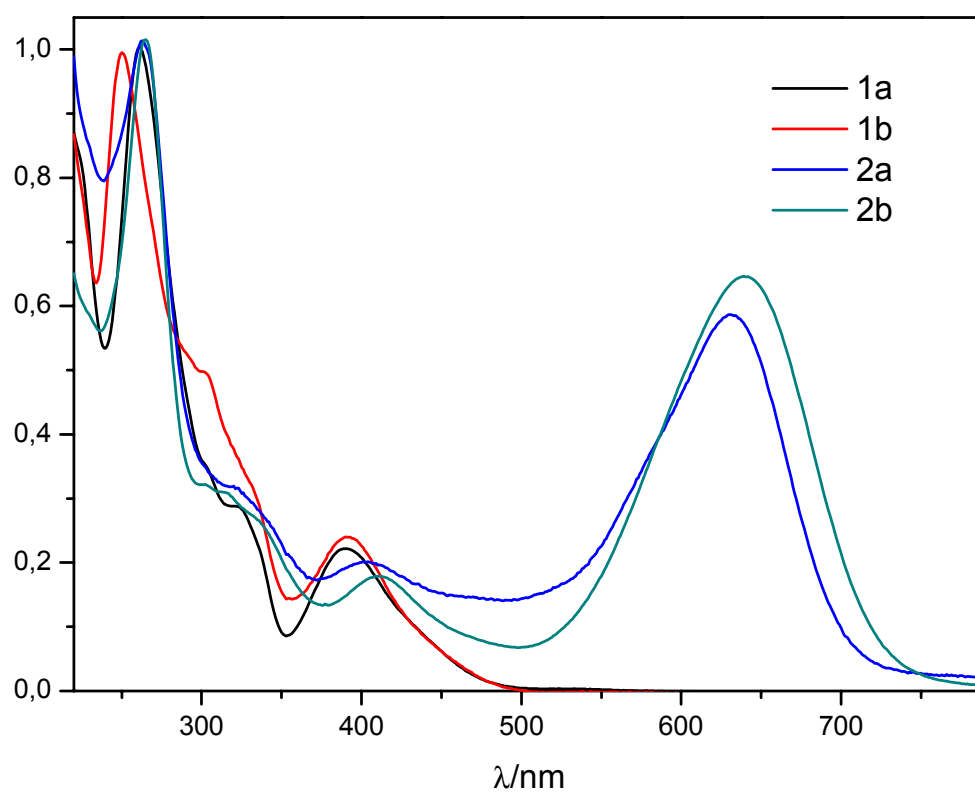


Fig. S2. Absorption spectra of Pt(IV) compounds **1a,b** and **2a,b** in acetonitrile solution.

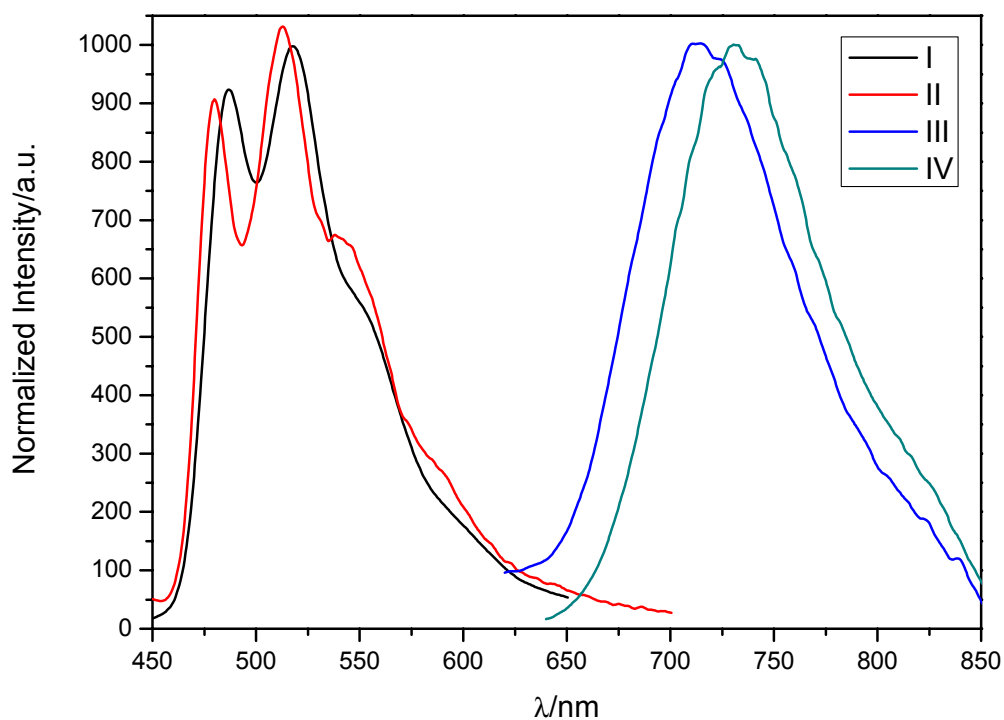


Fig. S3. Emission spectra of Pt(II) compounds **I-IV** in degassed acetonitrile solution at room temperature.

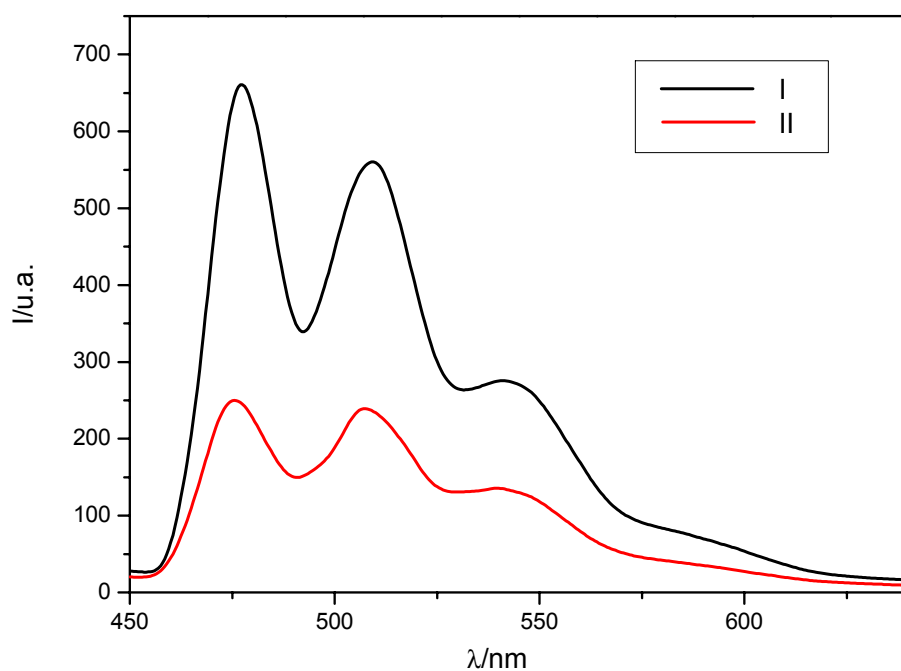


Fig. S4. Emission spectra of Pt(II) compounds **I** and **II** recorded in acetonitrile matrix at 77°K.

Table S1. Photophysical data in acetonitrile matrix at 77°K. Asterisk indicates a shoulder

Compounds	λ_{em}/nm	$\tau/\mu s$
I	475, 510, 545, 575*	7.3
II	475, 510, 540, 575*	1.7

Computational Results

In this section, a detailed presentation of the computational results is reported for all the studied compounds. All the computations have been performed with the MPW1PW91 xc functional, the SDD pseudopotential on the Pt and I atoms, SDD basis set on Pt and I and D95V(d) on the other atoms. The iodine basis set has been augmented with one d-type polarization function consisting in a single gaussian function with 0.302 exponent.

[(PhPy)Pt(acac)I₂], 1a

Table S2. Singlet excited states of **1a**. The computations have been performed by modelling the solvent effects with the PCM model on the structure optimized in vacuum. The following text lists the energy (in eV and nm), the oscillator strengths and percentage composition of the most important mono-electronic excitations for each excited state. Excited States composition has been expressed in two ways. The first one uses the Kohn-Sham orbital numerical label of the occupied and virtual orbital as produced by the computation (for instance, 119 → 120 for the HOMO → LUMO transition when the HOMO is the 119th orbital and the LUMO is the 120th one). The second way assigns the “0” label to the HOMO, the “-1” label to the HOMO-1 orbital and so on, the “0” label to the LUMO, “1” to LUMO+1 and so on (thus, 0 → 0 is the HOMO → LUMO transition, -2 → 1 is the HOMO-2 → LUMO+1 transition).

Excited State: 1				74 → 84	59.54 %	-9 → 0	
2.4793 eV	500.08 nm	19997.cm-1	f=0.0070	80 → 85	5.72 %	-3 → 1	
80 → 84	18.55 %	-3 → 0		81 → 85	3.14 %	-2 → 1	
82 → 84	35.13 %	-1 → 0		82 → 85	12.35 %	-1 → 1	
83 → 84	35.59 %	0 → 0		83 → 85	7.43 %	0 → 1	
Excited State: 2				Excited State: 11			
2.5412 eV	487.89 nm	20496.cm-1	f=0.0003	4.0680 eV	304.78 nm	32811.cm-1	f=0.1314
79 → 84	5.99 %	-4 → 0		70 → 84	3.34 %	-13 → 0	
81 → 84	80.72 %	-2 → 0		72 → 84	18.02 %	-11 → 0	
83 → 84	3.34 %	0 → 0		73 → 84	37.37 %	-10 → 0	
Excited State: 3				76 → 84	23.97 %	-7 → 0	
2.6447 eV	468.80 nm	21331.cm-1	f=0.0011	83 → 84	2.51 %	0 → 0	
80 → 84	9.56 %	-3 → 0		Excited State: 12			
81 → 84	2.71 %	-2 → 0		4.0768 eV	304.12 nm	32882.cm-1	f=0.0149
82 → 84	60.23 %	-1 → 0		80 → 85	4.71 %	-3 → 1	
83 → 84	23.30 %	0 → 0		81 → 85	61.59 %	-2 → 1	
Excited State: 4				82 → 85	27.50 %	-1 → 1	
2.8046 eV	442.07 nm	22621.cm-1	f=0.0308	Excited State: 13			
76 → 84	3.91 %	-7 → 0		4.0965 eV	302.66 nm	33040.cm-1	f=0.0543
80 → 84	63.35 %	-3 → 0		74 → 84	19.75 %	-9 → 0	
83 → 84	27.55 %	0 → 0		80 → 85	7.85 %	-3 → 1	
Excited State: 5				81 → 85	29.76 %	-2 → 1	
2.9082 eV	426.32 nm	23457.cm-1	f=0.0002	82 → 85	26.91 %	-1 → 1	
78 → 84	93.76 %	-5 → 0		83 → 85	4.18 %	0 → 1	
Excited State: 6				Excited State: 14			
3.0019 eV	413.01 nm	24212.cm-1	f=0.0011	4.2358 eV	292.71 nm	34164.cm-1	f=0.0035
77 → 84	93.33 %	-6 → 0		80 → 85	78.41 %	-3 → 1	
Excited State: 7				82 → 85	14.80 %	-1 → 1	
3.1687 eV	391.28 nm	25557.cm-1	f=0.0263	83 → 85	4.58 %	0 → 1	
76 → 84	4.50 %	-7 → 0		Excited State: 15			
79 → 84	84.47 %	-4 → 0		4.3703 eV	283.69 nm	35250.cm-1	f=0.0179
81 → 84	7.38 %	-2 → 0		78 → 85	92.87 %	-5 → 1	
Excited State: 8				Excited State: 16			
3.8314 eV	323.60 nm	30902.cm-1	f=0.0071	4.3753 eV	283.37 nm	35290.cm-1	f=0.1338
75 → 84	83.79 %	-8 → 0		79 → 85	78.16 %	-4 → 1	
82 → 85	2.77 %	-1 → 1		82 → 87	2.41 %	-1 → 3	
83 → 85	9.04 %	0 → 1		83 → 87	4.15 %	0 → 3	
Excited State: 9				Excited State: 17			
3.9753 eV	311.88 nm	32064.cm-1	f=0.0907	4.4330 eV	279.68 nm	35755.cm-1	f=0.2109
74 → 84	2.03 %	-9 → 0		72 → 84	3.49 %	-11 → 0	
75 → 84	11.10 %	-8 → 0		73 → 84	2.61 %	-10 → 0	
82 → 85	10.25 %	-1 → 1		76 → 84	20.65 %	-7 → 0	
83 → 85	67.44 %	0 → 1		78 → 85	4.89 %	-5 → 1	
Excited State: 10				82 → 88	11.91 %	-1 → 4	
4.0512 eV	306.04 nm	32675.cm-1	f=0.0065	83 → 88	44.20 %	0 → 4	
71 → 84	3.26 %	-12 → 0		Excited State: 18			
				4.4484 eV	278.72 nm	35878.cm-1	f=0.0002

77 -> 85 97.98 % -6 -> 1

Excited State: 19

4.4594 eV 278.03 nm 35967.cm-1 f=0.0163

71 -> 84 2.24 % -12 -> 0

80 -> 86 9.13 % -3 -> 2

81 -> 86 2.89 % -2 -> 2

82 -> 86 8.22 % -1 -> 2

83 -> 86 65.36 % 0 -> 2

Excited State: 20

4.4894 eV 276.17 nm 36210.cm-1 f=0.0612

72 -> 84 4.42 % -11 -> 0

76 -> 84 3.20 % -7 -> 0

79 -> 88 6.24 % -4 -> 4

80 -> 88 2.60 % -3 -> 4

81 -> 88 12.24 % -2 -> 4

82 -> 88 56.13 % -1 -> 4

83 -> 88 4.93 % 0 -> 4

Excited State: 21

4.5210 eV 274.24 nm 36464.cm-1 f=0.0077

81 -> 86 59.70 % -2 -> 2

82 -> 86 31.22 % -1 -> 2

Excited State: 22

4.5962 eV 269.76 nm 37070.cm-1 f=0.2034

73 -> 84 12.68 % -10 -> 0

76 -> 84 9.34 % -7 -> 0

78 -> 86 3.77 % -5 -> 2

81 -> 88 33.64 % -2 -> 4

82 -> 88 6.27 % -1 -> 4

83 -> 88 19.98 % 0 -> 4

Excited State: 23

4.6001 eV 269.52 nm 37103.cm-1 f=0.0639

71 -> 84 4.04 % -12 -> 0

80 -> 86 27.13 % -3 -> 2

81 -> 86 21.93 % -2 -> 2

82 -> 86 25.70 % -1 -> 2

83 -> 86 5.94 % 0 -> 2

83 -> 87 2.20 % 0 -> 3

Excited State: 24

4.6584 eV 266.15 nm 37573.cm-1 f=0.0320

79 -> 85 3.10 % -4 -> 1

80 -> 86 45.90 % -3 -> 2

81 -> 86 3.44 % -2 -> 2

82 -> 86 4.92 % -1 -> 2

82 -> 87 4.07 % -1 -> 3

83 -> 86 12.74 % 0 -> 2

83 -> 87 16.69 % 0 -> 3

Excited State: 25

4.6613 eV 265.99 nm 37595.cm-1 f=0.0001

75 -> 86 11.92 % -8 -> 2

78 -> 86 69.22 % -5 -> 2

78 -> 87 3.58 % -5 -> 3

81 -> 88 5.62 % -2 -> 4

82 -> 88 5.13 % -1 -> 4

Excited State: 26

4.6992 eV 263.84 nm 37902.cm-1 f=0.0172

72 -> 84 59.34 % -11 -> 0

73 -> 84 24.45 % -10 -> 0

83 -> 88 6.98 % 0 -> 4

Excited State: 27

4.7189 eV 262.74 nm 38060.cm-1 f=0.0322

79 -> 85 2.51 % -4 -> 1

80 -> 86 10.58 % -3 -> 2

81 -> 86 5.59 % -2 -> 2

82 -> 86 10.16 % -1 -> 2

82 -> 87 5.65 % -1 -> 3

83 -> 86 3.51 % 0 -> 2

83 -> 87 57.68 % 0 -> 3

Excited State: 28

4.7497 eV 261.04 nm 38308.cm-1 f=0.3352

72 -> 84 2.27 % -11 -> 0

73 -> 84 10.22 % -10 -> 0

76 -> 84 10.48 % -7 -> 0

78 -> 86 2.39 % -5 -> 2

79 -> 88 3.59 % -4 -> 4

80 -> 88 3.47 % -3 -> 4

81 -> 88 24.96 % -2 -> 4

82 -> 88 10.22 % -1 -> 4

83 -> 88 18.86 % 0 -> 4

Excited State: 29

4.7872 eV 258.99 nm 38612.cm-1 f=0.0002

80 -> 87 12.83 % -3 -> 3

81 -> 87 13.91 % -2 -> 3

82 -> 87 60.60 % -1 -> 3

83 -> 87 8.16 % 0 -> 3

Excited State: 30

4.8078 eV 257.88 nm 38778.cm-1 f=0.0180

80 -> 88 86.87 % -3 -> 4

81 -> 88 7.21 % -2 -> 4

Excited State: 31

4.8109 eV 257.71 nm 38803.cm-1 f=0.0387

76 -> 85 2.45 % -7 -> 1

80 -> 87 2.73 % -3 -> 3

81 -> 87 78.29 % -2 -> 3

82 -> 87 7.46 % -1 -> 3

Excited State: 32

4.8882 eV 253.64 nm 39426.cm-1 f=0.0191

77 -> 86 94.54 % -6 -> 2

Excited State: 33

4.9375 eV 251.11 nm 39823.cm-1 f=0.0013

80 -> 86 2.58 % -3 -> 2

80 -> 87 77.83 % -3 -> 3

82 -> 87 12.15 % -1 -> 3

83 -> 87 2.47 % 0 -> 3

Excited State: 34

4.9909 eV 248.42 nm 40254.cm-1 f=0.0070

79 -> 86 75.75 % -4 -> 2

79 -> 87 13.03 % -4 -> 3

81 -> 86 2.40 % -2 -> 2

Excited State: 35

5.0440 eV 245.81 nm 40682.cm-1 f=0.0152

79 -> 88 84.48 % -4 -> 4

80 -> 88 3.45 % -3 -> 4

81 -> 88 7.05 % -2 -> 4

Excited State: 36

5.0799 eV 244.07 nm 40972.cm-1 f=0.0450

71 -> 84 60.35 % -12 -> 0

74 -> 84 6.45 % -9 -> 0

77 -> 88 19.37 % -6 -> 4

Excited State: 37

5.0893 eV 243.62 nm 41048.cm-1 f=0.0098

75 -> 86 5.76 % -8 -> 2

78 -> 86 11.29 % -5 -> 2

78 -> 87 79.79 % -5 -> 3

Excited State: 38

5.0983 eV 243.19 nm 41120.cm-1 f=0.0039

76 -> 85 12.19 % -7 -> 1

78 -> 88 8.68 % -5 -> 4

79 -> 86 12.14 % -4 -> 2

79 -> 87 59.97 % -4 -> 3

Excited State: 39

5.1162 eV 242.34 nm 41264.cm-1 f=0.0402

71 -> 84 2.85 % -12 -> 0

78 -> 88 82.72 % -5 -> 4

79 -> 86 2.57 % -4 -> 2
79 -> 87 5.63 % -4 -> 3

Excited State: 40

5.1224 eV 242.04 nm 41315.cm-1 f=0.0068
59 -> 84 3.27 % -24 -> 0
68 -> 84 2.85 % -15 -> 0
70 -> 84 84.08 % -13 -> 0

Excited State: 41

5.1652 eV 240.04 nm 41660.cm-1 f=0.0015
75 -> 86 3.96 % -8 -> 2
77 -> 86 2.23 % -6 -> 2
77 -> 87 89.68 % -6 -> 3

Excited State: 42

5.1798 eV 239.36 nm 41778.cm-1 f=0.0768
71 -> 84 10.85 % -12 -> 0
76 -> 85 2.14 % -7 -> 1
77 -> 88 75.50 % -6 -> 4

Excited State: 43

5.1853 eV 239.11 nm 41822.cm-1 f=0.0112
75 -> 85 12.94 % -8 -> 1
75 -> 86 50.11 % -8 -> 2
75 -> 87 4.16 % -8 -> 3
77 -> 87 7.64 % -6 -> 3
78 -> 86 8.61 % -5 -> 2
78 -> 87 12.90 % -5 -> 3

Excited State: 44

5.2231 eV 237.37 nm 42128.cm-1 f=0.0464
76 -> 85 72.17 % -7 -> 1
77 -> 88 2.80 % -6 -> 4
79 -> 87 12.13 % -4 -> 3

Excited State: 45

5.2771 eV 234.95 nm 42562.cm-1 f=0.0002
75 -> 85 82.67 % -8 -> 1

75 -> 86 11.86 % -8 -> 2

Excited State: 46

5.5969 eV 221.52 nm 45143.cm-1 f=0.0058
67 -> 88 4.02 % -16 -> 4
71 -> 88 10.80 % -12 -> 4
74 -> 88 64.03 % -9 -> 4
76 -> 86 12.88 % -7 -> 2

Excited State: 47

5.6392 eV 219.86 nm 45483.cm-1 f=0.0232
68 -> 84 51.37 % -15 -> 0
70 -> 84 2.37 % -13 -> 0
72 -> 84 4.60 % -11 -> 0
73 -> 84 2.60 % -10 -> 0
76 -> 88 30.96 % -7 -> 4

Excited State: 48

5.6566 eV 219.18 nm 45625.cm-1 f=0.0010
69 -> 84 69.72 % -14 -> 0
74 -> 88 3.22 % -9 -> 4
76 -> 86 18.94 % -7 -> 2

Excited State: 49

5.6724 eV 218.57 nm 45752.cm-1 f=0.0178
69 -> 84 22.75 % -14 -> 0
71 -> 88 2.10 % -12 -> 4
73 -> 85 5.45 % -10 -> 1
74 -> 88 4.18 % -9 -> 4
76 -> 86 53.35 % -7 -> 2

Excited State: 50

5.6775 eV 218.38 nm 45792.cm-1 f=0.0004
74 -> 85 36.95 % -9 -> 1
74 -> 86 49.79 % -9 -> 2
74 -> 87 3.94 % -9 -> 3
76 -> 88 2.33 % -7 -> 4

Table S3. Singlet excited states of **1a**. The computations have been made in vacuum.

