Spectroscopy and electrochemical properties of a homologous series of acetylacetonato and hexafluoroacetylacetonato cyclopalladated and cycloplatinated complexes[†]

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Received 17th March 2008, Accepted 9th May 2008 First published as an Advance Article on the web 23rd June 2008 DOI: 10.1039/b804478c

A photophysical, electrochemical and computational study has been performed on a homologous series of cyclometallated Pd(II) (**1a–f**) and Pt(II) (**2a–f**) complexes of general formula [(C,N)M(O,O)]; (H(C,N) = azobenzene, 2-phenylpyridine, benzo[*h*]quinoline; M = Pd, Pt; H(O,O) = acetylacetone, hexafluoroacetylacetone). Experimental and computational data have shown the strong influence exerted by electronegativity of the ancillary ligand on the frontier orbitals of the complexes, such an effect being enhanced for the Pt(II) species.

Introduction

Square-planar cyclometallated palladium and platinum complexes are currently studied for purposes which include the preparation of bio-active molecules and the synthesis of new photo-active materials whose applications as advanced materials require species with luminescent, or strictly related, properties.¹ Luminescent palladium complexes have received until now less attention than platinum complexes;² however, several investigations are presently focused on such complexes.³

In this context, we have recently reported efficient luminescent cyclopalladated Nile Red (9-diethylamino-5H-benzo[a]phenoxazine-5-one) complexes, comprising as ancillary ligands deprotonated acetylacetone or hexafluoroacetylacetone (1,1,1,5,5,5-hexafuoro-2,4-pentanendionato(1-)), which show the highest emission quantum yield ever reported for cyclopalladated complexes (12% and 50% in cyclohexane respectively).⁴ For these complexes, the lower energy excited states are ligand-centered (LC) and are not influenced by competing non-emissive excited states located at the metal center. In contrast, in a recent study performed on cyclometallated Pd(II) complexes of general formula [(C,N)Pd(O,O)](H(C,N) = azobenzene, 2-phenylpyridine)or benzo[h]quinoline; H(O,O) = acetylacetone or hexafluoroacetylacetone), on the bases of photophysical and cyclovoltammetric data, we drew the conclusion that the frontier molecular orbitals HOMO and LUMO could be mainly centered on the acetylacetonato and on the cyclopalladated ligands respectively.5

The available literature data suggests that the lack of room temperature luminescence for cyclopalladated compounds is likely due to a rapid non-radiative deactivation of the excited levels, as a consequence of population of metal-centered states (MC), geometrically distorted with respect to their ground states.^{3a} Thus, in order to better understand the properties exhibited by squareplanar complexes which feature both a metallacycle and an ancillary chelating ligand, particular attention has to be deserved to the metal-mediated fine interplay among states originating from the molecular orbitals of the two chelated rings. Moreover, an accurate HOMO and LUMO description, in terms of atomic orbital composition, absolute energy, and relative energy gap, affords a set of parameters which are connected to relevant photophysical properties (i.e. luminescence, photorefractivity or charge photogeneration) these complexes display.^{1e} Thus ultimately, such studies could be of help for the design of new ligands and the tuning of specific desired properties of the complexes they form.

Given the potential of these compounds as photo-active materials, we have performed an experimental and theoretical comparative study on some homologous series of cyclometallated Pd(II) and Pt(II) complexes. This paper provides an account of the synthesis, spectroscopic and electrochemical characterisation, and the computational results on the electronic structure of the acety-lacetonato (acac) and hexafluoroacetylacetonato (hfacac) Pd(II) and Pt(II) complexes (Chart 1). In this series of complexes, the cyclometallated ligands are azobenzene (HAzo), 2-phenylpyridine (HPhPy) and benzo[*h*]quinoline (HBzQ), (**1a–f**, **2a–f**,).