Excited State: 1

2.3556 eV 526.34 nm 18999.cm-1 f=0.0004
78 -> 84 2.25 % -5 -> 0
82 -> 84 5.96 % -1 -> 0
83 -> 84 81.76 % 0 -> 0

Excited State: 2

2.3827 eV 520.34 nm 19218.cm-1 f=0.0011
82 -> 84 84.38 % -1 -> 0
83 -> 84 5.21 % 0 -> 0

Excited State: 3

2.7233 eV 455.28 nm 21965.cm-1 f=0.0001
81 -> 84 92.59 % -2 -> 0

Excited State: 4

2.8147 eV 440.49 nm 22702.cm-1 f=0.0007
79 -> 84 92.31 % -4 -> 0

Excited State: 5

2.8587 eV 433.70 nm 23057.cm-1 f=0.0055
77 -> 84 2.46 % -6 -> 0
78 -> 84 47.26 % -5 -> 0
80 -> 84 46.24 % -3 -> 0

Excited State: 6

3.0484 eV 406.72 nm 24587.cm-1 f=0.0355
76 -> 84 10.90 % -7 -> 0
77 -> 84 3.73 % -6 -> 0
78 -> 84 42.09 % -5 -> 0
80 -> 84 34.95 % -3 -> 0
83 -> 84 3.04 % 0 -> 0

Excited State: 7

3.3934 eV 365.37 nm 27370.cm-1 f=0.0015
83 -> 85 98.67 % 0 -> 1

Excited State: 8

3.4513 eV 359.23 nm 27837.cm-1 f=0.0021
82 -> 85 98.56 % -1 -> 1

Excited State: 9

3.4992 eV 354.33 nm 28222.cm-1 f=0.0213
76 -> 84 8.63 % -7 -> 0
77 -> 84 86.51 % -6 -> 0

Excited State: 10

3.7219 eV 333.12 nm 30019.cm-1 f=0.0001
81 -> 85 99.21 % -2 -> 1

Excited State: 11

3.7864 eV 327.45 nm 30539.cm-1 f=0.0002
79 -> 85 99.42 % -4 -> 1

Excited State: 12

3.8190 eV 324.65 nm 30802.cm-1 f=0.0453
78 -> 85 39.11 % -5 -> 1
80 -> 85 51.43 % -3 -> 1

Excited State: 13

3.9049 eV 317.51 nm 31495.cm-1 f=0.0232
78 -> 85 46.20 % -5 -> 1
80 -> 85 46.75 % -3 -> 1

Excited State: 14
 3.9714 eV 312.20 nm 32031.cm-1 f=0.0022
 83 -> 86 89.64 % 0 -> 2
 83 -> 87 8.35 % 0 -> 3

Excited State: 15
 4.0242 eV 308.10 nm 32457.cm-1 f=0.0022
 82 -> 86 89.44 % -1 -> 2
 82 -> 87 7.29 % -1 -> 3

Excited State: 16
 4.0897 eV 303.16 nm 32986.cm-1 f=0.0034
 75 -> 84 78.71 % -8 -> 0
 77 -> 85 3.33 % -6 -> 1
 80 -> 87 3.87 % -3 -> 3
 82 -> 86 2.16 % -1 -> 2
 83 -> 87 3.87 % 0 -> 3

Excited State: 17
 4.0970 eV 302.63 nm 33044.cm-1 f=0.0000
 75 -> 84 4.23 % -8 -> 0
 83 -> 86 7.90 % 0 -> 2
 83 -> 87 85.27 % 0 -> 3

Excited State: 18
 4.1628 eV 297.84 nm 33575.cm-1 f=0.0010
 82 -> 86 6.16 % -1 -> 2
 82 -> 87 89.22 % -1 -> 3

Excited State: 19
 4.1942 eV 295.61 nm 33828.cm-1 f=0.0495
 73 -> 84 6.66 % -10 -> 0
 76 -> 84 13.84 % -7 -> 0
 82 -> 88 4.51 % -1 -> 4
 83 -> 88 64.26 % 0 -> 4

Excited State: 20
 4.2445 eV 292.10 nm 34235.cm-1 f=0.0111
 73 -> 84 11.26 % -10 -> 0
 78 -> 88 2.32 % -5 -> 4
 81 -> 86 16.14 % -2 -> 2
 81 -> 87 7.96 % -2 -> 3
 82 -> 88 37.65 % -1 -> 4
 83 -> 88 14.62 % 0 -> 4

Excited State: 21
 4.2549 eV 291.39 nm 34318.cm-1 f=0.0341
 71 -> 84 2.46 % -12 -> 0
 74 -> 84 65.39 % -9 -> 0
 75 -> 84 2.81 % -8 -> 0
 77 -> 85 10.03 % -6 -> 1
 80 -> 86 4.38 % -3 -> 2
 80 -> 87 3.49 % -3 -> 3

Excited State: 22
 4.2642 eV 290.76 nm 34393.cm-1 f=0.0006
 73 -> 84 3.43 % -10 -> 0
 81 -> 86 50.66 % -2 -> 2
 81 -> 87 18.51 % -2 -> 3
 82 -> 88 22.01 % -1 -> 4

Excited State: 23
 4.2724 eV 290.20 nm 34459.cm-1 f=0.0772
 74 -> 84 10.60 % -9 -> 0
 77 -> 85 58.74 % -6 -> 1
 78 -> 86 10.04 % -5 -> 2
 80 -> 87 2.83 % -3 -> 3

Excited State: 24
 4.3565 eV 284.60 nm 35137.cm-1 f=0.0051
 79 -> 86 84.64 % -4 -> 2
 79 -> 87 8.89 % -4 -> 3
 81 -> 87 2.19 % -2 -> 3

Excited State: 25
 4.3940 eV 282.17 nm 35440.cm-1 f=0.0073
 79 -> 86 2.40 % -4 -> 2

81 -> 86 30.04 % -2 -> 2
 81 -> 87 60.22 % -2 -> 3
 82 -> 88 2.06 % -1 -> 4

Excited State: 26
 4.4036 eV 281.55 nm 35518.cm-1 f=0.0028
 74 -> 84 3.54 % -9 -> 0
 77 -> 85 4.21 % -6 -> 1
 78 -> 86 10.83 % -5 -> 2
 80 -> 86 70.79 % -3 -> 2

Excited State: 27
 4.4074 eV 281.31 nm 35548.cm-1 f=0.0907
 72 -> 84 2.11 % -11 -> 0
 73 -> 84 28.96 % -10 -> 0
 76 -> 84 8.60 % -7 -> 0
 78 -> 88 5.27 % -5 -> 4
 79 -> 86 5.43 % -4 -> 2
 80 -> 88 3.88 % -3 -> 4
 81 -> 87 5.96 % -2 -> 3
 82 -> 88 21.82 % -1 -> 4
 83 -> 88 5.43 % 0 -> 4

Excited State: 28
 4.4784 eV 276.85 nm 36121.cm-1 f=0.1009
 71 -> 84 2.22 % -12 -> 0
 74 -> 84 3.31 % -9 -> 0
 75 -> 84 3.59 % -8 -> 0
 76 -> 85 3.43 % -7 -> 1
 77 -> 85 5.41 % -6 -> 1
 78 -> 86 50.39 % -5 -> 2
 79 -> 88 2.69 % -4 -> 4
 80 -> 86 3.53 % -3 -> 2
 80 -> 87 10.30 % -3 -> 3
 81 -> 88 3.84 % -2 -> 4

Excited State: 29
 4.4910 eV 276.07 nm 36223.cm-1 f=0.0022
 73 -> 84 5.35 % -10 -> 0
 79 -> 86 6.79 % -4 -> 2
 79 -> 87 80.35 % -4 -> 3
 82 -> 88 2.45 % -1 -> 4

Excited State: 30
 4.5267 eV 273.89 nm 36511.cm-1 f=0.0364
 73 -> 84 9.68 % -10 -> 0
 76 -> 84 4.82 % -7 -> 0
 78 -> 88 27.79 % -5 -> 4
 79 -> 87 7.60 % -4 -> 3
 80 -> 88 36.62 % -3 -> 4
 82 -> 88 4.99 % -1 -> 4

Excited State: 31
 4.5484 eV 272.59 nm 36685.cm-1 f=0.0020
 78 -> 86 14.65 % -5 -> 2
 80 -> 86 16.43 % -3 -> 2
 80 -> 87 52.62 % -3 -> 3
 81 -> 88 4.73 % -2 -> 4

Excited State: 32
 4.5682 eV 271.41 nm 36845.cm-1 f=0.0002
 78 -> 88 47.16 % -5 -> 4
 80 -> 88 41.38 % -3 -> 4
 83 -> 88 4.68 % 0 -> 4

Excited State: 33
 4.6796 eV 264.95 nm 37743.cm-1 f=0.0187
 78 -> 87 31.34 % -5 -> 3
 80 -> 87 4.40 % -3 -> 3
 81 -> 88 57.86 % -2 -> 4

Excited State: 34
 4.7144 eV 262.99 nm 38024.cm-1 f=0.0002
 78 -> 87 33.59 % -5 -> 3
 79 -> 88 39.07 % -4 -> 4
 81 -> 88 22.26 % -2 -> 4

Excited State: 35
 4.7482 eV 261.12 nm 38297.cm-1 f=0.0037
 76 -> 85 45.33 % -7 -> 1
 77 -> 86 41.16 % -6 -> 2
 78 -> 86 2.99 % -5 -> 2
 79 -> 88 3.38 % -4 -> 4

Excited State: 36
 4.7697 eV 259.94 nm 38470.cm-1 f=0.0220
 77 -> 86 2.66 % -6 -> 2
 78 -> 87 24.63 % -5 -> 3
 79 -> 88 51.52 % -4 -> 4
 80 -> 87 3.37 % -3 -> 3
 81 -> 88 7.46 % -2 -> 4

Excited State: 37
 4.7799 eV 259.39 nm 38552.cm-1 f=0.5829
 68 -> 84 2.81 % -15 -> 0
 73 -> 84 10.10 % -10 -> 0
 76 -> 84 30.83 % -7 -> 0
 77 -> 84 2.23 % -6 -> 0
 78 -> 88 7.47 % -5 -> 4

80 -> 88 11.39 % -3 -> 4
 83 -> 88 6.93 % 0 -> 4

Excited State: 38
 4.8815 eV 253.99 nm 39372.cm-1 f=0.0779
 76 -> 85 40.86 % -7 -> 1
 77 -> 86 43.45 % -6 -> 2
 78 -> 86 2.26 % -5 -> 2

Excited State: 39
 5.0364 eV 246.18 nm 40621.cm-1 f=0.0038
 75 -> 85 70.61 % -8 -> 1
 75 -> 86 4.38 % -8 -> 2
 75 -> 87 20.24 % -8 -> 3

Excited State: 40
 5.1006 eV 243.08 nm 41139.cm-1 f=0.0028
 72 -> 84 26.44 % -11 -> 0
 73 -> 84 3.37 % -10 -> 0
 77 -> 88 61.39 % -6 -> 4

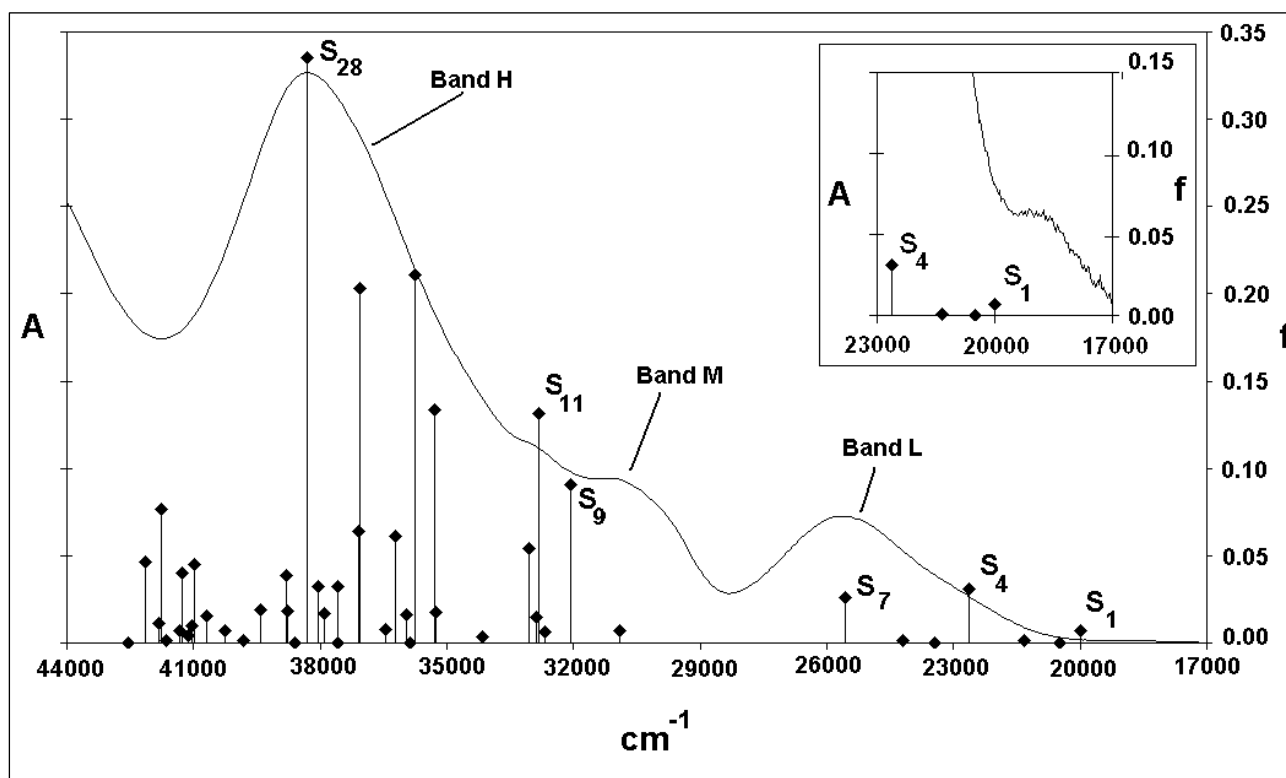


Fig. S5. The following figure compares the **1a** experimental spectrum recorded in acetonitrile and the computed electronic transitions listed above. The insert shows the first experimental band assigned by us to the S_1 excited state.

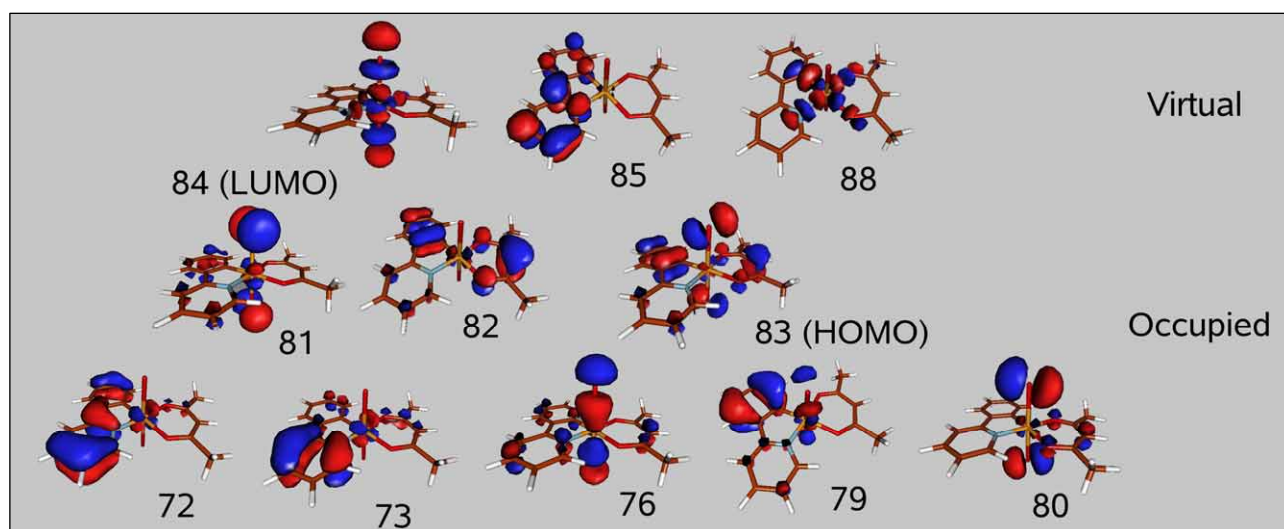


Fig. S6. In the following picture, some **1a** Kohn-Sham orbitals are reported that are relevant in describing the low-energy electronic transitions toward S_1 , S_4 , S_7 , S_9 , S_{11} and S_{28} .

Table S4. Optimized structure of **1a**. Cartesian coordinates in angstrom.

C	-3.457824	0.000091	3.018648	H	-4.563048	-0.000679	-3.437450
C	-3.653550	-0.000071	1.644169	H	-2.333064	-0.000609	-4.534478
C	-2.549608	-0.000100	0.784104	H	-0.257148	-0.000308	-3.166637
N	-1.299726	0.000048	1.315565	O	1.604829	0.000003	-1.489363
C	-1.094542	0.000193	2.638973	C	2.962815	0.000543	1.234994
C	-2.156152	0.000220	3.530370	C	3.541222	0.000307	-0.052565
C	-2.581517	-0.000255	-0.672130	C	2.871372	0.000167	-1.279145
C	-3.752225	-0.000423	-1.445047	C	3.668610	-0.000349	-2.556620
H	-4.731009	-0.000448	-0.971410	C	3.868110	0.000299	2.439979
H	-4.654628	-0.000168	1.227180	H	4.623367	0.000144	-0.098640
C	-3.660147	-0.000550	-2.832732	H	4.743842	-0.000597	-2.370381
C	-2.401870	-0.000509	-3.448949	H	3.401136	-0.883961	-3.145101
C	-1.231264	-0.000338	-2.687137	H	3.401601	0.883158	-3.145464
C	-1.320743	-0.000214	-1.299562	H	4.925799	0.000199	2.170401
Pt	0.216387	0.000027	-0.020992	H	3.649583	0.883766	3.048827
O	1.722254	0.000299	1.496921	H	3.649405	-0.883213	3.048711
H	-0.056886	0.000291	2.955242	I	0.243236	-2.703237	-0.014889
H	-1.959640	0.000344	4.597209	I	0.242800	2.703294	-0.015385
H	-4.312150	0.000120	3.690399				

[(PhPy)Pt(hfacac)I₂], 1b

Table S5. Singlet excited states of **1b**. The computations have been performed by modelling the solvent effects with the PCM model on the structure optimized in vacuum. The following text lists the energy (in eV and nm), the oscillator strengths and percentage composition of the most important mono-electronic excitations for each excited state. Excited States composition has been expressed in two ways. The first one uses the Kohn-Sham orbital numerical label of the occupied and virtual orbital as produced by the computation (for instance, 119 → 120 for the HOMO → LUMO transition when the HOMO is the 119th orbital and the LUMO is the 120th one). The second way assigns the “0” label to the HOMO, the “-1” label to the HOMO-1 orbital and so on, the “0” label to the LUMO, “1” to LUMO+1 and so on (thus, 0 → 0 is the HOMO → LUMO transition, -2 → 1 is the HOMO-2 → LUMO+1 transition).