Results and discussion

Electrochemical study

The electrochemical properties of the complexes were examined using cyclic voltammetry (CV), and the redox data are reported in Table 1. All of the electrochemical potentials were measured relative to an internal ferrocene reference (Cp_2Fe/Cp_2Fe^+). All complexes show a single irreversible oxidation wave between +1.33 and +0.34 V. Such irreversibility has been observed by us in the

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[†] Electronic supplementary information (ESI) available: Synthetic procedures and full characterizations of all studied compounds, spectroscopic characterization in various solvents and theoretical calculations. See DOI: 10.1039/b804478c



free ligands BzQ, Azo and PhPy. Pt(II) complexes are oxidized more easily than their corresponding Pd(II) analogues (ca. 200-300 mV negative shift). The introduction of the high electronegative fluorinated groups influences the oxidation potentials of all complexes. A typical shift of ca. 400-600 mV at higher potentials is observed for all complexes with respect to their non-fluorinated analogues. All complexes have shown a reduction wave between -1.2 and -2.4 V. Complexes of 2-phenylpyridine have shown a reversible or quasi-reversible reduction, whereas all complexes of benzo[h]quinoline have a tendency for irreversible behaviour. The introduction of the high electronegative CF_3 groups on the azobenzene complexes lead to the irreversibility of the reduction wave. According to our measurements, the free ligands Azo, BzQ and PhPy always show irreversible CV reductions. The nature of the metal center (Pd(II) or Pt(II)) has a weak influence on reduction potentials but slightly larger when electronegativity of the ligand is increased (shift of ca. 10-70 mV for acetylacetonate and ca. 100-200 mV for hexafluoroacetylacetonates). Reduction potentials are strongly affected by the electronegativity of the ancillary ligand, a significant positive shift of ca. 800-900 mV being observed for the hfacac complexes 1e-f and 2e-f with respect to their acac analogues 1b-c and 2b-c respectively. Only in the case of azobenzene as cyclometallated ligand (1a,1d with respect to 2a,2d) is this shift clearly less pronounced (ca. 170 mV).

Table 1 and Fig. 1 further compare the Kohn-Sham orbital energies evaluated *in vacuo* against those deduced from CV

measurements in the case of all the studied complexes. The performed computations are able to reproduce the experimental trend for the HOMO and LUMO energies of all the compounds. The high electronegativity of the fluorinated groups seems to greatly influence the HOMO energy of all complexes and, mostly in the case of PhPy-based and BzQ-based complexes, also the LUMO energy. The computed HOMO–LUMO gap is always overestimated by the computations, a fact possibly associated to the lack of solvation effects in the computations. This explanation can be extended to the inaccuracy in the computed HOMO energy. The LUMO energies are in better agreement with the computations when the ancillary ligand is hfacac. This result will be discussed below.

Fig. 2 shows the HOMO and LUMO orbitals in terms of the AO contribution in the case of **1a**, **2a**, **1e**, and **1d**. It is possible to see that, in all the compounds, the HOMO is mostly localised on the cyclometallated ring, though the contribution of the ancillary ligand is significant. A comparison of the **1a** and **2a** HOMOs highlights that the localisation is more evident in Pt-based complexes than in Pd-based ones. This feature has been found in all the studied complexes (the interested reader is referred to the ESI[†] for the HOMO in terms of the AO contribution of the remaining compounds), whereas the LUMO shows an uneven behaviour. From Fig. 2, in **1a** and **2a** the LUMO is principally localised on the cyclometallated ligand. This is found in all the complexes with an acac ancillary ligand. In contrast, in all the

Table 1 Electrochemical and computational data for 1a-f and 2a-f

Complexes	Oxidation E^{Ox}/V^{a}	Reduction E^{Red}/V^{a}	HOMO/eV ^e	LUMO/eV ^e	HOMO/eV ^f	LUMO/eV ^f
1a	$+0.82^{b}$	-1.33 ^c	-5.68	-3.74	-6.34	-2.74
1b	$+0.68^{b}$	-2.49^{d}	-5.58	-2.31	-5.97	-1.64
1c	$+0.55^{b}$	-2.20^{b}	-5.35	-2.60	-5.87	-1.84
1d	+1.33 ^b	-1.50^{b}	-6.13	-3.65	-7.02	-3.33
1e	$+1.18^{b}$	-1.63°	-5.95	-3.17	-6.78	-3.11
1f	$+0.95^{b}$	-1.35^{b}	-5.75	-3.45	-6.59	-3.12
2a	$+0.65^{b}$	-1.40°	-5.45	-3.40	-6.19	-2.62
2b	$+0.34^{b}$	-2.40°	-5.14	-2.40	-5.77	-1.66
2c	$+0.38^{b}$	-2.19^{b}	-5.18	-2.60	-5.69	-1.86
2d	$+0.98^{b}$	-1.23^{b}	-5.78	-3.57	-6.92	-3.44
2e	+0.67	-1.49^{c}	-5.47	-3.31	-6.59	-3.24
2f	$+0.57^{b}$	-1.53^{d}	-5.38	-3.27	-6.45	-3.25