Excited State: 1				102 → 109	5.02 %	-5 → 1	
2.4376 eV	508.62 nm	19661.cm-1	f=0.0000	103 → 109	92.27 %	-4 → 1	
104 → 108	4.16 %	-3 → 0					
105 → 108	2.47 %	-2 → 0					
106 → 108	82.76 %	-1 → 0					
Excited State: 2				Excited State: 12			
2.4687 eV	502.21 nm	19912.cm-1	f=0.0030	3.7106 eV	334.14 nm	29928.cm-1	f=0.0000
104 → 108	2.23 %	-3 → 0		102 → 109	94.55 %	-5 → 1	
105 → 108	57.11 %	-2 → 0		103 → 109	4.84 %	-4 → 1	
107 → 108	31.84 %	0 → 0					
Excited State: 3				Excited State: 13			
2.6238 eV	472.54 nm	21162.cm-1	f=0.0092	3.8182 eV	324.72 nm	30796.cm-1	f=0.0003
101 → 108	3.91 %	-6 → 0		101 → 109	2.58 %	-6 → 1	
105 → 108	29.52 %	-2 → 0		104 → 109	88.00 %	-3 → 1	
106 → 108	3.36 %	-1 → 0		106 → 109	4.40 %	-1 → 1	
107 → 108	58.93 %	0 → 0					
Excited State: 4				Excited State: 14			
2.8495 eV	435.11 nm	22983.cm-1	f=0.0002	3.9616 eV	312.97 nm	31952.cm-1	f=0.1235
103 → 108	93.28 %	-4 → 0		98 → 108	2.88 %	-9 → 0	
Excited State: 5				101 → 109	8.51 %	-6 → 1	
2.9088 eV	426.24 nm	23461.cm-1	f=0.0010	107 → 110	78.94 %	0 → 2	
102 → 108	93.06 %	-5 → 0					
Excited State: 6				Excited State: 15			
3.0288 eV	409.35 nm	24429.cm-1	f=0.0056	4.0242 eV	308.10 nm	32457.cm-1	f=0.0105
101 → 108	17.42 %	-6 → 0		98 → 108	3.57 %	-9 → 0	
104 → 108	71.19 %	-3 → 0		101 → 109	63.64 %	-6 → 1	
105 → 108	3.54 %	-2 → 0		104 → 109	3.42 %	-3 → 1	
106 → 108	5.92 %	-1 → 0		106 → 110	2.62 %	-1 → 2	
Excited State: 7				107 → 110	11.45 %	0 → 2	
3.2823 eV	377.73 nm	26474.cm-1	f=0.0769				
100 → 108	19.82 %	-7 → 0		Excited State: 16			
101 → 108	59.62 %	-6 → 0		4.0498 eV	306.15 nm	32664.cm-1	f=0.2156
104 → 108	12.69 %	-3 → 0		92 → 108	2.31 %	-15 → 0	
Excited State: 8				97 → 108	18.57 %	-10 → 0	
3.3094 eV	374.64 nm	26692.cm-1	f=0.0009	100 → 108	39.75 %	-7 → 0	
105 → 109	12.47 %	-2 → 1		101 → 108	7.11 %	-6 → 0	
106 → 109	34.07 %	-1 → 1		106 → 111	9.20 %	-1 → 3	
107 → 109	51.67 %	0 → 1		107 → 111	6.89 %	0 → 3	
Excited State: 9				Excited State: 17			
3.3634 eV	368.62 nm	27128.cm-1	f=0.0016	4.0731 eV	304.40 nm	32852.cm-1	f=0.0289
105 → 109	40.63 %	-2 → 1		101 → 109	2.04 %	-6 → 1	
106 → 109	50.32 %	-1 → 1		106 → 110	92.19 %	-1 → 2	
107 → 109	7.74 %	0 → 1					
Excited State: 10				Excited State: 18			
3.5191 eV	352.32 nm	28383.cm-1	f=0.0069	4.1498 eV	298.77 nm	33471.cm-1	f=0.0325
104 → 109	5.14 %	-3 → 1		105 → 110	93.60 %	-2 → 2	
105 → 109	44.46 %	-2 → 1					
106 → 109	10.46 %	-1 → 1		Excited State: 19			
107 → 109	39.19 %	0 → 1		4.1592 eV	298.10 nm	33546.cm-1	f=0.0014
Excited State: 11				104 → 111	7.67 %	-3 → 3	
3.6290 eV	341.65 nm	29270.cm-1	f=0.0000	105 → 111	6.54 %	-2 → 3	
				106 → 111	22.24 %	-1 → 3	
				107 → 111	56.95 %	0 → 3	
				Excited State: 20			
				4.2931 eV	288.80 nm	34626.cm-1	f=0.0107
				97 → 108	7.67 %	-10 → 0	
				104 → 111	4.16 %	-3 → 3	
				105 → 111	37.30 %	-2 → 3	
				106 → 111	16.63 %	-1 → 3	
				107 → 111	26.82 %	0 → 3	
				Excited State: 21			

4.3465 eV	285.25 nm	35057.cm-1	f=0.0461	4.7584 eV	260.56 nm	38379.cm-1	f=0.3041
96 -> 108	11.61 % -11 -> 0			92 -> 108	2.28 % -15 -> 0		
98 -> 108	26.52 % -9 -> 0			97 -> 108	23.17 % -10 -> 0		
104 -> 110	49.26 % -3 -> 2			100 -> 108	12.16 % -7 -> 0		
107 -> 112	2.08 % 0 -> 4			101 -> 111	41.39 % -6 -> 3		
107 -> 113	2.08 % 0 -> 5			105 -> 111	4.52 % -2 -> 3		
Excited State: 22				Excited State: 33			
4.3668 eV	283.92 nm	35221.cm-1	f=0.0358	4.7589 eV	260.53 nm	38383.cm-1	f=0.0130
97 -> 108	5.60 % -10 -> 0			100 -> 109	2.88 % -7 -> 1		
100 -> 108	3.48 % -7 -> 0			101 -> 110	31.40 % -6 -> 2		
105 -> 111	40.85 % -2 -> 3			102 -> 111	20.92 % -5 -> 3		
106 -> 111	40.83 % -1 -> 3			103 -> 111	24.22 % -4 -> 3		
Excited State: 23				Excited State: 34			
4.3788 eV	283.15 nm	35317.cm-1	f=0.0607	4.7708 eV	259.88 nm	38479.cm-1	f=0.0086
96 -> 108	41.65 % -11 -> 0			101 -> 110	41.36 % -6 -> 2		
98 -> 108	15.32 % -9 -> 0			102 -> 111	9.98 % -5 -> 3		
104 -> 110	29.13 % -3 -> 2			103 -> 111	35.83 % -4 -> 3		
107 -> 112	2.03 % 0 -> 4			106 -> 112	4.65 % -1 -> 4		
Excited State: 24				Excited State: 35			
4.4168 eV	280.71 nm	35624.cm-1	f=0.0330	4.8108 eV	257.72 nm	38802.cm-1	f=0.0071
96 -> 108	30.35 % -11 -> 0			100 -> 109	18.35 % -7 -> 1		
98 -> 108	45.43 % -9 -> 0			101 -> 110	3.16 % -6 -> 2		
100 -> 109	4.21 % -7 -> 1			102 -> 111	37.24 % -5 -> 3		
101 -> 109	3.30 % -6 -> 1			103 -> 111	6.15 % -4 -> 3		
104 -> 110	3.03 % -3 -> 2			106 -> 112	25.45 % -1 -> 4		
Excited State: 25				Excited State: 36			
4.4260 eV	280.13 nm	35698.cm-1	f=0.0000	4.8185 eV	257.31 nm	38864.cm-1	f=0.0679
103 -> 110	98.71 % -4 -> 2			100 -> 109	6.40 % -7 -> 1		
Excited State: 26				Excited State: 37			
4.4584 eV	278.09 nm	35960.cm-1	f=0.0002	4.8827 eV	253.93 nm	39381.cm-1	f=0.0164
102 -> 110	98.46 % -5 -> 2			105 -> 112	92.18 % -2 -> 4		
Excited State: 27				Excited State: 38			
4.5599 eV	271.90 nm	36778.cm-1	f=0.0116	4.8836 eV	253.88 nm	39389.cm-1	f=0.4809
98 -> 109	10.65 % -9 -> 1			97 -> 108	19.70 % -10 -> 0		
99 -> 108	58.93 % -8 -> 0			100 -> 108	9.31 % -7 -> 0		
104 -> 111	24.98 % -3 -> 3			101 -> 111	50.86 % -6 -> 3		
Excited State: 28				Excited State: 39			
4.5647 eV	271.62 nm	36816.cm-1	f=0.0011	5.0759 eV	244.26 nm	40940.cm-1	f=0.0027
94 -> 109	2.05 % -13 -> 1			100 -> 110	4.05 % -7 -> 2		
98 -> 109	77.99 % -9 -> 1			104 -> 112	88.89 % -3 -> 4		
99 -> 108	7.72 % -8 -> 0			Excited State: 40			
104 -> 111	3.08 % -3 -> 3			5.1083 eV	242.71 nm	41201.cm-1	f=0.0004
Excited State: 29				Excited State: 41			
4.6377 eV	267.34 nm	37406.cm-1	f=0.0008	5.1664 eV	239.98 nm	41670.cm-1	f=0.0050
97 -> 108	5.73 % -10 -> 0			102 -> 112	3.56 % -5 -> 4		
99 -> 108	26.28 % -8 -> 0			103 -> 112	95.81 % -4 -> 4		
104 -> 111	55.44 % -3 -> 3			Excited State: 42			
105 -> 111	3.73 % -2 -> 3			5.1958 eV	238.62 nm	41908.cm-1	f=0.0049
106 -> 111	4.65 % -1 -> 3			102 -> 112	96.06 % -5 -> 4		
107 -> 111	2.20 % 0 -> 3			103 -> 112	3.47 % -4 -> 4		
Excited State: 30				Excited State: 43			
4.6909 eV	264.31 nm	37834.cm-1	f=0.0313	5.3487 eV	231.80 nm	43141.cm-1	f=0.0009
100 -> 109	50.98 % -7 -> 1			87 -> 108	5.12 % -20 -> 0		
102 -> 111	14.96 % -5 -> 3			93 -> 108	82.85 % -14 -> 0		
103 -> 111	18.12 % -4 -> 3			97 -> 108	2.34 % -10 -> 0		
107 -> 112	7.56 % 0 -> 4			Excited State: 44			
Excited State: 31				5.3911 eV			
4.7043 eV	263.56 nm	37942.cm-1	f=0.0439	229.98 nm	43482.cm-1	f=0.1025	
100 -> 109	4.30 % -7 -> 1						
100 -> 110	2.29 % -7 -> 2						
101 -> 110	16.90 % -6 -> 2						
103 -> 111	6.44 % -4 -> 3						
104 -> 110	4.76 % -3 -> 2						
107 -> 112	60.17 % 0 -> 4						
Excited State: 32							

99 -> 109 4.54 % -8 -> 1
 100 -> 110 74.01 % -7 -> 2
 104 -> 112 2.67 % -3 -> 4

Excited State: 45
 5.4045 eV 229.41 nm 43590.cm-1 f=0.0141
 95 -> 108 37.93 % -12 -> 0
 97 -> 109 12.98 % -10 -> 1
 99 -> 109 42.24 % -8 -> 1

Excited State: 46
 5.4451 eV 227.70 nm 43917.cm-1 f=0.0060
 95 -> 108 30.61 % -12 -> 0
 97 -> 109 3.93 % -10 -> 1
 99 -> 109 51.50 % -8 -> 1
 100 -> 110 6.37 % -7 -> 2

Excited State: 47
 5.4484 eV 227.56 nm 43944.cm-1 f=0.0353
 92 -> 108 3.16 % -15 -> 0
 100 -> 111 87.60 % -7 -> 3

Excited State: 48
 5.4784 eV 226.32 nm 44185.cm-1 f=0.0109
 100 -> 110 2.20 % -7 -> 2
 101 -> 112 93.84 % -6 -> 4

Excited State: 49
 5.5761 eV 222.35 nm 44974.cm-1 f=0.0756
 94 -> 108 2.31 % -13 -> 0
 95 -> 108 5.23 % -12 -> 0
 96 -> 108 2.11 % -11 -> 0
 96 -> 111 27.46 % -11 -> 3
 97 -> 109 53.33 % -10 -> 1

Excited State: 50
 5.6363 eV 219.98 nm 45459.cm-1 f=0.0701
 91 -> 111 4.17 % -16 -> 3
 95 -> 108 11.20 % -12 -> 0
 95 -> 111 3.39 % -12 -> 3
 96 -> 111 50.43 % -11 -> 3
 97 -> 109 19.61 % -10 -> 1

Table S6. Singlet excited states of **1b**. The computations have been made in vacuum..

Excited State: 1
 2.2706 eV 546.05 nm 18313.cm-1 f=0.0002
 106 -> 108 8.15 % -1 -> 0
 107 -> 108 80.48 % 0 -> 0

Excited State: 2
 2.3242 eV 533.45 nm 18746.cm-1 f=0.0008
 106 -> 108 81.74 % -1 -> 0
 107 -> 108 7.11 % 0 -> 0

Excited State: 3
 2.6664 eV 464.98 nm 21506.cm-1 f=0.0002
 105 -> 108 92.37 % -2 -> 0

Excited State: 4
 2.7452 eV 451.65 nm 22141.cm-1 f=0.0007
 104 -> 108 92.20 % -3 -> 0

Excited State: 5
 2.9424 eV 421.37 nm 23732.cm-1 f=0.0105
 101 -> 108 10.93 % -6 -> 0
 102 -> 108 10.02 % -5 -> 0
 103 -> 108 70.47 % -4 -> 0
 107 -> 108 2.73 % 0 -> 0

Excited State: 6
 3.0595 eV 405.24 nm 24677.cm-1 f=0.0002
 107 -> 109 98.10 % 0 -> 1

Excited State: 7
 3.1263 eV 396.59 nm 25215.cm-1 f=0.0004
 106 -> 109 98.73 % -1 -> 1

Excited State: 8
 3.3036 eV 375.30 nm 26645.cm-1 f=0.0129
 100 -> 108 6.86 % -7 -> 0
 101 -> 108 77.84 % -6 -> 0
 102 -> 108 2.24 % -5 -> 0
 103 -> 108 6.03 % -4 -> 0
 3.3710 eV 367.79 nm 27189.cm-1 f=0.0039
 101 -> 108 2.35 % -6 -> 0
 102 -> 108 11.34 % -5 -> 0
 104 -> 109 2.38 % -3 -> 1
 105 -> 109 82.22 % -2 -> 1

Excited State: 10
 3.4021 eV 364.43 nm 27440.cm-1 f=0.0017
 107 -> 110 98.59 % 0 -> 2

Excited State: 11
 3.4350 eV 360.95 nm 27705.cm-1 f=0.0431

100 -> 108 12.17 % -7 -> 0
 102 -> 108 49.13 % -5 -> 0
 103 -> 108 2.70 % -4 -> 0
 104 -> 109 25.97 % -3 -> 1
 105 -> 109 4.47 % -2 -> 1

Excited State: 12
 3.4680 eV 357.51 nm 27971.cm-1 f=0.0135
 100 -> 108 5.18 % -7 -> 0
 102 -> 108 12.46 % -5 -> 0
 104 -> 109 71.26 % -3 -> 1
 105 -> 109 8.65 % -2 -> 1

Excited State: 13
 3.4687 eV 357.44 nm 27977.cm-1 f=0.0022
 106 -> 110 98.67 % -1 -> 2

Excited State: 14
 3.6473 eV 339.93 nm 29418.cm-1 f=0.0078
 102 -> 109 5.51 % -5 -> 1
 103 -> 109 90.46 % -4 -> 1

Excited State: 15
 3.7599 eV 329.75 nm 30326.cm-1 f=0.0001
 105 -> 110 98.15 % -2 -> 2

Excited State: 16
 3.8105 eV 325.37 nm 30734.cm-1 f=0.0003
 104 -> 110 98.87 % -3 -> 2

Excited State: 17
 3.8609 eV 321.12 nm 31141.cm-1 f=0.0616
 102 -> 109 2.75 % -5 -> 1
 103 -> 110 86.08 % -4 -> 2

Excited State: 18
 3.9172 eV 316.52 nm 31594.cm-1 f=0.0018
 100 -> 108 7.91 % -7 -> 0
 107 -> 112 84.01 % 0 -> 4

Excited State: 19
 3.9523 eV 313.70 nm 31878.cm-1 f=0.0144
 101 -> 109 15.15 % -6 -> 1
 102 -> 109 64.58 % -5 -> 1
 103 -> 109 6.71 % -4 -> 1

Excited State: 20
 4.0121 eV 309.02 nm 32360.cm-1 f=0.0025
 106 -> 112 92.87 % -1 -> 4

Excited State: 21

4.0522 eV 305.97 nm 32683.cm-1 f=0.0020
107 -> 111 97.64 % 0 -> 3

Excited State: 22

4.1121 eV 301.51 nm 33166.cm-1 f=0.0055
101 -> 109 7.11 % -6 -> 1
102 -> 109 2.88 % -5 -> 1
102 -> 110 4.00 % -5 -> 2
106 -> 111 83.42 % -1 -> 3

Excited State: 23

4.1272 eV 300.41 nm 33288.cm-1 f=0.0287
99 -> 108 2.33 % -8 -> 0
101 -> 109 54.27 % -6 -> 1
102 -> 109 18.98 % -5 -> 1
102 -> 110 2.70 % -5 -> 2
106 -> 111 14.15 % -1 -> 3

Excited State: 24

4.2258 eV 293.40 nm 34083.cm-1 f=0.0398
100 -> 108 8.96 % -7 -> 0
101 -> 112 2.38 % -6 -> 4
103 -> 112 78.12 % -4 -> 4

Excited State: 25

4.2263 eV 293.36 nm 34088.cm-1 f=0.0736
105 -> 109 3.08 % -2 -> 1
101 -> 109 6.61 % -6 -> 1
102 -> 110 78.26 % -5 -> 2
103 -> 111 2.27 % -4 -> 3

Excited State: 26

4.3403 eV 285.66 nm 35007.cm-1 f=0.0183
100 -> 110 2.14 % -7 -> 2
101 -> 110 77.06 % -6 -> 2
103 -> 111 9.81 % -4 -> 3
105 -> 112 3.07 % -2 -> 4

Excited State: 27

4.3921 eV 282.29 nm 35425.cm-1 f=0.0041
101 -> 110 2.04 % -6 -> 2
105 -> 112 91.84 % -2 -> 4

Excited State: 28

4.3997 eV 281.80 nm 35486.cm-1 f=0.0702
97 -> 108 7.48 % -10 -> 0
100 -> 108 6.38 % -7 -> 0
103 -> 112 4.38 % -4 -> 4
105 -> 111 68.45 % -2 -> 3
107 -> 112 2.46 % 0 -> 4

Excited State: 29

4.4256 eV 280.15 nm 35695.cm-1 f=0.0010
99 -> 108 2.79 % -8 -> 0
104 -> 112 93.50 % -3 -> 4

Excited State: 30

4.4276 eV 280.02 nm 35712.cm-1 f=0.1360
97 -> 108 19.08 % -10 -> 0
100 -> 108 11.25 % -7 -> 0
102 -> 112 2.85 % -5 -> 4
103 -> 112 5.79 % -4 -> 4
104 -> 111 9.05 % -3 -> 3
105 -> 111 27.84 % -2 -> 3
107 -> 112 4.72 % 0 -> 4

Excited State: 31

4.4617 eV 277.88 nm 35987.cm-1 f=0.0142
97 -> 108 2.35 % -10 -> 0
104 -> 111 90.65 % -3 -> 3
105 -> 111 3.16 % -2 -> 3

Excited State: 32

4.5007 eV 275.48 nm 36300.cm-1 f=0.0141
96 -> 108 12.77 % -11 -> 0
99 -> 108 32.88 % -8 -> 0

100 -> 109 2.42 % -7 -> 1
101 -> 110 6.25 % -6 -> 2
103 -> 111 39.59 % -4 -> 3

Excited State: 33

4.5358 eV 273.35 nm 36583.cm-1 f=0.0325
96 -> 108 33.56 % -11 -> 0
99 -> 108 14.66 % -8 -> 0
101 -> 110 5.99 % -6 -> 2
103 -> 111 34.25 % -4 -> 3

Excited State: 34

4.5498 eV 272.50 nm 36697.cm-1 f=0.0224
95 -> 108 2.29 % -12 -> 0
96 -> 108 34.78 % -11 -> 0
99 -> 108 34.05 % -8 -> 0
100 -> 109 9.04 % -7 -> 1
101 -> 109 2.02 % -6 -> 1
103 -> 111 5.01 % -4 -> 3

Excited State: 35

4.5920 eV 270.00 nm 37037.cm-1 f=0.0026
99 -> 109 82.24 % -8 -> 1
101 -> 112 2.89 % -6 -> 4
102 -> 112 2.71 % -5 -> 4

Excited State: 36

4.6448 eV 266.93 nm 37463.cm-1 f=0.0000
97 -> 108 8.09 % -10 -> 0
99 -> 109 7.87 % -8 -> 1
101 -> 112 27.62 % -6 -> 4
102 -> 112 47.61 % -5 -> 4

Excited State: 37

4.7803 eV 259.37 nm 38555.cm-1 f=0.0728
99 -> 108 2.87 % -8 -> 0
100 -> 109 16.77 % -7 -> 1
100 -> 110 9.13 % -7 -> 2
102 -> 111 59.01 % -5 -> 3
103 -> 111 5.01 % -4 -> 3

Excited State: 35

4.5920 eV 270.00 nm 37037.cm-1 f=0.0026
99 -> 109 82.24 % -8 -> 1
101 -> 112 2.89 % -6 -> 4
102 -> 112 2.71 % -5 -> 4

Excited State: 36

4.6448 eV 266.93 nm 37463.cm-1 f=0.0000
97 -> 108 8.09 % -10 -> 0
99 -> 109 7.87 % -8 -> 1
101 -> 112 27.62 % -6 -> 4
102 -> 112 47.61 % -5 -> 4

Excited State: 37

4.7803 eV 259.37 nm 38555.cm-1 f=0.0728
99 -> 108 2.87 % -8 -> 0
100 -> 109 16.77 % -7 -> 1
100 -> 110 9.13 % -7 -> 2
102 -> 111 59.01 % -5 -> 3

Excited State: 38

4.7928 eV 258.69 nm 38656.cm-1 f=0.0042
101 -> 112 55.74 % -6 -> 4
102 -> 112 37.49 % -5 -> 4
103 -> 112 2.38 % -4 -> 4

Excited State: 39

4.8408 eV 256.12 nm 39044.cm-1 f=0.0107
99 -> 108 3.75 % -8 -> 0
100 -> 109 57.10 % -7 -> 1
102 -> 111 18.78 % -5 -> 3

Excited State: 40

4.9466 eV 250.65 nm 39896.cm-1 f=0.5254
92 -> 108 4.97 % -15 -> 0
97 -> 108 34.56 % -10 -> 0

100 -> 108 23.51 % -7 -> 0
 101 -> 112 4.17 % -6 -> 4
 102 -> 108 2.53 % -5 -> 0

102 -> 112 4.38 % -5 -> 4
 103 -> 112 2.13 % -4 -> 4

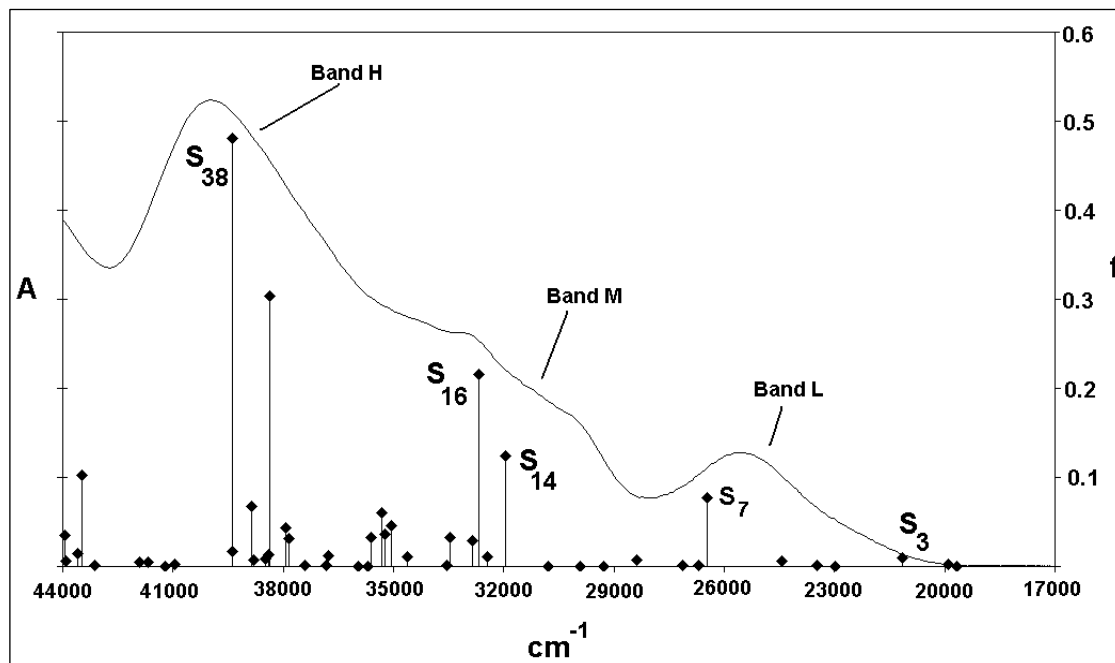


Fig. S7. The following figure compares the **1b** experimental spectrum recorded in acetonitrile and the computed electronic transitions computed in acetonitrile.

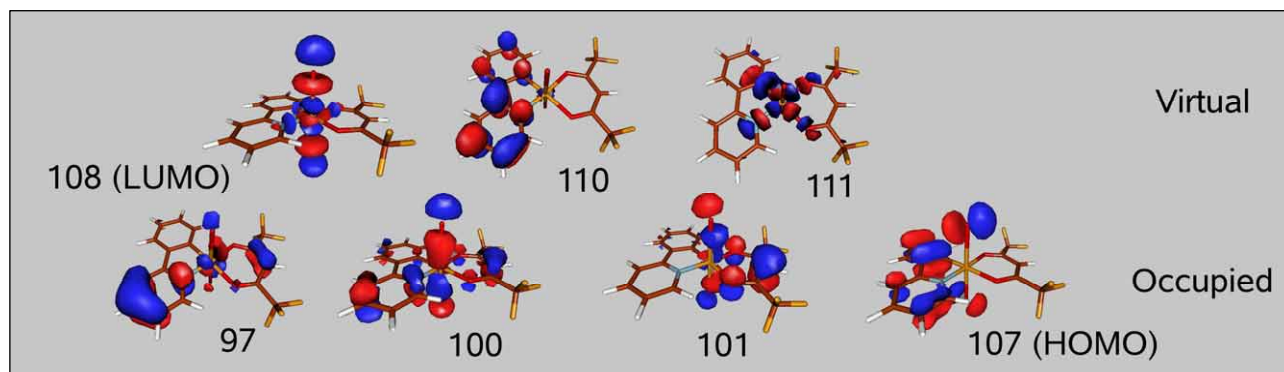


Fig. S8. In the following picture, some **1b** Kohn-Sham orbitals are reported that are relevant in describing the low-energy electronic transitions toward S_3 , S_7 , S_{14} , S_{16} , and S_{38} .

Table S7. Optimized structure of **1b**. Cartesian coordinates in angstrom.

C	-3.962250	-3.054340	-0.000387	C	-1.768015	2.663642	-0.000001
C	-4.170775	-1.681713	-0.000407	C	-1.862148	1.278094	-0.000077
C	-3.075587	-0.811751	-0.000286	Pt	-0.324461	0.007234	0.000048
N	-1.820516	-1.332949	-0.000139	O	1.241083	-1.502211	0.000182
C	-1.601839	-2.655426	-0.000119	H	-0.563780	-2.968636	0.000007
C	-2.656180	-3.554490	-0.000240	H	-2.449184	-4.619210	-0.000211
C	-3.117525	0.642687	-0.000252	H	-4.810185	-3.733891	-0.000472
C	-4.289098	1.413658	-0.000346	H	-5.102068	3.404642	-0.000340
H	-5.266651	0.937890	-0.000464	H	-2.874971	4.506355	-0.000043
H	-5.175349	-1.273303	-0.000501	H	-0.796899	3.148605	0.000135
C	-4.198322	2.801535	-0.000273	O	1.080960	1.482461	0.000244
C	-2.942210	3.421043	-0.000105	C	2.456810	-1.198628	0.000423

C	3.048224	0.075947	0.000419	F	2.801621	3.313843	1.082795
C	2.331706	1.268359	0.000447	F	4.681437	-2.102591	-0.000011
C	3.115325	2.596207	0.000084	F	3.148288	-3.181148	1.082868
C	3.384514	-2.432722	0.000019	F	3.148084	-3.180640	-1.083140
H	4.127094	0.136781	0.000287	I	-0.291694	-0.003269	-2.699546
F	4.439481	2.404429	-0.000064	I	-0.292278	-0.003407	2.699640
F	2.801303	3.313485	-1.082773				

[(NR)Pt(acac)I₂], 2a

Table S8. Singlet excited states of **2a**. The computations have been performed by modelling the solvent effects with the PCM model on the structure optimized in vacuum. The following text lists the energy (in eV and nm), the oscillator strengths and percentage composition of the most important mono-electronic excitations for each excited state. Excited States composition has been expressed in two ways. The first one uses the Kohn-Sham orbital numerical label of the occupied and virtual orbital as produced by the computation (for instance, 119 → 120 for the HOMO → LUMO transition when the HOMO is the 119th orbital and the LUMO is the 120th one). The second way assign the “0” label to the HOMO, the “-1” label to the HOMO-1 orbital and so on, the “0” label to the LUMO, “1” to LUMO+1 and so on (thus, 0 → 0 is the HOMO → LUMO transition, -2 → 1 is the HOMO-2 → LUMO+1 transition).

Excited State: 1 1.8150 eV 683.11 nm 14639.cm-1 f=0.0005 126 → 127 88.55 % 0 → 0 126 → 128 9.50 % 0 → 1	Excited State: 8 2.8384 eV 436.82 nm 22893.cm-1 f=0.0023 119 → 127 19.92 % -7 → 0 119 → 128 2.51 % -7 → 1 121 → 127 3.78 % -5 → 0 122 → 128 10.86 % -4 → 1 124 → 128 12.01 % -2 → 1 125 → 127 4.29 % -1 → 0 125 → 128 37.14 % -1 → 1
Excited State: 2 2.1851 eV 567.41 nm 17624.cm-1 f=0.6241 126 → 127 7.20 % 0 → 0 126 → 128 69.46 % 0 → 1	Excited State: 9 2.8787 eV 430.70 nm 23218.cm-1 f=0.0105 119 → 127 25.66 % -7 → 0 119 → 128 2.90 % -7 → 1 121 → 127 6.36 % -5 → 0 123 → 127 6.68 % -3 → 0 123 → 128 44.94 % -3 → 1 125 → 128 5.31 % -1 → 1
Excited State: 3 2.3739 eV 522.28 nm 19147.cm-1 f=0.0053 122 → 127 16.65 % -4 → 0 123 → 127 3.74 % -3 → 0 124 → 127 7.37 % -2 → 0 125 → 127 53.96 % -1 → 0 125 → 128 6.07 % -1 → 1	Excited State: 10 2.9096 eV 426.12 nm 23468.cm-1 f=0.0047 119 → 127 31.39 % -7 → 0 119 → 128 2.96 % -7 → 1 122 → 128 3.74 % -4 → 1 123 → 127 3.45 % -3 → 0 123 → 128 23.01 % -3 → 1 125 → 127 2.80 % -1 → 0 125 → 128 24.51 % -1 → 1
Excited State: 4 2.4340 eV 509.38 nm 19632.cm-1 f=0.0014 120 → 127 5.43 % -6 → 0 123 → 127 45.82 % -3 → 0 123 → 128 5.19 % -3 → 1 124 → 127 20.91 % -2 → 0 124 → 128 2.31 % -2 → 1 125 → 127 9.63 % -1 → 0	Excited State: 11 2.9530 eV 419.85 nm 23818.cm-1 f=0.0009 120 → 127 4.83 % -6 → 0 122 → 127 7.14 % -4 → 0 123 → 127 17.79 % -3 → 0 123 → 128 4.05 % -3 → 1 124 → 127 54.61 % -2 → 0 124 → 128 8.39 % -2 → 1
Excited State: 5 2.6369 eV 470.19 nm 21268.cm-1 f=0.0119 120 → 127 2.81 % -6 → 0 122 → 127 56.88 % -4 → 0 122 → 128 5.88 % -4 → 1 123 → 127 9.11 % -3 → 0 125 → 127 15.12 % -1 → 0	Excited State: 12 3.0098 eV 411.94 nm 24275.cm-1 f=0.0002 118 → 127 8.93 % -8 → 0 118 → 128 67.04 % -8 → 1 118 → 131 2.60 % -8 → 4 121 → 128 13.14 % -5 → 1
Excited State: 6 2.7689 eV 447.77 nm 22333.cm-1 f=0.0007 121 → 127 70.30 % -5 → 0 121 → 128 7.54 % -5 → 1 123 → 128 7.79 % -3 → 1 124 → 128 5.53 % -2 → 1	Excited State: 13 3.0357 eV 408.43 nm 24484.cm-1 f=0.0328 114 → 127 3.90 % -12 → 0 117 → 127 2.45 % -9 → 0 120 → 127 57.17 % -6 → 0 120 → 128 5.06 % -6 → 1 122 → 127 5.86 % -4 → 0 122 → 128 7.16 % -4 → 1
Excited State: 7 2.8200 eV 439.67 nm 22744.cm-1 f=0.0045 117 → 128 2.06 % -9 → 1 119 → 127 4.34 % -7 → 0 121 → 127 2.08 % -5 → 0 122 → 128 3.43 % -4 → 1 123 → 128 3.36 % -3 → 1 124 → 127 8.64 % -2 → 0 124 → 128 60.98 % -2 → 1 125 → 128 6.04 % -1 → 1	

123 -> 127	4.38 %	-3 -> 0	
125 -> 127	3.91 %	-1 -> 0	
Excited State: 14			
3.0416 eV	407.62 nm	24533.cm-1	f=0.0062
119 -> 127	2.57 %	-7 -> 0	
120 -> 127	7.76 %	-6 -> 0	
122 -> 127	3.70 %	-4 -> 0	
122 -> 128	63.13 %	-4 -> 1	
125 -> 128	14.67 %	-1 -> 1	
Excited State: 15			
3.1800 eV	389.89 nm	25648.cm-1	f=0.0001
118 -> 128	11.72 %	-8 -> 1	
121 -> 127	8.07 %	-5 -> 0	
121 -> 128	76.49 %	-5 -> 1	
Excited State: 16			
3.2331 eV	383.49 nm	26076.cm-1	f=0.0008
119 -> 127	9.20 %	-7 -> 0	
119 -> 128	86.79 %	-7 -> 1	
Excited State: 17			
3.2431 eV	382.30 nm	26157.cm-1	f=0.0511
120 -> 127	8.40 %	-6 -> 0	
120 -> 128	80.30 %	-6 -> 1	
Excited State: 18			
3.5006 eV	354.18 nm	28234.cm-1	f=0.0198
117 -> 127	78.37 %	-9 -> 0	
117 -> 128	8.21 %	-9 -> 1	
Excited State: 19			
3.5294 eV	351.29 nm	28467.cm-1	f=0.0015
117 -> 127	2.08 %	-9 -> 0	
126 -> 129	10.76 %	0 -> 2	
126 -> 130	82.98 %	0 -> 3	
Excited State: 20			
3.5508 eV	349.17 nm	28639.cm-1	f=0.0037
115 -> 127	25.57 %	-11 -> 0	
115 -> 128	2.74 %	-11 -> 1	
117 -> 127	5.49 %	-9 -> 0	
117 -> 128	7.52 %	-9 -> 1	
118 -> 127	42.97 %	-8 -> 0	
118 -> 128	6.47 %	-8 -> 1	
Excited State: 21			
3.5958 eV	344.80 nm	29002.cm-1	f=0.0384
115 -> 127	2.47 %	-11 -> 0	
116 -> 128	14.71 %	-10 -> 1	
117 -> 127	2.28 %	-9 -> 0	
117 -> 128	51.40 %	-9 -> 1	
118 -> 127	10.21 %	-8 -> 0	
126 -> 131	6.25 %	0 -> 4	
Excited State: 22			
3.7469 eV	330.90 nm	30221.cm-1	f=0.0035
116 -> 128	7.54 %	-10 -> 1	
126 -> 129	78.09 %	0 -> 2	
126 -> 130	9.78 %	0 -> 3	
Excited State: 23			
3.7984 eV	326.41 nm	30636.cm-1	f=0.0161
116 -> 127	8.39 %	-10 -> 0	
116 -> 128	51.52 %	-10 -> 1	
117 -> 128	7.82 %	-9 -> 1	
118 -> 127	2.14 %	-8 -> 0	
126 -> 129	9.38 %	0 -> 2	
126 -> 131	12.06 %	0 -> 4	
Excited State: 24			
3.8524 eV	321.84 nm	31071.cm-1	f=0.0031
115 -> 127	51.66 %	-11 -> 0	
115 -> 128	4.92 %	-11 -> 1	
116 -> 127	4.26 %	-10 -> 0	
118 -> 127	29.03 %	-8 -> 0	
118 -> 128	4.17 %	-8 -> 1	
Excited State: 25			
3.8953 eV	318.29 nm	31418.cm-1	f=0.0097
114 -> 127	5.00 %	-12 -> 0	
116 -> 127	74.48 %	-10 -> 0	
116 -> 128	13.26 %	-10 -> 1	
Excited State: 26			
4.0034 eV	309.70 nm	32289.cm-1	f=0.1497
114 -> 127	2.48 %	-12 -> 0	
114 -> 128	17.56 %	-12 -> 1	
116 -> 128	5.44 %	-10 -> 1	
117 -> 128	7.64 %	-9 -> 1	
126 -> 131	56.05 %	0 -> 4	
Excited State: 27			
4.0675 eV	304.81 nm	32807.cm-1	f=0.0007
115 -> 127	9.09 %	-11 -> 0	
115 -> 128	86.10 %	-11 -> 1	
Excited State: 28			
4.0864 eV	303.40 nm	32960.cm-1	f=0.0056
114 -> 127	3.66 %	-12 -> 0	
125 -> 129	8.78 %	-1 -> 2	
125 -> 130	78.26 %	-1 -> 3	
Excited State: 29			
4.1684 eV	297.44 nm	33620.cm-1	f=0.0006
110 -> 127	2.14 %	-16 -> 0	
113 -> 127	63.96 %	-13 -> 0	
113 -> 128	7.00 %	-13 -> 1	
125 -> 129	7.00 %	-1 -> 2	
Excited State: 30			
4.2097 eV	294.52 nm	33954.cm-1	f=0.0618
114 -> 127	17.14 %	-12 -> 0	
114 -> 128	39.03 %	-12 -> 1	
123 -> 130	14.06 %	-3 -> 3	
124 -> 130	7.28 %	-2 -> 3	
126 -> 131	8.95 %	0 -> 4	
Excited State: 31			
4.2153 eV	294.13 nm	33999.cm-1	f=0.0426
114 -> 128	27.74 %	-12 -> 1	
123 -> 129	4.31 %	-3 -> 2	
123 -> 130	32.17 %	-3 -> 3	
124 -> 129	2.25 %	-2 -> 2	
124 -> 130	17.71 %	-2 -> 3	
126 -> 131	3.52 %	0 -> 4	
Excited State: 32			
4.3723 eV	283.57 nm	35265.cm-1	f=0.0055
122 -> 129	9.54 %	-4 -> 2	
122 -> 130	75.80 %	-4 -> 3	
123 -> 130	6.99 %	-3 -> 3	
Excited State: 33			
4.4103 eV	281.12 nm	35572.cm-1	f=0.3284
107 -> 127	2.01 %	-19 -> 0	
114 -> 127	23.90 %	-12 -> 0	
114 -> 128	3.70 %	-12 -> 1	
120 -> 129	3.86 %	-6 -> 2	
120 -> 130	41.11 %	-6 -> 3	
121 -> 129	2.08 %	-5 -> 2	
124 -> 130	2.14 %	-2 -> 3	
Excited State: 34			
4.4700 eV	277.37 nm	36053.cm-1	f=0.0312
122 -> 129	3.49 %	-4 -> 2	
125 -> 129	30.27 %	-1 -> 2	
125 -> 130	3.28 %	-1 -> 3	
126 -> 132	34.72 %	0 -> 5	
126 -> 133	8.53 %	0 -> 6	
Excited State: 35			
4.4774 eV	276.91 nm	36113.cm-1	f=0.0090