^{*a*} Potentials were obtained in dry dimethyl formamide solution using tetrabutylammonium hexafluorophosphate (0.1 M) as supporting electrolyte; values are reported relative to Cp_2Fe/Cp_2Fe^+ , using a glassy carbon working electrode *vs.* Ag wire as a pseudoreference electrode. ^{*b*} Irreversible. ^{*c*} Reversible. ^{*d*} Quasi-reversible. ^{*e*} Values calculated using -4.8 eV for ferrocene. ^{*f*} Our computations at the MPW1PW91/SDD level of approximation.



Fig. 1 Comparison of the experimental (dashed line) and computed (solid line) HOMO and LUMO energies of the studied complexes.



Fig. 2 Computed HOMO and LUMO Kohn-Sham orbitals of complexes 1a, 2a, 1e and 1d.

complexes with hfacac (*e.g.* **1e** in Fig. 2), the LUMO is mostly localised on the ancillary ligand. One exception has been found in **1d** (Fig. 2), whose LUMO also shows a large contribution from the cyclometallated ring (see ESI for a visual description of the LUMO in all the complexes).

The change in LUMO localisation can be related to a definite shift in the experimental LUMO energy when the ancillary ligand is changed from acac to hfacac. This is particularly evident comparing 2c and 2f. Fig. 3 shows that the LUMO and LUMO + 1 orbitals of 2c are mostly localised on the cyclometallated ring and ancillary ligand, respectively. When the acac ligand is replaced by hfacac (2f compound), the LUMO and LUMO + 1 energy order is reversed. This fact can be directly explained as a consequence of the electronegativity of the fluorine atoms, which induces a large stabilization of all the fragment orbitals of the hfacac ligand.

The change in LUMO localization and energy lowering of the LUMO is found in all the compounds based on the BzQ and PhPy cyclometallated ligand, and agrees with the experimental strong influence of the ancillary ligand electronegativity on the reduction peak.

In the azo-based complexes, the hfacac electronegativity is not enough to produce such an evident change. Fig. 1 shows that the LUMO energy is more negative in acac-based complexes **1a** and **2a** and less sensitive to the fluorine introduction than in the other complexes. As mentioned above, such a LUMO is localised on the cyclometallated ligand (as in all the acac-containing complexes), which contains twice as many electronegative atoms (two nitrogen atoms) than the other ligands, *i.e.* PhPy and BzQ. Thus, the replacement of acac with hfacac leads to a smaller change in the LUMO energy. In fact, in the case of **1a** and **1d**, we do not



Fig. 3 The exchange of LUMO and LUMO + 1 orbitals by replacing the acac ligand with the hfacac ligand (from 2c to 2f). The HOMO and LUMO orbitals of 2c are lowered in energy by hfacac. The LUMO + 1 orbitals of 2c undergoes a much greater energy lowering, so as to become the LUMO in 2f. A similar behaviour has been observed in all the complexes apart from azo-based complexes.

observe the sharp change in LUMO localisation passing from acac to hfacac. This explains the lower influence of the ancillary ligand electronegativity on the experimental reduction peak in CV experiments of azo-based complexes.

Another point inferred from Fig. 2 is the larger contribution of the central metal to the HOMO rather than to the LUMO. This finding explains the greater importance of the central metal nature on the computed and the experimental HOMO energy in comparison of its relevance on the LUMO.

In particular, concerning the HOMO composition, the Pt(II) atomic orbitals (mostly a d_{π} orbital) seems to be significantly more important than the Pd(II) atomic orbitals in Pd-based complexes. The fact that Pt(II) atomic orbitals show a larger contribution in the HOMO is in line with the less negative HOMO energy in the cases of Pt(II)-based complexes. In fact, the interaction between the central metal and the cyclometallated ligand is anti-bonding, thus it is a destabilising interaction.

From the above discussions, the replacement of acac with hfacac in complexes based on BzQ and PhPy has the most dramatic effect on the LUMO energy. As a consequence, a reduction in HOMO– LUMO gap is induced by the fluorine electronegativity of hfacac. The HOMO–LUMO reduction spreads in range from 0.25 eV to 0.58 eV passing from acac-based compounds **1b**, **2b**, **1c** and **2c** to the respective hfacac-based compounds **1e**, **2e**, **1f** and **2f**. The azobased complexes are different; their HOMO–LUMO gap increases by 0.54 eV passing from **1a** to **1d** and by 0.16 eV passing from **1d** to **2d**. Such trends in the HOMO–LUMO gap have been reproduced by DFT computations; furthermore, they have been evidenced by UV-Vis spectroscopy (see below).

Photophysical properties

Absorption and low-temperature (77 K) emission spectra were recorded for all complexes of the Pd(II) and Pt(II) series, and, in all cases, no emission was detected at room temperature. The relevant data are collected in Table 2. Absorption maxima, λ_{abs} , and extinction coefficients, ε are similar to those of other cyclometallated complexes reported in the literature.⁶ Representative absorption spectra (those for 2d,e) are shown in Fig. 4. In order to assess the nature of the various absorption bands, the solvatochromism of each member of the series 1 and 2 was investigated by recording spectra in solvents spanning a large range of Reichardt's polarity parameter⁷ (e.g., cyclohexane, $E_{\rm T} = 0.006$, dichloromethane, $E_{\rm T} =$ 0.309; dimethyl formamide, $E_{\rm T} = 0.404$; methanol, $E_{\rm T} = 0.762$). However, no substantial band shift was evidenced (Table S2 in ESI). In particular, the high energy ($\lambda < 360$ nm), more intense absorption bands do not show any appreciable solvatochromism, suggesting the assignment to π - π * mainly ligand-centered (¹LC) transitions. As a consequence of the ligand-metal orbital mixing, these transitions are red-shifted with respect to what happens for free ligand absorption. Also for the absorption bands falling in the range 360–500 nm (with ε between 2700 and 6600 M⁻¹ cm⁻¹,

Table 2 Photophysical results obtained in dichloromethane solution

Complex	Absorption (RT)	Emission (77 K) ^a		
	$\lambda_{abs}/nm (\epsilon/M^{-1} cm^{-1})$	$\lambda_{\rm em}/\rm nm$	τ/μs	
1a	250 (28300.sh), 311 (23852), 354 (18187), 410 (8850.sh), 490 (5190.sh)	Ь	b	
1b	259 (63168), 305 (30360,sh), 316 (33649), 360 (10700,sh)	461	138.0	
1c	240 (41500,sh), 297 (21608), 315 (13900,sh), 370(3250,sh), 393 (4814)	500	2130.0	
1d	248 (16200,sh), 280 (8430,sh), 330 (16183), 365 (13200,sh), 385 (10658), 445 (4759), 480 (3230,sh)	b	b	
1e	261 (23087), 300(8900.sh), 315 (10182), 340 (8400.sh), 358 (5100.sh)	462	83.0	
1f	250 (54200,sh), 280 (33500,sh), 281 (36033), 315 (22700,sh), 365 (10400,sh), 390 (9200,sh)	b	b	
2a	252 (17450), 300 (10448), 351 (9855), 395 (6300,sh), 448 (4255)	b	b	
2b	249 (22810), 276 (16046), 315 (7750,sh), 330 (6900,sh), 363 (4724), 400 (2200,sh)	480	7.3	
2c	246 (52633), 255 (38700,sh), 319 (19949), 370 (9300,sh), 420 (7405)	500	26.0	
2d	246 (22274), 282 (9809), 340 (13800,sh), 364 (15478), 388 (13936), 430 (5150,sh), 502 (2705)	b	b	
2e	241 (24268), 251 (23300), 265 (19000,sh), 310 (7100,sh), 323 (7113), 366 (6585), 390 (4780,sh)	546	1.7	
2f	243 (55689), 290(18400,sh), 305 (19820), 320 (15300,sh), 382 (14330), 410 (11550,sh)	552	2.9, 1.0 ^e	

^a Highest energy peak, excitation performed at 337 nm for both emission spectra and lifetimes. ^b No emission detected. ^c Dual exponential emission.



Fig. 4 Absorption spectra of 2d and 2e recorded in dichloromethane solution.