121 -> 130 2.59 % -5 -> 3
 122 -> 129 3.11 % -4 -> 2
 123 -> 129 5.80 % -3 -> 2
 125 -> 129 25.85 % -1 -> 2
 125 -> 130 2.71 % -1 -> 3
 126 -> 132 39.11 % 0 -> 5
 126 -> 133 5.83 % 0 -> 6

Excited State: 36
 4.5038 eV 275.29 nm 36325.cm-1 f=0.0021
 123 -> 129 49.04 % -3 -> 2
 123 -> 130 5.16 % -3 -> 3
 124 -> 129 32.07 % -2 -> 2
 124 -> 130 2.94 % -2 -> 3

Excited State: 37
 4.5849 eV 270.42 nm 36980.cm-1 f=0.0087
 110 -> 127 2.41 % -16 -> 0
 119 -> 130 3.30 % -7 -> 3
 121 -> 129 7.58 % -5 -> 2
 121 -> 130 15.00 % -5 -> 3
 122 -> 129 44.69 % -4 -> 2
 122 -> 130 5.90 % -4 -> 3
 123 -> 129 2.41 % -3 -> 2
 124 -> 129 4.51 % -2 -> 2
 126 -> 133 2.71 % 0 -> 6

Excited State: 38
 4.5917 eV 270.02 nm 37034.cm-1 f=0.0735
 107 -> 127 3.88 % -19 -> 0
 111 -> 127 27.01 % -15 -> 0
 111 -> 128 2.98 % -15 -> 1
 112 -> 127 5.21 % -14 -> 0
 114 -> 127 2.91 % -12 -> 0
 115 -> 129 2.34 % -11 -> 2
 120 -> 129 2.21 % -6 -> 2
 120 -> 130 14.78 % -6 -> 3
 121 -> 129 13.26 % -5 -> 2
 123 -> 130 4.55 % -3 -> 3
 125 -> 130 4.13 % -1 -> 3

Excited State: 39
 4.5991 eV 269.58 nm 37095.cm-1 f=0.0741
 111 -> 127 22.84 % -15 -> 0
 111 -> 128 2.91 % -15 -> 1
 112 -> 127 4.83 % -14 -> 0
 114 -> 127 3.51 % -12 -> 0
 115 -> 129 4.73 % -11 -> 2
 120 -> 130 6.13 % -6 -> 3
 121 -> 129 25.42 % -5 -> 2
 121 -> 130 4.35 % -5 -> 3
 124 -> 130 6.33 % -2 -> 3

Excited State: 40
 4.6170 eV 268.54 nm 37238.cm-1 f=0.0336
 121 -> 130 2.57 % -5 -> 3
 122 -> 129 2.19 % -4 -> 2
 123 -> 131 2.11 % -3 -> 4
 124 -> 131 11.32 % -2 -> 4
 126 -> 132 13.06 % 0 -> 5
 126 -> 133 55.02 % 0 -> 6

Excited State: 41
 4.6332 eV 267.60 nm 37369.cm-1 f=0.2853
 114 -> 127 12.50 % -12 -> 0
 115 -> 129 7.35 % -11 -> 2
 120 -> 130 13.94 % -6 -> 3
 121 -> 129 27.84 % -5 -> 2
 122 -> 129 3.09 % -4 -> 2
 123 -> 130 2.19 % -3 -> 3
 124 -> 130 6.86 % -2 -> 3

Excited State: 42
 4.6818 eV 264.82 nm 37761.cm-1 f=0.0138
 119 -> 129 2.68 % -7 -> 2
 119 -> 130 18.63 % -7 -> 3
 121 -> 130 38.80 % -5 -> 3

122 -> 129 7.08 % -4 -> 2
 123 -> 130 6.56 % -3 -> 3
 124 -> 130 13.95 % -2 -> 3

Excited State: 43
 4.6947 eV 264.09 nm 37866.cm-1 f=0.0443
 111 -> 127 2.42 % -15 -> 0
 119 -> 130 7.14 % -7 -> 3
 121 -> 130 13.74 % -5 -> 3
 122 -> 130 7.79 % -4 -> 3
 123 -> 129 2.82 % -3 -> 2
 123 -> 130 19.59 % -3 -> 3
 124 -> 129 4.87 % -2 -> 2
 124 -> 130 30.10 % -2 -> 3

Excited State: 44
 4.7483 eV 261.11 nm 38298.cm-1 f=0.0197
 119 -> 129 8.79 % -7 -> 2
 119 -> 130 50.38 % -7 -> 3
 121 -> 130 11.19 % -5 -> 3
 122 -> 129 7.65 % -4 -> 2
 125 -> 129 6.01 % -1 -> 2

Excited State: 45
 4.7777 eV 259.51 nm 38534.cm-1 f=0.0009
 113 -> 127 9.40 % -13 -> 0
 113 -> 128 85.19 % -13 -> 1

Excited State: 46
 4.8575 eV 255.24 nm 39179.cm-1 f=0.1705
 122 -> 129 5.24 % -4 -> 2
 123 -> 129 20.56 % -3 -> 2
 123 -> 130 2.67 % -3 -> 3
 123 -> 131 6.67 % -3 -> 4
 124 -> 129 37.41 % -2 -> 2
 124 -> 130 5.36 % -2 -> 3
 124 -> 131 6.38 % -2 -> 4
 126 -> 133 5.74 % 0 -> 6

Excited State: 47
 4.8730 eV 254.43 nm 39304.cm-1 f=0.0152
 119 -> 129 81.54 % -7 -> 2
 119 -> 130 13.34 % -7 -> 3

Excited State: 48
 4.9080 eV 252.62 nm 39585.cm-1 f=0.0274
 122 -> 131 2.09 % -4 -> 4
 123 -> 129 2.78 % -3 -> 2
 123 -> 131 43.94 % -3 -> 4
 124 -> 129 6.18 % -2 -> 2
 125 -> 131 37.79 % -1 -> 4

Excited State: 49
 4.9262 eV 251.68 nm 39733.cm-1 f=0.2851
 123 -> 129 3.26 % -3 -> 2
 123 -> 131 3.31 % -3 -> 4
 124 -> 129 4.53 % -2 -> 2
 124 -> 131 70.22 % -2 -> 4
 126 -> 133 6.14 % 0 -> 6

Excited State: 50
 4.9512 eV 250.41 nm 39935.cm-1 f=0.0802
 122 -> 131 14.16 % -4 -> 4
 123 -> 131 34.88 % -3 -> 4
 125 -> 131 42.58 % -1 -> 4

Excited State: 51
 5.0216 eV 246.90 nm 40502.cm-1 f=0.0056
 110 -> 127 2.41 % -16 -> 0
 120 -> 129 81.51 % -6 -> 2
 120 -> 130 7.80 % -6 -> 3

Excited State: 52
 5.0479 eV 245.62 nm 40713.cm-1 f=0.0003
 110 -> 128 2.62 % -16 -> 1
 118 -> 128 3.16 % -8 -> 1
 118 -> 129 3.13 % -8 -> 2

118 -> 131	68.01 %	-8 -> 4	
121 -> 131	11.12 %	-5 -> 4	
Excited State: 53			
5.0911 eV	243.53 nm	41063.cm-1	f=0.0152
110 -> 128	13.69 %	-16 -> 1	
112 -> 127	4.74 %	-14 -> 0	
112 -> 128	9.31 %	-14 -> 1	
117 -> 129	5.74 %	-9 -> 2	
117 -> 130	48.97 %	-9 -> 3	
118 -> 131	2.92 %	-8 -> 4	
Excited State: 54			
5.0942 eV	243.38 nm	41088.cm-1	f=0.0174
110 -> 127	3.60 %	-16 -> 0	
112 -> 128	9.03 %	-14 -> 1	
122 -> 131	66.08 %	-4 -> 4	
125 -> 131	9.78 %	-1 -> 4	
Excited State: 55			
5.1061 eV	242.82 nm	41183.cm-1	f=0.0507
112 -> 127	5.03 %	-14 -> 0	
112 -> 128	48.79 %	-14 -> 1	
117 -> 130	13.80 %	-9 -> 3	
122 -> 131	11.00 %	-4 -> 4	
125 -> 131	3.28 %	-1 -> 4	
Excited State: 56			
5.1293 eV	241.72 nm	41370.cm-1	f=0.0059
115 -> 129	51.73 %	-11 -> 2	
115 -> 130	3.32 %	-11 -> 3	
118 -> 129	12.29 %	-8 -> 2	
121 -> 129	17.00 %	-5 -> 2	
121 -> 131	3.31 %	-5 -> 4	
Excited State: 57			
5.1358 eV	241.41 nm	41423.cm-1	f=0.1164
109 -> 127	2.53 %	-17 -> 0	
110 -> 127	39.40 %	-16 -> 0	
112 -> 127	7.12 %	-14 -> 0	
112 -> 128	2.19 %	-14 -> 1	
113 -> 127	4.73 %	-13 -> 0	
113 -> 130	5.07 %	-13 -> 3	
117 -> 130	2.66 %	-9 -> 3	
126 -> 134	20.39 %	0 -> 7	
Excited State: 58			
5.1472 eV	240.87 nm	41516.cm-1	f=0.0026
110 -> 128	37.03 %	-16 -> 1	
111 -> 127	7.83 %	-15 -> 0	
112 -> 127	37.18 %	-14 -> 0	
117 -> 130	5.35 %	-9 -> 3	
Excited State: 59			
5.1639 eV	240.10 nm	41649.cm-1	f=0.0160
107 -> 127	3.71 %	-19 -> 0	
110 -> 128	21.14 %	-16 -> 1	
111 -> 127	8.86 %	-15 -> 0	
111 -> 128	5.77 %	-15 -> 1	
112 -> 127	24.41 %	-14 -> 0	
112 -> 128	16.51 %	-14 -> 1	
117 -> 130	3.39 %	-9 -> 3	
126 -> 134	6.59 %	0 -> 7	
Excited State: 60			
5.2066 eV	238.13 nm	41994.cm-1	f=0.1046
110 -> 127	7.07 %	-16 -> 0	
110 -> 128	3.85 %	-16 -> 1	
111 -> 127	2.20 %	-15 -> 0	
113 -> 127	2.53 %	-13 -> 0	
113 -> 130	8.66 %	-13 -> 3	
118 -> 130	6.50 %	-8 -> 3	
126 -> 134	48.73 %	0 -> 7	

Table S9. Singlet excited states of **2a**. The computations have been made in vacuum.

Excited State: 1			
2.1832 eV	567.90 nm	17609.cm-1	f=0.0006
124 -> 128	7.81 %	-2 -> 1	
125 -> 128	6.09 %	-1 -> 1	
126 -> 128	80.87 %	0 -> 1	
Excited State: 2			
2.2728 eV	545.52 nm	18331.cm-1	f=0.0005
125 -> 128	78.66 %	-1 -> 1	
126 -> 128	10.16 %	0 -> 1	
Excited State: 3			
2.2955 eV	540.13 nm	18514.cm-1	f=0.0006
124 -> 128	80.14 %	-2 -> 1	
125 -> 128	3.37 %	-1 -> 1	
126 -> 128	6.06 %	0 -> 1	
Excited State: 4			
2.4071 eV	515.08 nm	19414.cm-1	f=0.4594
124 -> 127	2.07 %	-2 -> 0	
126 -> 127	72.43 %	0 -> 0	
Excited State: 5			
2.4695 eV	502.06 nm	19918.cm-1	f=0.0027
123 -> 128	4.89 %	-3 -> 1	
125 -> 127	92.35 %	-1 -> 0	
Excited State: 6			
2.5272 eV	490.60 nm	20383.cm-1	f=0.0124
121 -> 128	2.21 %	-5 -> 1	
124 -> 127	92.74 %	-2 -> 0	
Excited State: 7			
2.6456 eV	468.65 nm	21338.cm-1	f=0.0035
123 -> 128	86.63 %	-3 -> 1	
125 -> 127	5.55 %	-1 -> 0	
Excited State: 8			
2.7319 eV	453.83 nm	22035.cm-1	f=0.0013
121 -> 128	62.62 %	-5 -> 1	
122 -> 128	25.71 %	-4 -> 1	
124 -> 127	3.86 %	-2 -> 0	
Excited State: 9			
2.7511 eV	450.67 nm	22189.cm-1	f=0.0000
118 -> 127	65.16 %	-8 -> 0	
118 -> 131	2.25 %	-8 -> 4	
123 -> 127	26.09 %	-3 -> 0	
Excited State: 10			
2.8231 eV	439.17 nm	22770.cm-1	f=0.0023
118 -> 127	18.94 %	-8 -> 0	
119 -> 128	2.22 %	-7 -> 1	
121 -> 127	2.90 %	-5 -> 0	
121 -> 128	3.93 %	-5 -> 1	
122 -> 128	6.24 %	-4 -> 1	
123 -> 127	59.38 %	-3 -> 0	
Excited State: 11			
2.8383 eV	436.83 nm	22892.cm-1	f=0.0092
118 -> 127	5.52 %	-8 -> 0	
119 -> 128	10.98 %	-7 -> 1	
120 -> 128	9.25 %	-6 -> 1	
121 -> 127	6.96 %	-5 -> 0	
121 -> 128	14.71 %	-5 -> 1	
122 -> 127	5.81 %	-4 -> 0	
122 -> 128	28.24 %	-4 -> 1	
123 -> 127	12.57 %	-3 -> 0	
Excited State: 12			

2.8740 eV 431.41 nm 23180.cm-1 f=0.0029
 119 -> 128 3.06 % -7 -> 1
 120 -> 128 2.39 % -6 -> 1
 121 -> 127 59.96 % -5 -> 0
 122 -> 127 21.03 % -4 -> 0
 122 -> 128 9.76 % -4 -> 1

Excited State: 13

2.9828 eV 415.66 nm 24058.cm-1 f=0.0148
 117 -> 127 2.58 % -9 -> 0
 119 -> 127 3.85 % -7 -> 0
 120 -> 127 43.12 % -6 -> 0
 121 -> 127 12.91 % -5 -> 0
 122 -> 127 29.78 % -4 -> 0

Excited State: 14

2.9912 eV 414.50 nm 24125.cm-1 f=0.0031
 119 -> 127 9.44 % -7 -> 0
 120 -> 127 31.02 % -6 -> 0
 121 -> 127 14.84 % -5 -> 0
 122 -> 127 38.62 % -4 -> 0

Excited State: 15

3.1671 eV 391.48 nm 25544.cm-1 f=0.0429
 116 -> 128 7.09 % -10 -> 1
 117 -> 128 4.76 % -9 -> 1
 119 -> 127 8.67 % -7 -> 0
 119 -> 128 35.13 % -7 -> 1
 120 -> 128 14.71 % -6 -> 1
 121 -> 128 4.23 % -5 -> 1
 122 -> 128 12.42 % -4 -> 1

Excited State: 16

3.1814 eV 389.72 nm 25659.cm-1 f=0.0566
 119 -> 127 68.34 % -7 -> 0
 119 -> 128 4.81 % -7 -> 1
 120 -> 127 9.51 % -6 -> 0
 120 -> 128 2.50 % -6 -> 1

Excited State: 17

3.3108 eV 374.49 nm 26703.cm-1 f=0.0007
 119 -> 128 33.80 % -7 -> 1
 120 -> 128 63.34 % -6 -> 1

Excited State: 18

3.6184 eV 342.65 nm 29184.cm-1 f=0.0006
 114 -> 128 9.18 % -12 -> 1
 117 -> 127 4.93 % -9 -> 0
 118 -> 128 81.97 % -8 -> 1

Excited State: 19

3.6583 eV 338.91 nm 29506.cm-1 f=0.0218
 115 -> 127 7.88 % -11 -> 0
 116 -> 127 3.74 % -10 -> 0
 117 -> 127 67.24 % -9 -> 0
 118 -> 128 6.15 % -8 -> 1
 120 -> 127 2.84 % -6 -> 0
 126 -> 131 3.43 % 0 -> 4

Excited State: 20

3.7393 eV 331.57 nm 30160.cm-1 f=0.0108
 116 -> 128 2.46 % -10 -> 1
 117 -> 128 54.63 % -9 -> 1
 125 -> 130 3.41 % -1 -> 3
 126 -> 130 28.11 % 0 -> 3

Excited State: 21

3.7549 eV 330.19 nm 30286.cm-1 f=0.0063
 117 -> 128 30.09 % -9 -> 1
 126 -> 129 3.07 % 0 -> 2
 126 -> 130 58.54 % 0 -> 3

Excited State: 22

3.8412 eV 322.78 nm 30981.cm-1 f=0.0026
 116 -> 127 2.60 % -10 -> 0
 126 -> 129 89.76 % 0 -> 2
 126 -> 130 3.94 % 0 -> 3

Excited State: 23

3.8812 eV 319.45 nm 31304.cm-1 f=0.0182
 115 -> 127 6.09 % -11 -> 0
 116 -> 127 75.34 % -10 -> 0
 117 -> 127 6.35 % -9 -> 0
 126 -> 129 4.17 % 0 -> 2

Excited State: 24

3.9133 eV 316.83 nm 31563.cm-1 f=0.0003
 116 -> 128 6.86 % -10 -> 1
 124 -> 130 2.00 % -2 -> 3
 125 -> 129 4.05 % -1 -> 2
 125 -> 130 80.08 % -1 -> 3

Excited State: 25

3.9774 eV 311.72 nm 32080.cm-1 f=0.0002
 124 -> 129 5.35 % -2 -> 2
 124 -> 130 80.27 % -2 -> 3

Excited State: 26

3.9912 eV 310.64 nm 32192.cm-1 f=0.0011
 113 -> 128 3.12 % -13 -> 1
 114 -> 128 58.49 % -12 -> 1
 118 -> 128 8.50 % -8 -> 1
 124 -> 130 2.80 % -2 -> 3
 125 -> 129 13.02 % -1 -> 2

Excited State: 27

4.0078 eV 309.36 nm 32325.cm-1 f=0.0002
 114 -> 128 10.76 % -12 -> 1
 124 -> 129 3.24 % -2 -> 2
 125 -> 129 78.45 % -1 -> 2
 125 -> 130 2.82 % -1 -> 3

Excited State: 28

4.0251 eV 308.03 nm 32464.cm-1 f=0.0072
 114 -> 128 2.98 % -12 -> 1
 115 -> 127 47.34 % -11 -> 0
 116 -> 127 9.01 % -10 -> 0
 126 -> 131 33.39 % 0 -> 4

Excited State: 29

4.0626 eV 305.19 nm 32766.cm-1 f=0.0011
 124 -> 129 88.98 % -2 -> 2
 124 -> 130 4.13 % -2 -> 3
 125 -> 129 2.00 % -1 -> 2

Excited State: 30

4.1152 eV 301.28 nm 33192.cm-1 f=0.0005
 114 -> 127 93.34 % -12 -> 0

Excited State: 31

4.2044 eV 294.89 nm 33911.cm-1 f=0.0260
 115 -> 128 49.57 % -11 -> 1
 116 -> 128 30.50 % -10 -> 1
 122 -> 130 3.81 % -4 -> 3
 123 -> 129 4.70 % -3 -> 2

Excited State: 32

4.2465 eV 291.97 nm 34250.cm-1 f=0.0018
 114 -> 129 3.23 % -12 -> 2
 115 -> 128 6.45 % -11 -> 1
 121 -> 129 3.18 % -5 -> 2
 123 -> 129 81.19 % -3 -> 2

Excited State: 33

4.2600 eV 291.05 nm 34358.cm-1 f=0.0131
 113 -> 128 7.76 % -13 -> 1
 115 -> 128 8.95 % -11 -> 1
 121 -> 129 3.12 % -5 -> 2
 121 -> 130 14.59 % -5 -> 3
 122 -> 129 7.16 % -4 -> 2
 122 -> 130 43.11 % -4 -> 3
 123 -> 130 2.93 % -3 -> 3
 124 -> 130 3.08 % -2 -> 3

Excited State: 34
 4.2724 eV 290.20 nm 34459.cm-1 f=0.0054
 113 -> 128 24.03 % -13 -> 1
 115 -> 128 2.13 % -11 -> 1
 122 -> 129 13.82 % -4 -> 2
 122 -> 130 19.16 % -4 -> 3
 123 -> 129 4.22 % -3 -> 2
 123 -> 130 23.46 % -3 -> 3

Excited State: 35
 4.3193 eV 287.04 nm 34838.cm-1 f=0.1490
 115 -> 127 26.54 % -11 -> 0
 117 -> 127 5.59 % -9 -> 0
 126 -> 131 44.13 % 0 -> 4
 126 -> 133 2.96 % 0 -> 6

Excited State: 36
 4.3759 eV 283.33 nm 35295.cm-1 f=0.0042
 121 -> 129 43.74 % -5 -> 2
 121 -> 130 19.44 % -5 -> 3
 122 -> 129 2.90 % -4 -> 2
 122 -> 130 12.70 % -4 -> 3
 123 -> 130 16.61 % -3 -> 3

Excited State: 37
 4.3828 eV 282.89 nm 35349.cm-1 f=0.0127
 113 -> 128 17.75 % -13 -> 1
 121 -> 129 9.70 % -5 -> 2
 122 -> 129 12.44 % -4 -> 2
 123 -> 130 50.08 % -3 -> 3

Excited State: 38
 4.4021 eV 281.65 nm 35505.cm-1 f=0.0049
 113 -> 128 6.97 % -13 -> 1
 121 -> 129 17.70 % -5 -> 2
 121 -> 130 48.15 % -5 -> 3
 122 -> 129 12.35 % -4 -> 2
 122 -> 130 6.65 % -4 -> 3

Excited State: 39
 4.4206 eV 280.47 nm 35654.cm-1 f=0.0509
 115 -> 128 4.30 % -11 -> 1
 116 -> 128 3.71 % -10 -> 1
 119 -> 130 48.56 % -7 -> 3
 120 -> 130 22.37 % -6 -> 3
 121 -> 129 2.97 % -5 -> 2
 122 -> 130 2.67 % -4 -> 3
 126 -> 130 2.61 % 0 -> 3

Excited State: 40
 4.5606 eV 271.86 nm 36784.cm-1 f=0.0250
 110 -> 128 3.63 % -16 -> 1
 113 -> 128 15.32 % -13 -> 1
 114 -> 128 4.95 % -12 -> 1
 119 -> 129 3.10 % -7 -> 2
 121 -> 129 12.46 % -5 -> 2
 121 -> 130 7.47 % -5 -> 3
 122 -> 129 31.04 % -4 -> 2
 126 -> 132 2.23 % 0 -> 5

Excited State: 41
 4.5782 eV 270.82 nm 36925.cm-1 f=0.0062
 125 -> 131 95.91 % -1 -> 4

Excited State: 42
 4.5999 eV 269.54 nm 37100.cm-1 f=0.0043
 120 -> 131 2.29 % -6 -> 4
 126 -> 131 2.79 % 0 -> 4
 126 -> 132 65.21 % 0 -> 5
 126 -> 133 12.66 % 0 -> 6

Excited State: 43
 4.6471 eV 266.80 nm 37481.cm-1 f=0.0021
 124 -> 131 94.53 % -2 -> 4

Excited State: 44
 4.6879 eV 264.48 nm 37810.cm-1 f=0.5261

109 -> 128 2.51 % -17 -> 1
 115 -> 128 10.64 % -11 -> 1
 116 -> 128 26.49 % -10 -> 1
 116 -> 130 3.98 % -10 -> 3
 119 -> 130 9.67 % -7 -> 3
 121 -> 130 2.27 % -5 -> 3
 122 -> 130 6.00 % -4 -> 3
 125 -> 130 4.84 % -1 -> 3

Excited State: 45
 4.7631 eV 260.30 nm 38417.cm-1 f=0.0067
 109 -> 128 4.00 % -17 -> 1
 111 -> 128 48.34 % -15 -> 1
 112 -> 128 11.46 % -14 -> 1
 113 -> 127 7.36 % -13 -> 0
 115 -> 128 3.53 % -11 -> 1
 126 -> 133 5.53 % 0 -> 6

Excited State: 46
 4.7662 eV 260.13 nm 38442.cm-1 f=0.0148
 111 -> 128 5.03 % -15 -> 1
 113 -> 127 2.51 % -13 -> 0
 119 -> 131 5.71 % -7 -> 4
 120 -> 129 4.74 % -6 -> 2
 120 -> 131 5.63 % -6 -> 4
 126 -> 132 15.38 % 0 -> 5
 126 -> 133 45.75 % 0 -> 6

Excited State: 47
 4.7741 eV 259.70 nm 38506.cm-1 f=0.0013
 111 -> 128 6.23 % -15 -> 1
 113 -> 127 74.90 % -13 -> 0
 118 -> 131 6.78 % -8 -> 4

Excited State: 48
 4.7909 eV 258.79 nm 38641.cm-1 f=0.0320
 119 -> 129 37.59 % -7 -> 2
 120 -> 129 44.27 % -6 -> 2
 126 -> 133 3.56 % 0 -> 6

Excited State: 49
 4.8534 eV 255.46 nm 39145.cm-1 f=0.0014
 113 -> 127 9.57 % -13 -> 0
 118 -> 127 2.99 % -8 -> 0
 118 -> 131 51.51 % -8 -> 4
 123 -> 131 26.61 % -3 -> 4

Excited State: 50
 4.8773 eV 254.21 nm 39338.cm-1 f=0.0073
 117 -> 130 5.43 % -9 -> 3
 119 -> 129 3.58 % -7 -> 2
 119 -> 130 23.44 % -7 -> 3
 120 -> 129 2.42 % -6 -> 2
 120 -> 130 59.81 % -6 -> 3

Excited State: 51
 4.9139 eV 252.31 nm 39634.cm-1 f=0.0022
 114 -> 129 10.79 % -12 -> 2
 118 -> 129 5.69 % -8 -> 2
 118 -> 131 16.06 % -8 -> 4
 123 -> 131 59.22 % -3 -> 4

Excited State: 52
 4.9416 eV 250.90 nm 39857.cm-1 f=0.0133
 119 -> 129 45.95 % -7 -> 2
 119 -> 130 2.50 % -7 -> 3
 120 -> 129 37.66 % -6 -> 2
 120 -> 130 3.49 % -6 -> 3
 123 -> 131 2.04 % -3 -> 4

Excited State: 53
 4.9663 eV 249.65 nm 40056.cm-1 f=0.0129
 114 -> 129 56.80 % -12 -> 2
 118 -> 129 13.38 % -8 -> 2
 118 -> 131 6.56 % -8 -> 4
 119 -> 129 2.54 % -7 -> 2
 123 -> 129 2.86 % -3 -> 2

123 -> 131 8.84 % -3 -> 4

Excited State: 54

4.9883 eV 248.55 nm 40233.cm-1 f=0.0046

121 -> 131 65.11 % -5 -> 4

122 -> 131 31.84 % -4 -> 4

Excited State: 55

5.0307 eV 246.45 nm 40576.cm-1 f=0.1102

118 -> 130 4.13 % -8 -> 3

120 -> 131 38.31 % -6 -> 4

121 -> 131 16.30 % -5 -> 4

122 -> 131 26.07 % -4 -> 4

126 -> 133 3.35 % 0 -> 6

Excited State: 56

5.0960 eV 243.29 nm 41103.cm-1 f=0.1621

118 -> 130 3.16 % -8 -> 3

120 -> 131 29.73 % -6 -> 4

121 -> 131 14.96 % -5 -> 4

122 -> 131 37.66 % -4 -> 4

126 -> 133 5.08 % 0 -> 6

Excited State: 57

5.1376 eV 241.33 nm 41437.cm-1 f=0.0015

125 -> 132 89.89 % -1 -> 5

125 -> 133 3.01 % -1 -> 6

Excited State: 58

5.1610 eV 240.23 nm 41627.cm-1 f=0.0259

110 -> 127 47.22 % -16 -> 0

116 -> 130 2.26 % -10 -> 3

117 -> 130 34.59 % -9 -> 3

Excited State: 59

5.1889 eV 238.94 nm 41852.cm-1 f=0.0947

110 -> 130 2.46 % -16 -> 3

113 -> 130 16.45 % -13 -> 3

114 -> 130 4.91 % -12 -> 3

118 -> 130 48.72 % -8 -> 3

120 -> 131 6.07 % -6 -> 4

124 -> 132 5.54 % -2 -> 5

Excited State: 60

5.2117 eV 237.90 nm 42034.cm-1 f=0.0155

109 -> 128 3.86 % -17 -> 1

110 -> 127 35.41 % -16 -> 0

116 -> 130 2.98 % -10 -> 3

117 -> 130 30.78 % -9 -> 3

124 -> 132 11.74 % -2 -> 5

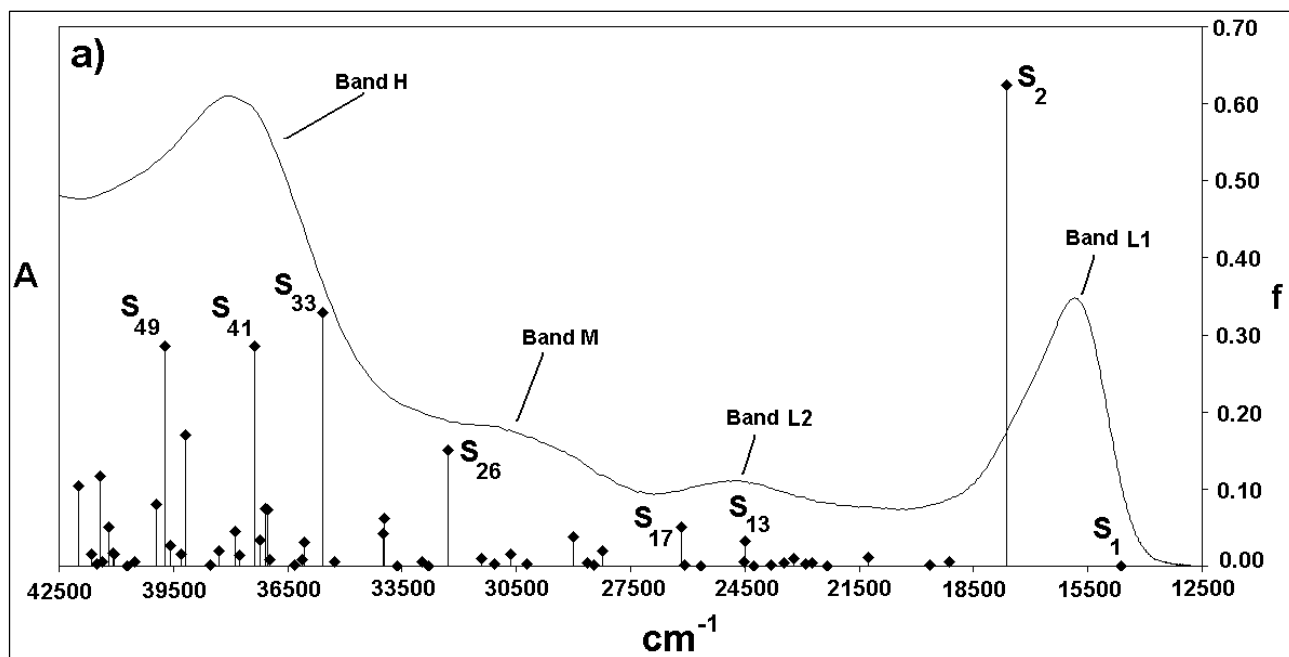


Fig. S9. The following figure compares the $[(acac)_2(NR)Pt]$ (**2a**) experimental spectrum recorded in acetonitrile and the computed electronic transitions in acetonitrile.

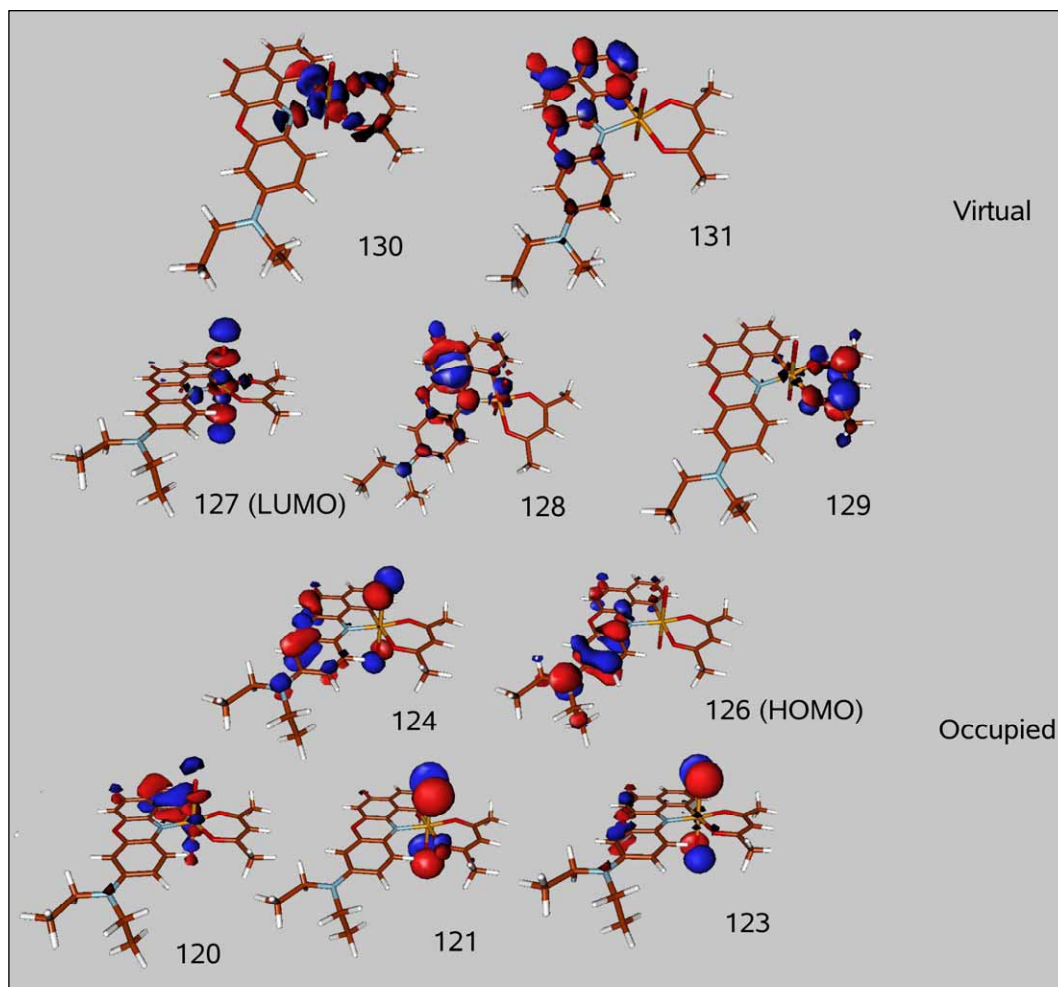


Fig. S10. In the following picture, some 2) Kohn-Sham orbitals are reported that are relevant in describing the low-energy electronic transitions toward S_2 , S_{13} , S_{17} , S_{26} , S_{33} , S_{41} , and S_{49} .

Table S10. Optimized structure of **2a**. Cartesian coordinates in angstrom.

C	-2.116919	1.330585	0.113683	C	-3.234197	-2.600054	-0.105640
C	-1.219952	2.404342	0.113549	C	-4.704414	-2.923226	-0.096889
C	-1.643521	3.739724	0.178190	C	-2.300079	-3.628155	-0.212881
C	-3.011003	3.998130	0.247011	C	6.452847	-1.781723	-0.067295
C	-3.912360	2.928607	0.249613	C	6.545554	-2.158266	1.412934
C	-3.479308	1.595616	0.182511	H	1.530611	5.198707	0.084871
C	-0.627129	4.828572	0.172003	H	-3.351139	5.028126	0.298023
C	0.779166	4.415512	0.096578	H	-4.979736	3.130077	0.304642
C	1.148697	3.110349	0.040749	H	-4.198457	0.782932	0.184703
C	0.161211	2.053101	0.051485	H	4.818776	2.035262	-0.145619
N	0.477639	0.772157	0.010785	H	3.932634	-2.220563	-0.094193
C	1.823461	0.430487	-0.037005	H	1.577747	-1.700631	0.002265
C	2.799218	1.449979	-0.071716	H	-2.690480	-4.635441	-0.288364
O	2.457796	2.770885	-0.035969	H	6.567242	1.417746	-1.037809
C	4.154971	1.180290	-0.137832	H	6.881507	1.195175	0.683408
C	4.625987	-0.151413	-0.179757	H	8.924796	1.262651	-0.672420
C	3.642495	-1.177028	-0.631763	H	8.818113	-0.309487	0.116987
C	2.294576	-0.890757	-0.041069	H	8.429151	-0.148482	-1.612835
N	5.965219	-0.431125	-0.308859	H	7.435168	-1.876937	-0.532098
C	6.906616	0.687855	-0.294162	H	5.814921	-2.490620	-0.602017
C	8.347749	0.333353	-0.633119	H	6.912872	-3.184791	1.520724
Pt	-1.206787	-0.447260	-0.003559	H	7.235959	-1.494453	1.944015
O	-0.265365	-2.383210	-0.146786	H	5.569597	-2.091059	1.903216
C	-0.897992	-3.477308	-0.222866	H	-0.620205	-5.625206	-0.415499
C	-0.034156	-4.708617	-0.326575	H	0.621971	-4.611623	-1.197605
O	-0.943687	6.014290	0.225990	H	0.601278	-4.772320	0.563140
O	-3.010921	-1.338639	-0.005856	H	-4.886334	-3.996006	-0.179212

H -5.149466 -2.548830 0.830624
H -5.189737 -2.406800 -0.931380

I -1.269323 -0.320602 -2.701807
I -1.117264 -0.620619 2.689714

[(NR)Pt(hfacac)I₂], 2b

Table S11. Singlet excited states of **2b**. The computations have been performed by modelling the solvent effects with the PCM model on the structure optimized in vacuum. The following text lists the energy (in eV and nm), the oscillator strengths and percentage composition of the most important mono-electronic excitations for each excited state. Excited States composition has been expressed in two ways. The first one uses the Kohn-Sham orbital numerical label of the occupied and virtual orbital as produced by the computation (for instance, 119 → 120 for the HOMO → LUMO transition when the HOMO is the 119th orbital and the LUMO is the 120th one). The second way assign the “0” label to the HOMO, the “-1” label to the HOMO-1 orbital and so on, the “0” label to the LUMO, “1” to LUMO+1 and so on (thus, 0 → 0 is the HOMO → LUMO transition, -2 → 1 is the HOMO-2 → LUMO+1 transition).