Table 2), which are not observed in the cyclometallating ligand precursors (Table S1 in ESI), the registered absorption features in the solvents employed do not show the relevant solvatochromism (see ESI). In principle, these low energy bands could be due to (i) metal-to-ligand charge transfer (¹MLCT) transitions and possibly include some ligand-to-ligand character (¹LLCT, from metallated to heterocontaining ligand fragments), or to (ii) perturbed ligand localized (¹LC) transitions involving the metallacycle.^{3b,8} However, the solvatochromic studies did not allow clear-cut conclusions about the nature of the low-energy absorption bands for the complexes of both **1** (Pd(II)) and **2** (Pt(II)) series.

Absorption spectra: the benzol//lquinoline complexes. We will thoroughly discuss the 1(c,f) and 2(c,f) series of molecules due to their photophysical properties and novelty. Further details and decomposition in terms of the Gaussian functions of this group of molecules are reported in Table 3. All the decomposed spectra are reproduced quite well as concerns the excitation energies even though the number of Gaussian functions is well below the number of computed transitions. On the other hand, the intensities do not show the same level of agreement. In fact, in all the instances where vibronic and spin-orbit (SO) coupling play a relevant role in determining the transition intensities and structure of the spectra, our computational results give only a qualitative indication of their relative oscillatory strength especially in the low energy region of the spectra. Our computations neither take into account explicitly SO interactions, nor couple electronic and vibronic transitions, and thus they can be particularly inaccurate in computing band intensities in case of large geometry deformations associated to the electronic transitions. On the other hand, inspection of composition of the states involved in the transitions in terms of one-electron MO transitions and analysis of the computed harmonic vibration normal modes can give some hint on the origin of some of these disagreements.

All the spectra are characterized by four major features of decreasing intensity: an high energy region (H), a middle and low energy region (M) and (L) respectively, and a tail at lower energy (T) that extends into the visible spectrum. Fig. 5 and 6 compare the UV-Vis spectra of **1c**,**1f** and **2c**,**2f** in cyclohexane solution. In all the reported spectra, the results of our TD-DFT computations are included for comparison.

According to the computations, transitions that are uniquely localized on the benzoquinoline ligand are pushed toward the high energy region of the spectrum, beyond band H, so that only some of their tails fall under band H. In case of **1c**, the onsets of band M and band L are at 28000 cm^{-1} and 24000 cm^{-1} respectively. The presence of the hfacac ligand in **1f** shifts the onset of band M to higher energy by 500 cm^{-1} . In the case of Pt(II) complexes **2c** and **2f**, the hfacac ligand moves the onset of band M and band L from 28000 cm^{-1} to 29000 cm^{-1} and from $22000 \text{ to } 22500 \text{ cm}^{-1}$ respectively.

Band H is due to high energy singlet states that starts from singlet S_{20} and S_{19} for **1c** and **1f** respectively. In addition, the first transitions in the case of **2c** and **2f** are S_{15} and S_{18} . Being deep in the UV region, band H is not very interesting as regards luminescence properties and will not be further discussed.

1c. In the case of **1c**, the main features of band M, as represented by the fitting Gaussians g17, g15, g14, g13 and g11, well match the computed transitions. g17 takes into account of S_{19} and S_{20} and half of its contribution belongs to band H. g15 includes a group of transitions mainly represented by S_{16} . g14 corresponds to S_{12} , g13 to S_{10} and g11 to S_6 . Transition toward S_{10} is the most important excitation in determining the intensity of band M. Its composition is substantially a π - π * LC transition with MLCT character which involves charge flow toward the cyclometallated

Table 3Fitting functions and TD-DFT results for 1c, 1f, 2c, and 2f

	Decomposition					TD-DFT		
	Function	$\tilde{v}_{(max)}/cm^{-1}$	$\lambda_{(max)}/nm$	Γ/cm^{-1}	$\epsilon_{\rm max}$	State	$\tilde{v}_{(max)}/cm^{-1}$	f
1c						_		
Band H						S_{40}	46515	0.0159
						S ₃₉	46511	0.0003
	a21	11126.85	227	1804 46	20502.22	S ₃₈	46138	0.0510
	g21	44120.85	227	1604.40	20392.23	S 337	45590	0.3233
						S	44783	< 0.0002
						S.4	44744	0.0599
						S ₂₂	44128	0.0002
						S ₃₂	43711	0.0283
						S ₃₁	43310	0.0998
						S_{30}	43263	0.0028
	g20	41226.77	243	1038.27	5907.29	S_{29}	42769	0.0308
						S_{28}	42740	0.0002
						S_{27}	42207	0.0502
						S_{26}	42095	0.0013
						S_{25}	41736	0.0016
						S_{24}	41423	0.0009
	g19	40275.05	248	1165.13	8263.92	S ₂₃	40599	0.0550
						S ₂₂	40095	0.0424
	10					S_{21}	39076	0.0001
	g18	39435.29	254	605.91	2195.35	S_{20}	38725	0.0617
Band M	g17	37939.93	264	1223.50	5080.22	S19	38150	0.0792
	0					S_{18}	37387	0.0001
	g16	37260.52	268	504.04	323.84	S_{17}	36704	0.0005
	g15	36228.58	276	828.84	2850.49	S_{16}	36584	0.0332
	-					S ₁₅	35632	0.0001
						T ₂₀	35601	
						S_{14}	35524	0.0086
						T ₁₉	35397	
						S_{13}	35056	0.0009
	g14	34624.49	289	1110.19	4604.85	S_{12}	34640	0.0345
						T_{18}	34225	
						T ₁₇	34085	
						S ₁₁	33455	0.0022
	10	22100.24	202	000 00	1055 51	T_{16}	33374	0.00.55
	g13	33100.24	302	929.09	4877.74	S_{10}	33088	0.0857
						S ₉	32934	<0.0001
	-12	22400 51	200	256 60	229 50	1 ₁₅	32689	0.0242
	g12	52409.51	509	550.00	238.39	38 T	21015	0.0242
						1 ₁₄ T	21642	
						1 13 S	31580	0.0004
	a11	31538 73	317	006 52	3807 72	37 S	31385	0.0004
	gII	51556.75	517	990.52	5607.72	S -	31049	<0.0743
						55 T.,	30854	<0.0001
	σ10	30430 29	329	570.04	1056.08	S.	30368	0.0097
	510	50150.25	52)	570.01	1020.00		30319	0.0007
	σ 9	29448 59	340	326.27	250.83	T ₁₀	30077	
	98	29245.89	342	980.64	1222.51	S ₂	29156	0.0183
	8-					T_9	28862	
Band L	g7	27241.46	367	988.32	871.14	S ₂	27267	0.0018
	g6	26656.72	375	207.81	58.99	T_8	26465	
	g5	25996.42	385	447.17	897.34	\mathbf{S}_{1}	26024	0.0471
	g4	24983.34	400	561.35	914.11	$\dot{T_7}$	26144	
	C					T ₆	25657	
	g3	24604.50	406	264.12	730.29	T ₅	25656	
	g 2	24137.28	414	1126.95	125.21	T_4	23474	
Band T	g1	21598.67	463	3094.94	238.80	T ₃	23163	
						T_2	22954	
						T_1	19928	
1f						_		
Band H	g20	41808.08	239	239.19	1133.97	S ₂₅	41235	0.0636
						S_{24}	4103/	<0.0001

Table 3(Contd.)