Excited State: 1 1.6179 eV 766.33 nm 13049.cm-1 f=0.0003 150 → 151 98.31 % 0 → 0	148 → 151 4.31 % -2 → 0
Excited State: 2 2.1449 eV 578.05 nm 17300.cm-1 f=0.6229 150 → 152 75.83 % 0 → 1	Excited State: 12 2.9393 eV 421.81 nm 23707.cm-1 f=0.0014 144 → 151 5.50 % -6 → 0 145 → 151 3.05 % -5 → 0 147 → 152 85.93 % -3 → 1
Excited State: 3 2.3099 eV 536.75 nm 18631.cm-1 f=0.0000 147 → 151 33.44 % -3 → 0 148 → 151 49.91 % -2 → 0 149 → 151 5.88 % -1 → 0	Excited State: 13 2.9783 eV 416.29 nm 24022.cm-1 f=0.0000 143 → 152 87.24 % -7 → 1 143 → 155 2.98 % -7 → 4 146 → 152 3.19 % -4 → 1
Excited State: 4 2.3474 eV 528.17 nm 18933.cm-1 f=0.0015 145 → 151 3.00 % -5 → 0 147 → 151 54.67 % -3 → 0 148 → 151 32.84 % -2 → 0	Excited State: 14 3.0707 eV 403.76 nm 24767.cm-1 f=0.0007 150 → 154 94.49 % 0 → 3
Excited State: 5 2.5325 eV 489.58 nm 20426.cm-1 f=0.0128 150 → 153 99.30 % 0 → 2	Excited State: 15 3.1368 eV 395.26 nm 25300.cm-1 f=0.0545 139 → 151 7.93 % -11 → 0 141 → 151 33.12 % -9 → 0 142 → 151 32.76 % -8 → 0 145 → 151 13.06 % -5 → 0
Excited State: 6 2.7120 eV 457.17 nm 21874.cm-1 f=0.0004 145 → 151 5.37 % -5 → 0 146 → 151 80.51 % -4 → 0 148 → 152 4.78 % -2 → 1	Excited State: 16 3.2385 eV 382.85 nm 26120.cm-1 f=0.0006 143 → 152 3.51 % -7 → 1 145 → 152 2.27 % -5 → 1 146 → 152 91.48 % -4 → 1
Excited State: 7 2.7438 eV 451.87 nm 22130.cm-1 f=0.0005 147 → 151 2.26 % -3 → 0 148 → 151 3.21 % -2 → 0 149 → 151 90.88 % -1 → 0	Excited State: 17 3.2630 eV 379.97 nm 26318.cm-1 f=0.0318 144 → 152 24.49 % -6 → 1 145 → 152 65.25 % -5 → 1 146 → 152 3.33 % -4 → 1
Excited State: 8 2.7688 eV 447.78 nm 22332.cm-1 f=0.0009 144 → 151 85.49 % -6 → 0 147 → 152 6.11 % -3 → 1	Excited State: 18 3.2670 eV 379.51 nm 26350.cm-1 f=0.0110 144 → 152 72.05 % -6 → 1 145 → 152 24.10 % -5 → 1
Excited State: 9 2.7759 eV 446.65 nm 22389.cm-1 f=0.0120 141 → 152 2.93 % -9 → 1 149 → 152 85.86 % -1 → 1	Excited State: 19 3.3494 eV 370.17 nm 27015.cm-1 f=0.0001 148 → 153 93.55 % -2 → 2 149 → 153 3.80 % -1 → 2
Excited State: 10 2.8865 eV 429.52 nm 23282.cm-1 f=0.0073 146 → 151 4.50 % -4 → 0 148 → 152 91.78 % -2 → 1	Excited State: 20 3.3771 eV 367.13 nm 27238.cm-1 f=0.0397 139 → 151 2.39 % -11 → 0 141 → 151 61.14 % -9 → 0 142 → 151 25.12 % -8 → 0 145 → 151 3.99 % -5 → 0
Excited State: 11 2.9369 eV 422.17 nm 23687.cm-1 f=0.0128 142 → 151 25.44 % -8 → 0 145 → 151 53.92 % -5 → 0 146 → 151 2.68 % -4 → 0 147 → 152 6.07 % -3 → 1	Excited State: 21 3.3934 eV 365.37 nm 27370.cm-1 f=0.0007 147 → 153 92.75 % -3 → 2

149 -> 153	6.60 %	-1 -> 2		
Excited State: 22				
3.4964 eV	354.60 nm	28201.cm-1	f=0.0001	
143 -> 151	96.49 %	-7 -> 0		
Excited State: 23				
3.5808 eV	346.24 nm	28882.cm-1	f=0.0384	
140 -> 152	19.44 %	-10 -> 1		
141 -> 152	61.15 %	-9 -> 1		
150 -> 155	8.96 %	0 -> 4		
Excited State: 24				
3.5885 eV	345.51 nm	28943.cm-1	f=0.0003	
142 -> 152	93.64 %	-8 -> 1		
Excited State: 25				
3.6482 eV	339.85 nm	29425.cm-1	f=0.0004	
146 -> 153	21.54 %	-4 -> 2		
147 -> 153	4.55 %	-3 -> 2		
148 -> 153	3.36 %	-2 -> 2		
149 -> 153	66.07 %	-1 -> 2		
Excited State: 26				
3.6536 eV	339.35 nm	29468.cm-1	f=0.0001	
144 -> 153	7.46 %	-6 -> 2		
145 -> 153	5.30 %	-5 -> 2		
146 -> 153	59.69 %	-4 -> 2		
149 -> 153	21.83 %	-1 -> 2		
Excited State: 27				
3.7227 eV	333.05 nm	30026.cm-1	f=0.0084	
140 -> 151	82.40 %	-10 -> 0		
144 -> 153	10.53 %	-6 -> 2		
148 -> 154	2.80 %	-2 -> 3		
Excited State: 28				
3.7321 eV	332.21 nm	30101.cm-1	f=0.0018	
140 -> 151	9.15 %	-10 -> 0		
144 -> 153	79.45 %	-6 -> 2		
146 -> 153	8.84 %	-4 -> 2		
Excited State: 29				
3.7689 eV	328.97 nm	30398.cm-1	f=0.0047	
140 -> 152	65.35 %	-10 -> 1		
141 -> 152	7.47 %	-9 -> 1		
150 -> 155	20.78 %	0 -> 4		
Excited State: 30				
3.8483 eV	322.18 nm	31039.cm-1	f=0.0116	
142 -> 153	3.99 %	-8 -> 2		
145 -> 153	82.60 %	-5 -> 2		
146 -> 153	5.56 %	-4 -> 2		
Excited State: 31				
3.8578 eV	321.38 nm	31116.cm-1	f=0.0005	
139 -> 151	6.26 %	-11 -> 0		
140 -> 151	2.95 %	-10 -> 0		
145 -> 154	4.28 %	-5 -> 3		
148 -> 154	78.05 %	-2 -> 3		
149 -> 154	3.98 %	-1 -> 3		
Excited State: 32				
3.9167 eV	316.56 nm	31590.cm-1	f=0.0008	
147 -> 154	90.51 %	-3 -> 3		
149 -> 154	3.02 %	-1 -> 3		
Excited State: 33				
4.0020 eV	309.81 nm	32278.cm-1	f=0.1988	
139 -> 152	2.28 %	-11 -> 1		
140 -> 152	8.00 %	-10 -> 1		
141 -> 152	14.92 %	-9 -> 1		
150 -> 155	58.62 %	0 -> 4		
Excited State: 34				
4.0698 eV	304.64 nm	32826.cm-1	f=0.0215	
138 -> 151	12.72 %	-12 -> 0		
141 -> 153	3.82 %	-9 -> 2		
142 -> 153	60.52 %	-8 -> 2		
144 -> 154	2.10 %	-6 -> 3		
145 -> 153	6.03 %	-5 -> 2		
Excited State: 35				
4.1171 eV	301.15 nm	33206.cm-1	f=0.0106	
139 -> 151	6.83 %	-11 -> 0		
145 -> 154	72.35 %	-5 -> 3		
146 -> 154	6.25 %	-4 -> 3		
148 -> 154	4.46 %	-2 -> 3		
149 -> 154	3.68 %	-1 -> 3		
Excited State: 36				
4.2096 eV	294.52 nm	33954.cm-1	f=0.0086	
136 -> 151	18.92 %	-14 -> 0		
138 -> 151	58.94 %	-12 -> 0		
142 -> 153	6.18 %	-8 -> 2		
146 -> 154	3.84 %	-4 -> 3		
Excited State: 37				
4.2192 eV	293.85 nm	34031.cm-1	f=0.0001	
145 -> 154	4.95 %	-5 -> 3		
147 -> 154	3.17 %	-3 -> 3		
149 -> 154	86.60 %	-1 -> 3		
Excited State: 38				
4.2964 eV	288.58 nm	34652.cm-1	f=0.0003	
141 -> 153	72.89 %	-9 -> 2		
142 -> 153	8.71 %	-8 -> 2		
146 -> 154	12.89 %	-4 -> 3		
Excited State: 39				
4.3231 eV	286.80 nm	34868.cm-1	f=0.0051	
141 -> 153	6.31 %	-9 -> 2		
144 -> 154	32.73 %	-6 -> 3		
145 -> 154	4.03 %	-5 -> 3		
146 -> 154	52.51 %	-4 -> 3		
Excited State: 40				
4.3458 eV	285.29 nm	35052.cm-1	f=0.0033	
138 -> 153	17.90 %	-12 -> 2		
142 -> 154	2.09 %	-8 -> 3		
143 -> 153	72.56 %	-7 -> 2		
Excited State: 41				
4.3547 eV	284.71 nm	35123.cm-1	f=0.0091	
136 -> 151	3.14 %	-14 -> 0		
141 -> 153	9.21 %	-9 -> 2		
143 -> 153	2.58 %	-7 -> 2		
144 -> 154	56.64 %	-6 -> 3		
146 -> 154	17.22 %	-4 -> 3		
Excited State: 42				
4.3962 eV	282.03 nm	35457.cm-1	f=0.0574	
139 -> 151	11.81 %	-11 -> 0		
141 -> 154	6.11 %	-9 -> 3		
142 -> 154	66.18 %	-8 -> 3		
143 -> 153	2.72 %	-7 -> 2		
148 -> 154	2.63 %	-2 -> 3		
Excited State: 43				
4.4105 eV	281.11 nm	35573.cm-1	f=0.0051	
139 -> 152	84.22 %	-11 -> 1		
150 -> 156	4.70 %	0 -> 5		
150 -> 157	3.59 %	0 -> 6		
Excited State: 44				
4.4520 eV	278.49 nm	35908.cm-1	f=0.0286	
139 -> 152	7.61 %	-11 -> 1		
150 -> 156	72.31 %	0 -> 5		
150 -> 157	9.65 %	0 -> 6		
Excited State: 45				
4.5651 eV	271.59 nm	36820.cm-1	f=0.4584	
132 -> 151	4.17 %	-18 -> 0		
138 -> 152	4.68 %	-12 -> 1		

138 -> 153	7.70 %	-12 -> 2			
139 -> 151	28.16 %	-11 -> 0			
139 -> 154	2.88 %	-11 -> 3			
141 -> 154	13.47 %	-9 -> 3			
142 -> 154	5.40 %	-8 -> 3			
143 -> 153	4.41 %	-7 -> 2			
145 -> 151	2.65 %	-5 -> 0			
145 -> 154	3.71 %	-5 -> 3			
148 -> 154	3.01 %	-2 -> 3			
Excited State: 46					
4.5775 eV	270.86 nm	36919.cm-1	f=0.0089		
124 -> 151	2.37 %	-26 -> 0			
136 -> 151	50.99 %	-14 -> 0			
138 -> 151	15.28 %	-12 -> 0			
139 -> 153	4.97 %	-11 -> 2			
140 -> 153	9.39 %	-10 -> 2			
142 -> 153	2.54 %	-8 -> 2			
Excited State: 47					
4.5930 eV	269.94 nm	37045.cm-1	f=0.1170		
138 -> 152	18.05 %	-12 -> 1			
138 -> 153	41.71 %	-12 -> 2			
139 -> 151	6.48 %	-11 -> 0			
141 -> 154	2.71 %	-9 -> 3			
143 -> 153	14.74 %	-7 -> 2			
Excited State: 48					
4.5935 eV	269.91 nm	37049.cm-1	f=0.0121		
149 -> 155	15.81 %	-1 -> 4			
150 -> 156	11.09 %	0 -> 5			
150 -> 157	60.72 %	0 -> 6			
Excited State: 49					
4.6420 eV	267.09 nm	37441.cm-1	f=0.0042		
136 -> 151	4.81 %	-14 -> 0			
138 -> 151	2.18 %	-12 -> 0			
140 -> 153	88.51 %	-10 -> 2			
Excited State: 50					
4.7009 eV	263.75 nm	37915.cm-1	f=0.1105		
138 -> 152	6.99 %	-12 -> 1			
139 -> 151	5.77 %	-11 -> 0			
140 -> 154	2.53 %	-10 -> 3			
141 -> 154	61.03 %	-9 -> 3			
142 -> 154	13.19 %	-8 -> 3			
Excited State: 51					
4.7090 eV	263.29 nm	37981.cm-1	f=0.0087		
138 -> 152	61.72 %	-12 -> 1			
138 -> 153	20.12 %	-12 -> 2			
141 -> 154	7.46 %	-9 -> 3			
143 -> 155	2.07 %	-7 -> 4			
Excited State: 52					
4.8450 eV	255.90 nm	39078.cm-1	f=0.0992		
130 -> 151	11.51 %	-20 -> 0			
525.29 nm	39171.cm-1	f=0.4280			
143 -> 154	7.70 %	-7 -> 3			
148 -> 155	3.83 %	-2 -> 4			
149 -> 155	63.36 %	-1 -> 4			
150 -> 156	2.17 %	0 -> 5			
150 -> 157	12.85 %	0 -> 6			
Excited State: 54					
4.9353 eV	251.22 nm	39806.cm-1	f=0.0492		
139 -> 153	6.68 %	-11 -> 2			
143 -> 154	20.37 %	-7 -> 3			
148 -> 155	57.61 %	-2 -> 4			
149 -> 155	7.59 %	-1 -> 4			
Excited State: 55					
4.9552 eV	250.21 nm	39966.cm-1	f=0.0103		
136 -> 154	2.10 %	-14 -> 3			
137 -> 152	2.95 %	-13 -> 1			
139 -> 153	8.33 %	-11 -> 2			
143 -> 154	43.55 %	-7 -> 3			
148 -> 155	35.50 %	-2 -> 4			
Excited State: 56					
5.0038 eV	247.78 nm	40358.cm-1	f=0.0490		
139 -> 153	38.17 %	-11 -> 2			
143 -> 154	10.25 %	-7 -> 3			
147 -> 155	36.58 %	-3 -> 4			
Excited State: 57					
5.0118 eV	247.38 nm	40424.cm-1	f=0.0000		
138 -> 152	3.72 %	-12 -> 1			
143 -> 152	3.92 %	-7 -> 1			
143 -> 155	80.30 %	-7 -> 4			
146 -> 155	2.61 %	-4 -> 4			
Excited State: 58					
5.0156 eV	247.20 nm	40453.cm-1	f=0.0006		
130 -> 151	9.17 %	-20 -> 0			
132 -> 151	28.95 %	-18 -> 0			
137 -> 151	52.23 %	-13 -> 0			
Excited State: 59					
5.0254 eV	246.71 nm	40533.cm-1	f=0.1302		
139 -> 153	21.92 %	-11 -> 2			
143 -> 154	7.26 %	-7 -> 3			
147 -> 155	59.22 %	-3 -> 4			
Excited State: 60					
5.0844 eV	243.85 nm	41009.cm-1	f=0.0185		
137 -> 152	84.78 %	-13 -> 1			
139 -> 153	2.22 %	-11 -> 2			

Table S12. Singlet excited states of **2b**. The computations have been made in vacuum.

Excited State: 1					
1.9877 eV	623.77 nm	16032.cm-1	f=0.0002		
150 -> 152	95.15 %	0 -> 1			
Excited State: 2					
2.1779 eV	569.29 nm	17566.cm-1	f=0.0001		
148 -> 152	7.23 %	-2 -> 1			
149 -> 152	80.11 %	-1 -> 1			
150 -> 152	2.50 %	0 -> 1			
Excited State: 3					
2.2294 eV	556.12 nm	17982.cm-1	f=0.0006		
148 -> 152	81.01 %	-2 -> 1			
149 -> 152	7.35 %	-1 -> 1			
Excited State: 4					
2.3548 eV	526.52 nm	18993.cm-1	f=0.4776		
150 -> 151	73.88 %	0 -> 0			
Excited State: 5					
2.4977 eV	496.40 nm	20145.cm-1	f=0.0015		
147 -> 152	18.05 %	-3 -> 1			
149 -> 151	78.13 %	-1 -> 0			
Excited State: 6					
2.5653 eV	483.32 nm	20690.cm-1	f=0.0043		
145 -> 152	14.39 %	-5 -> 1			
148 -> 151	79.50 %	-2 -> 0			
Excited State: 7					