	Decomposition					TD-DFT		
	Function	$\tilde{v}_{(max)}/cm^{-1}$	$\lambda_{(max)}/nm$	Γ/cm^{-1}	\mathcal{E}_{\max}	State	$\tilde{v}_{(max)}/cm^{-1}$	f
	g19	39885.39	251	250.72	678.08	S ₂₃	40501	0.0359
	-					\mathbf{S}_{22}	40211	< 0.0001
	g18	39438.49	254	253.56	1226.94	S_{21}	39516	0.1490
	-					\mathbf{S}_{20}	39099	0.0005
Band M	g17	37659.58	266	265.54	815.95	S ₁₉	39030	0.0242
						S_{18}	36602	0.0028
	g16	36538.84	274	273.68	692.33	S_{17}	36121	0.0365
	g15	35269.52	284	283.53	868.80	S_{16}	35267	0.0169
						S ₁₅	34955	0.0039
	g14	33921.66	295	294.80	/63.03	S_{14}	34567	0.1017
						I 20	34522	
						1 19 S	22856	-0.0001
						S ₁₃	32630	< 0.0001
	g13	32528 23	307	307.43	834.86	S ₁₂	32567	0.0007
	g13 g12	31360.32	319	318 87	704.01	T	32407	0.0040
	512	51500.52	517	510.07	/04.01	S	31852	0.0017
						T_{17}	31671	010017
	g11	30258.24	330	330.49	1253.22	S ₉	31324	0.0001
	0					T ₁₆	30725	
						T ₁₅	30649	
						S_8	30453	0.0027
						S_7	30267	0.0051
						T ₁₄	30091	
						T ₁₃	29907	
						S_6	29622	< 0.0001
						T ₁₂	29433	
	σ10	29358 94	341	340.61	919 79	T ₁₁ S.	29297 29165	0 0244
	510	29330.91	511	510.01	,,,,,	55	27100	0.0211
Band L	g9	27707.75	361	360.91	943.94	S_4	27235	0.0636
	gð	26412.44	379	3/8.61	562.78	S ₃	2/1/2	0.0492
						I 10 T	26820	
	~7	25547 52	201	201 42	267 20	19 T	20344	
	g/ g6	25071.32	391	308.86	245.25		23924	
	go	25071.59	399	398.80	243.23		23599	
	g5	25026.23	400	399.58	553.66	\mathbf{S}_{2}	22880	< 0.0001
Band T	<u>g</u> 4	23975.14	417	417.10	1001.47	T,	22360	
	g3	21189.23	472	471.94	2519.68	T,	22210	
	0-					T_3	22064	
						\mathbf{S}_1	21807	0.0090
	g2	18642.97	536	536.40	967.96	T_2	20187	
	g1	16495.68	606	606.22	1681.59	T_1	17166	
2c								
Band H	g21	42069.23	238	1735.69	30902.20	S_{30}	43559	0.2230
						S ₂₉	42584	0.0893
						S_{28}	42163	0.0050
						S ₂₇	42093	0.0005
						S ₂₆	41818	0.0033
	a20	40136.00	240	1006.83	37115 40	S ₂₅	41013	0.0010
	g20	40150.07	249	1000.05	5/115.40	S ₂₄	40345	< 0.001
	g19	39265.29	255	585.78	9741.36	S23	40170	0.0686
	8				,,,,,,,,,,,,,,,,,,,,,,,,,,,,,,,,,,,,,,,	S ₂₁	39335	< 0.0001
	g18	38563.38	259	654.09	15713.47	\tilde{S}_{20}	39199	0.0264
	-					\mathbf{S}_{19}	38864	0.0002
						S_{18}	38735	0.0095
	g17	37638.21	266	931.91	11429.66	S_{17}	37728	0.0209
						S_{16}	37651	0.0459
						b_{15}	5/448	0.0006
						S.,	37271	0.0001
Band M						014	25015	~ ~ ~ ~ ~
Band M	-1(25924 57	270	1022 59	10546 51	S_{14} S_{13}	35915	< 0.0001

 Table 3 (Contd.)