2.6014 eV	476.60 nm	20982.cm-1	f=0.0012	
147 -> 152	72.33 %	-3 -> 1		
149 -> 151	19.86 %	-1 -> 0		
Excited State: 8				
2.6735 eV	463.75 nm	21563.cm-1	f=0.0011	
145 -> 152	77.21 %	-5 -> 1		
148 -> 151	16.98 %	-2 -> 0		
Excited State: 9				
2.7298 eV	454.18 nm	22018.cm-1	f=0.0000	
143 -> 151	87.24 %	-7 -> 0		
143 -> 155	2.97 %	-7 -> 4		
147 -> 151	2.97 %	-3 -> 0		
Excited State: 10				
2.7838 eV	445.38 nm	22453.cm-1	f=0.0088	
150 -> 153	99.10 %	0 -> 2		
Excited State: 11				
2.8825 eV	430.13 nm	23249.cm-1	f=0.0002	
143 -> 151	2.92 %	-7 -> 0		
147 -> 151	95.42 %	-3 -> 0		
Excited State: 12				
2.9267 eV	423.64 nm	23605.cm-1	f=0.0000	
145 -> 151	97.48 %	-5 -> 0		
Excited State: 13				
2.9337 eV	422.62 nm	23662.cm-1	f=0.0126	
141 -> 151	4.07 %	-9 -> 0		
144 -> 151	5.97 %	-6 -> 0		
146 -> 151	79.49 %	-4 -> 0		
Excited State: 14				
3.0339 eV	408.67 nm	24470.cm-1	f=0.0087	
142 -> 152	32.71 %	-8 -> 1		
144 -> 152	12.28 %	-6 -> 1		
146 -> 152	47.50 %	-4 -> 1		
Excited State: 15				
3.0609 eV	405.05 nm	24688.cm-1	f=0.0007	
149 -> 153	97.97 %	-1 -> 2		
Excited State: 16				
3.1222 eV	397.10 nm	25183.cm-1	f=0.0050	
142 -> 152	5.72 %	-8 -> 1		
144 -> 152	51.08 %	-6 -> 1		
146 -> 152	36.55 %	-4 -> 1		
Excited State: 17				
3.1227 eV	397.04 nm	25186.cm-1	f=0.0003	
148 -> 153	97.27 %	-2 -> 2		
Excited State: 18				
3.1448 eV	394.26 nm	25364.cm-1	f=0.0457	
144 -> 151	85.23 %	-6 -> 0		
146 -> 151	5.29 %	-4 -> 0		
Excited State: 19				
3.2657 eV	379.66 nm	26339.cm-1	f=0.0474	
139 -> 152	9.05 %	-11 -> 1		
140 -> 152	3.02 %	-10 -> 1		
141 -> 152	9.24 %	-9 -> 1		
142 -> 152	42.39 %	-8 -> 1		
144 -> 152	11.07 %	-6 -> 1		
146 -> 152	7.97 %	-4 -> 1		
147 -> 153	4.33 %	-3 -> 2		
149 -> 154	2.20 %	-1 -> 3		
Excited State: 20				
3.3424 eV	370.94 nm	26959.cm-1	f=0.0013	
150 -> 154	92.13 %	0 -> 3		
Excited State: 21				
3.3811 eV	366.70 nm	27270.cm-1	f=0.0020	
145 -> 153	7.52 %	-5 -> 2		
147 -> 153	85.81 %	-3 -> 2		
Excited State: 22				
3.4560 eV	358.75 nm	27875.cm-1	f=0.0002	
145 -> 153	91.73 %	-5 -> 2		
147 -> 153	7.28 %	-3 -> 2		
Excited State: 23				
3.4780 eV	356.48 nm	28052.cm-1	f=0.0063	
142 -> 151	91.44 %	-8 -> 0		
143 -> 152	2.88 %	-7 -> 1		
Excited State: 24				
3.4899 eV	355.27 nm	28148.cm-1	f=0.0005	
142 -> 151	2.82 %	-8 -> 0		
143 -> 152	95.20 %	-7 -> 1		
Excited State: 25				
3.5792 eV	346.40 nm	28868.cm-1	f=0.0067	
141 -> 152	53.09 %	-9 -> 1		
149 -> 154	39.83 %	-1 -> 3		
Excited State: 26				
3.6457 eV	340.08 nm	29405.cm-1	f=0.0221	
140 -> 151	14.59 %	-10 -> 0		
141 -> 151	69.04 %	-9 -> 0		
146 -> 151	2.45 %	-4 -> 0		
150 -> 155	4.35 %	0 -> 4		
Excited State: 27				
3.6627 eV	338.50 nm	29542.cm-1	f=0.0182	
139 -> 152	6.33 %	-11 -> 1		
140 -> 152	3.29 %	-10 -> 1		
141 -> 152	31.75 %	-9 -> 1		
149 -> 154	48.03 %	-1 -> 3		
Excited State: 28				
3.7061 eV	334.54 nm	29892.cm-1	f=0.0018	
148 -> 154	94.40 %	-2 -> 3		
Excited State: 29				
3.7131 eV	333.91 nm	29948.cm-1	f=0.0058	
142 -> 153	2.38 %	-8 -> 2		
144 -> 153	57.42 %	-6 -> 2		
146 -> 153	34.82 %	-4 -> 2		
Excited State: 30				
3.8792 eV	319.61 nm	31288.cm-1	f=0.0049	
140 -> 151	12.72 %	-10 -> 0		
144 -> 153	25.07 %	-6 -> 2		
146 -> 153	53.11 %	-4 -> 2		
150 -> 155	2.05 %	0 -> 4		
Excited State: 31				
3.8962 eV	318.22 nm	31425.cm-1	f=0.0051	
140 -> 151	55.29 %	-10 -> 0		
141 -> 151	6.46 %	-9 -> 0		
144 -> 153	7.31 %	-6 -> 2		
146 -> 153	9.97 %	-4 -> 2		
150 -> 155	15.14 %	0 -> 4		
Excited State: 32				
4.0228 eV	308.21 nm	32445.cm-1	f=0.0182	
140 -> 152	78.35 %	-10 -> 1		
144 -> 154	12.47 %	-6 -> 3		
146 -> 154	2.70 %	-4 -> 3		
Excited State: 33				
4.0397 eV	306.91 nm	32583.cm-1	f=0.0026	
142 -> 153	48.28 %	-8 -> 2		
144 -> 153	5.79 %	-6 -> 2		
145 -> 154	16.32 %	-5 -> 3		
147 -> 154	18.75 %	-3 -> 3		
Excited State: 34				
4.0771 eV	304.10 nm	32884.cm-1	f=0.0033	
142 -> 153	4.70 %	-8 -> 2		

145 -> 154	20.28 %	-5 -> 3		
147 -> 154	71.35 %	-3 -> 3		
Excited State: 35				
4.1035 eV	302.14 nm	33097.cm-1	f=0.0000	
139 -> 152	13.27 %	-11 -> 1		
140 -> 152	10.56 %	-10 -> 1		
144 -> 154	53.44 %	-6 -> 3		
146 -> 154	14.97 %	-4 -> 3		
Excited State: 36				
4.1365 eV	299.73 nm	33363.cm-1	f=0.0057	
138 -> 152	3.75 %	-12 -> 1		
142 -> 153	21.98 %	-8 -> 2		
145 -> 154	59.67 %	-5 -> 3		
147 -> 154	6.00 %	-3 -> 3		
Excited State: 37				
4.1526 eV	298.57 nm	33493.cm-1	f=0.1202	
139 -> 151	23.22 %	-11 -> 0		
140 -> 151	9.44 %	-10 -> 0		
141 -> 151	5.89 %	-9 -> 0		
142 -> 153	2.31 %	-8 -> 2		
150 -> 155	48.48 %	0 -> 4		
Excited State: 38				
4.2183 eV	293.92 nm	34023.cm-1	f=0.0000	
138 -> 153	8.21 %	-12 -> 2		
143 -> 153	90.18 %	-7 -> 2		
Excited State: 39				
4.3138 eV	287.41 nm	34794.cm-1	f=0.0036	
136 -> 152	19.96 %	-14 -> 1		
138 -> 152	64.54 %	-12 -> 1		
Excited State: 40				
4.3459 eV	285.29 nm	35052.cm-1	f=0.0466	
139 -> 151	68.73 %	-11 -> 0		
141 -> 151	2.15 %	-9 -> 0		
150 -> 155	14.80 %	0 -> 4		
150 -> 157	2.55 %	0 -> 6		
Excited State: 41				
4.3874 eV	282.59 nm	35387.cm-1	f=0.0136	
139 -> 152	8.74 %	-11 -> 1		
142 -> 154	81.30 %	-8 -> 3		
Excited State: 42				
4.4204 eV	280.48 nm	35653.cm-1	f=0.0027	
141 -> 153	93.98 %	-9 -> 2		
Excited State: 43				
4.4663 eV	277.60 nm	36023.cm-1	f=0.0021	
141 -> 154	3.75 %	-9 -> 3		
142 -> 154	2.17 %	-8 -> 3		
144 -> 154	19.64 %	-6 -> 3		
146 -> 154	70.46 %	-4 -> 3		
Excited State: 44				
4.5397 eV	273.11 nm	36615.cm-1	f=0.0007	
138 -> 151	33.20 %	-12 -> 0		
138 -> 153	51.00 %	-12 -> 2		
143 -> 153	7.41 %	-7 -> 2		
Excited State: 45				
4.5733 eV	271.11 nm	36885.cm-1	f=0.0041	
150 -> 155	2.49 %	0 -> 4		
150 -> 156	66.30 %	0 -> 5		
150 -> 157	16.00 %	0 -> 6		
Excited State: 46				
4.6274 eV	267.93 nm	37323.cm-1	f=0.0038	
136 -> 152	2.46 %	-14 -> 1		
149 -> 155	90.65 %	-1 -> 4		
Excited State: 47				
4.6444 eV	266.95 nm	37460.cm-1	f=0.0018	
Excited State: 48				
4.6574 eV	266.21 nm	37564.cm-1	f=0.0060	
136 -> 152	44.93 %	-14 -> 1		
136 -> 154	2.28 %	-14 -> 3		
138 -> 152	15.91 %	-12 -> 1		
139 -> 153	8.81 %	-11 -> 2		
140 -> 153	7.35 %	-10 -> 2		
149 -> 155	3.93 %	-1 -> 4		
Excited State: 49				
4.6821 eV	264.80 nm	37764.cm-1	f=0.4649	
134 -> 152	4.72 %	-16 -> 1		
139 -> 152	33.97 %	-11 -> 1		
139 -> 154	7.03 %	-11 -> 3		
141 -> 154	10.04 %	-9 -> 3		
142 -> 152	3.37 %	-8 -> 1		
142 -> 154	6.04 %	-8 -> 3		
144 -> 152	4.93 %	-6 -> 1		
144 -> 154	3.80 %	-6 -> 3		
149 -> 154	2.21 %	-1 -> 3		
Excited State: 50				
4.7009 eV	263.74 nm	37916.cm-1	f=0.0015	
146 -> 155	2.69 %	-4 -> 4		
148 -> 155	70.10 %	-2 -> 4		
150 -> 156	5.09 %	0 -> 5		
150 -> 157	14.80 %	0 -> 6		
Excited State: 51				
4.7373 eV	261.72 nm	38209.cm-1	f=0.0163	
144 -> 155	2.62 %	-6 -> 4		
146 -> 155	6.26 %	-4 -> 4		
148 -> 155	28.12 %	-2 -> 4		
149 -> 155	2.07 %	-1 -> 4		
150 -> 156	14.66 %	0 -> 5		
150 -> 157	36.82 %	0 -> 6		
Excited State: 52				
4.7906 eV	258.80 nm	38640.cm-1	f=0.0047	
136 -> 152	3.94 %	-14 -> 1		
138 -> 152	2.73 %	-12 -> 1		
140 -> 153	88.03 %	-10 -> 2		
Excited State: 53				
4.8313 eV	256.63 nm	38967.cm-1	f=0.0001	
138 -> 151	8.41 %	-12 -> 0		
143 -> 151	3.98 %	-7 -> 0		
143 -> 155	77.77 %	-7 -> 4		
147 -> 155	2.42 %	-3 -> 4		
Excited State: 54				
4.8547 eV	255.39 nm	39156.cm-1	f=0.1150	
139 -> 152	6.34 %	-11 -> 1		
141 -> 154	75.35 %	-9 -> 3		
146 -> 154	5.05 %	-4 -> 3		
Excited State: 55				
4.8624 eV	254.99 nm	39217.cm-1	f=0.0442	
136 -> 152	2.62 %	-14 -> 1		
143 -> 154	85.02 %	-7 -> 3		
150 -> 157	2.77 %	0 -> 6		
Excited State: 56				
4.9884 eV	248.54 nm	40235.cm-1	f=0.0066	
135 -> 152	2.59 %	-15 -> 1		
138 -> 152	2.46 %	-12 -> 1		
139 -> 153	60.84 %	-11 -> 2		
146 -> 155	11.59 %	-4 -> 4		
147 -> 155	4.90 %	-3 -> 4		
Excited State: 57				
4.9900 eV	248.46 nm	40248.cm-1	f=0.0259	
132 -> 152	8.77 %	-18 -> 1		

133 -> 152 6.26 % -17 -> 1
 134 -> 152 38.17 % -16 -> 1
 137 -> 152 4.46 % -13 -> 1
 139 -> 152 2.27 % -11 -> 1
 141 -> 154 2.79 % -9 -> 3
 147 -> 155 22.07 % -3 -> 4

Excited State: 60
 5.0593 eV 245.06 nm 40806.cm-1 f=0.0072
 145 -> 155 96.10 % -5 -> 4

Excited State: 58
 4.9948 eV 248.23 nm 40285.cm-1 f=0.0021
 132 -> 152 3.35 % -18 -> 1
 134 -> 152 12.25 % -16 -> 1
 147 -> 155 68.56 % -3 -> 4

Excited State: 59
 5.0476 eV 245.63 nm 40712.cm-1 f=0.3772
 139 -> 153 9.19 % -11 -> 2
 143 -> 154 4.16 % -7 -> 3
 146 -> 155 63.33 % -4 -> 4
 150 -> 157 7.09 % 0 -> 6

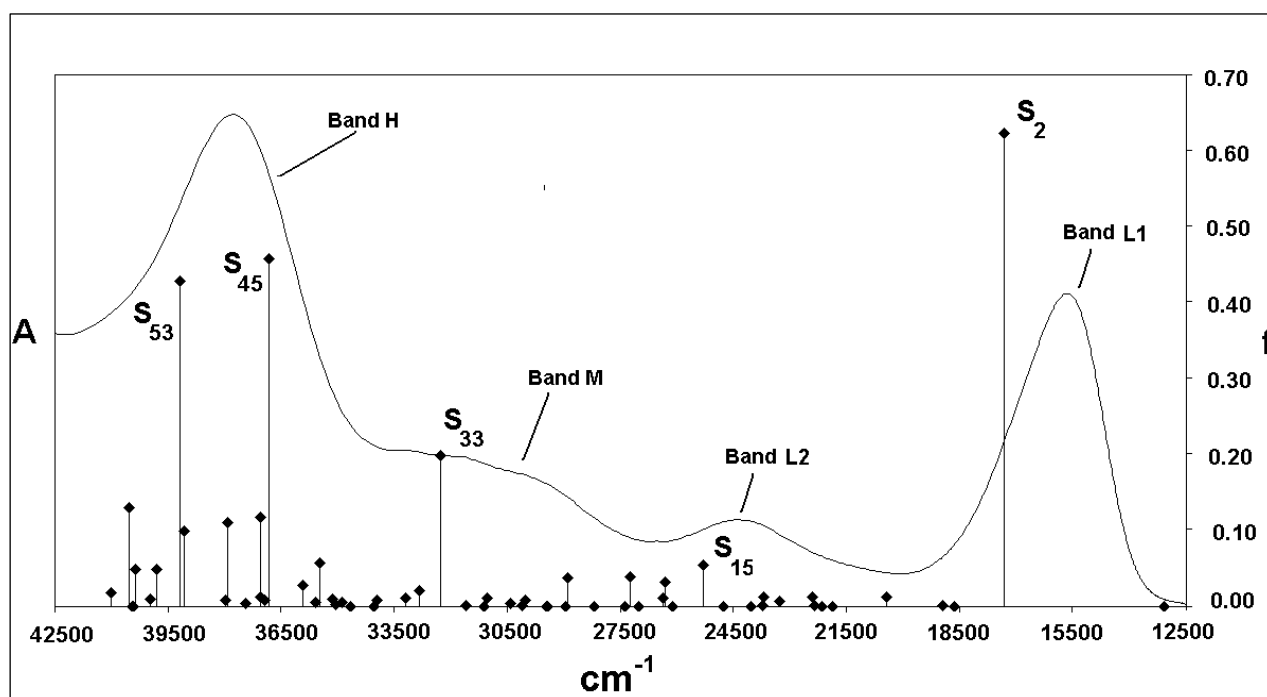


Fig. S11. The following figure compares **2b** the experimental spectrum recorded in acetonitrile and the computed electronic transitions listed above.

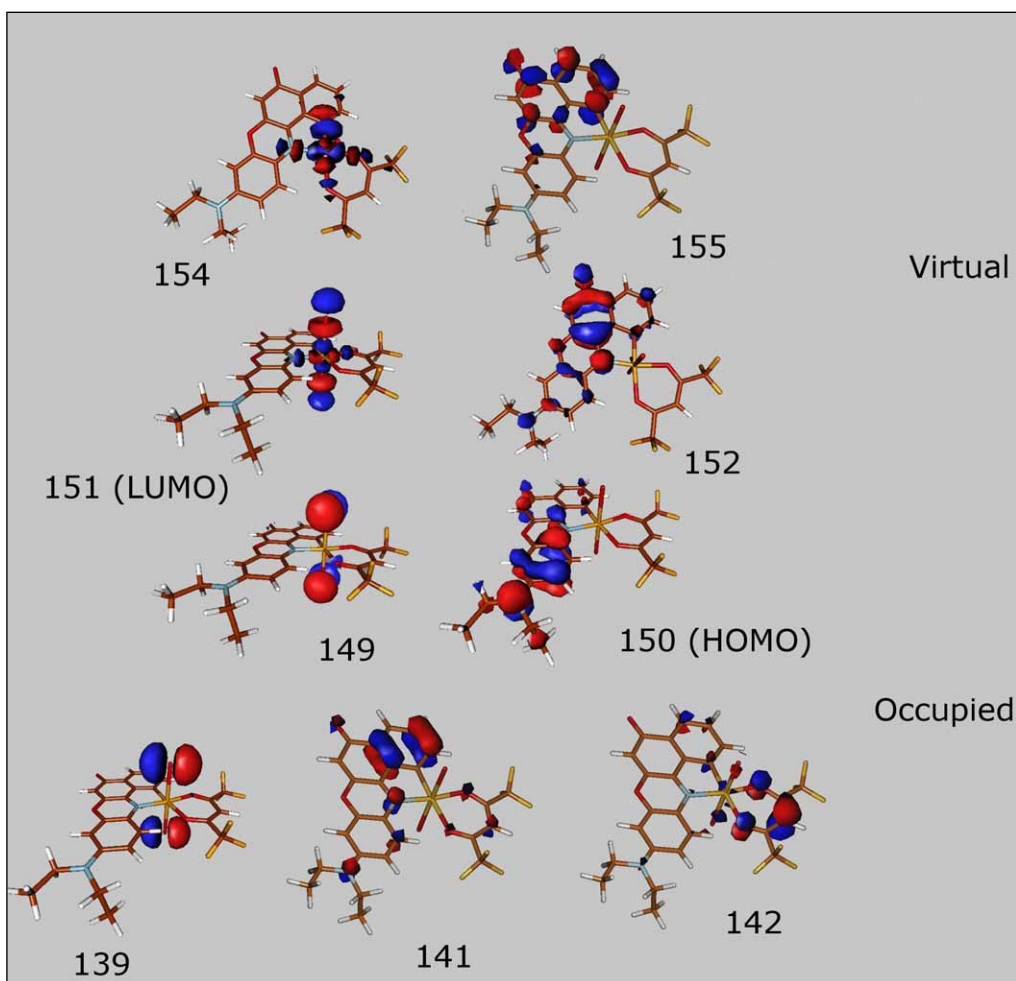


Figure S12. In the following picture, some **2b** Kohn-Sham orbitals are reported that are relevant in describing the low-energy electronic transitions toward S_2 , S_{15} , S_{33} , S_{45} and S_{53} .

Table S13. Optimized structure of **2b**. Cartesian coordinates in angstrom.

C	-1.493203	2.083740	0.086705	O	-2.860087	-0.402038	0.076156
C	-0.415519	2.973116	0.058207	C	-3.296892	-1.594588	0.068364
C	-0.591146	4.362687	0.107311	C	-4.835815	-1.611889	0.152272
C	-1.889596	4.862680	0.185674	C	-2.618981	-2.802545	-0.000894
C	-2.968513	3.973319	0.213565	C	6.327045	-2.574069	-0.037916
C	-2.786141	2.581850	0.164811	C	6.249895	-2.982196	1.434678
C	0.608727	5.246314	0.076389	H	2.797452	5.213748	-0.015865
C	1.915658	4.581023	0.002114	H	-2.039846	5.937428	0.224065
C	2.040338	3.229586	-0.040239	H	-3.981700	4.363244	0.274492
C	0.875031	2.375521	-0.019257	H	-3.641966	1.915491	0.187364
N	0.947872	1.057328	-0.061187	H	5.445460	1.485855	-0.158539
C	2.202906	0.466526	-0.119583	H	3.776739	-2.531675	-0.189877
C	3.352405	1.288293	-0.134192	H	1.569297	-1.586661	-0.134158
O	3.262743	2.650207	-0.103248	H	-3.195762	-3.716580	0.014656
C	4.633769	0.770034	-0.170979	H	7.104616	0.541995	-0.963534
C	4.849958	-0.627232	-0.204722	H	7.246208	0.292290	0.776900
C	3.689640	-1.452334	-0.181665	H	9.359815	-0.043671	-0.409055
C	2.419335	-0.919268	-0.145921	H	8.897934	-1.561585	0.358303
N	6.115393	-1.150800	-0.270662	H	8.685469	-1.343879	-1.396020
C	7.247694	-0.226242	-0.194715	H	7.303054	-2.843191	-0.443183
C	8.617820	-0.848191	-0.422423	H	5.604948	-3.141911	-0.630783
Pt	-0.915424	0.174558	-0.004115	H	6.407258	-4.061391	1.536569
O	-0.380855	-1.959996	-0.115752	H	7.017599	-2.470477	2.024546
C	-1.219115	-2.886624	-0.092505	H	5.274540	-2.737283	1.865540
C	-0.597174	-4.294224	-0.230203	F	-1.390693	-5.247271	0.272889
O	0.513888	6.469670	0.113472	F	-0.391241	-4.569052	-1.525440

F	0.577828	-4.357154	0.399501
F	-5.328325	-2.855204	0.127593
F	-5.240210	-1.028059	1.284247

F	-5.358957	-0.937775	-0.875907
I	-1.042232	0.232063	-2.696512
I	-0.763066	0.038941	2.686743