	Decompositio	Decomposition					TD-DFT		
	Function	$\tilde{v}_{(max)}/cm^{-1}$	$\lambda_{(max)}/nm$	Γ/cm^{-1}	\mathcal{E}_{\max}	State	$\tilde{v}_{(max)}/cm^{-1}$	f	
						T ₂₀	35336		
						T ₁₉	34483		
	g15	34734.00	288	1050.43	3052.14	\mathbf{S}_{11}	33834	0.0029	
	-					S_{10}	33772	0.0048	
						T ₁₈	33557		
						S.	33422	< 0.0001	
						T ₁₇	33249		
						T ₁₆	33177		
						T ₁₅	33075		
						T ₁₄	32895		
	g14	33467.26	299	1143.14	10011.50	S.	32796	0.0441	
	8-1						32680		
						T.,	32468		
	g13	31660.06	316	1147 65	10428.02	S ₇	32285	0.0285	
	515	51000.00	510	1117.05	10120.02	Б, Т.,	32258	0.0205	
						T.,	31447		
						S .	30657	0 0004	
	a12	30308 65	320	010.18	8836.86	S	30641	0.0004	
	g12 g11	20876 77	325	485.20	2527.24	55 T	30120	0.1100	
	gII	29870.77	555	405.20	2327.24	19 T	20674		
	α10	20144 61	3/3	532 24	7172.28	1 8 S	29074	0 1100	
	giu	29144.01	545	552.24	/1/2.20	54	29323	0.1190	
Band L	g9	28447.42	352	593.67	3195.64	S_3	27891	0.0149	
	g8	27117.96	369	1112.07	4642.38	\mathbf{S}_{2}	27083	0.0018	
	g7	26067.67	384	459.97	3165.67	$\tilde{T_7}$	28329		
	g6	25774.78	388	254.63	1176.52	T ₆	27855		
	g5	25574.25	391	480.46	1111.85	T₅	26178		
	o4	24015 91	416	1089 73	2887.97	Ŝ.	24233	0.0344	
	5'	21013.91	110	1009.75	2007.97	\mathbf{T}_{i}	24096	0.0511	
	g3	22738.99	440	520.74	2138.05	T_3^4	22936		
Band T	g2	21288.79	470	424.41	153.84	T ₂	21645		
	gl	18708.50	535	7558.94	101.44	T_1	19231		
•	C								
2f Band H	ø21	42657 04	234	2213 83	431 73	Sa	42276	0 1 5 4 0	
Dunu II	g20	40432.17	247	1123 51	285.90	S24	41897	0.0121	
	g19	40171.37	249	372.01	40.36	S.,	40688	0.0672	
	517	401/1.57	247	572.01	40.50	S	39270	< 0.0072	
	σ18	38373 38	261	774 32	80.44	S ₂₁	39231	0.0704	
	gio	56575.56	201	114.52	00.44	S_{19}^{20}	39035	0.0619	
Pand M	g17	26020 54	271	055 67	115.65	c	28775	0.0507	
Dallu IVI	gi/	50959.54	271	955.07	115.05	S ₁₈	27920	-0.0001	
						S ₁₇	3/839	< 0.0001	
						\mathbf{S}_{16}	3/140	0.0019	
						S ₁₅	3/109	0.0036	
						1 20	35/1/	0.0003	
	16	25020 75	205	1070 70	121.42	S ₁₄	35575	0.0002	
	g16	35029.75	285	12/2./3	131.42	S ₁₃	35027	0.0409	
	g15	33803.83	296	597.77	64.5/	S ₁₂	33982	0.006/	
		22565.05	205	000.07	106.06	T ₁₉	33594	0.1056	
	g14	32565.85	307	880.97	106.26	S ₁₁	33322	0.1076	
						S ₁₀	33148	0.0008	
						T_{18}	32950		
						T_{17}	32358		
						T_{16}	31706		
						T ₁₅	31505		
						T_{14}	31064		
	g13	31020.95	322	1500.02	99.63	S_9	30961	0.0697	
	g12	30185.60	331	328.88	3.72	T ₁₃	30685		
	g11	29882.98	335	835.87	17.36	S_8	30653	0.0127	
						T ₁₂	30526		
						S_7	30364	0.0028	
						T ₁₁	29885		
Band L						T_{10}	29295		
						\mathbf{S}_{6}	28743	< 0.0001	
						T ₉	28546		

 Table 3
 (Contd.)

	Decomposition						TD-DFT			
	Function	$\tilde{v}_{(max)}/cm^{-1}$	$\lambda_{(max)}/nm$	Γ/cm^{-1}	<i>E</i> _{max}	State	$\tilde{v}_{(max)}/cm^{-1}$	f		
	g10	27876.60	359	1092.77	77.98	S ₅	28179	0.0075		
	g9	26839.28	373	500.07	17.54	T_8	27268			
	g8	25788.60	388	881.85	69.89	S_4	25980	0.0876		
	e					T_7	25617			
						T ₆	25281			
	g 7	24356.29	411	851.12	56.63	S_3	25113	0.0757		
Band T	g6	23448.70	426	522.91	21.76	Ts	22498			
	g5	22430.96	446	356.72	4.02	\mathbf{S}_{2}	21969	< 0.0001		
	g4	21813.99	458	439.00	3.80	$\tilde{T_4}$	21338			
	C					T ₃	19961			
	g3	20944.17	477	762.84	2.87	S ₁	19484	0.0176		
	g2	19523.53	512	654.15	0.65	T_2	19007			
	gl	17504.14	571	5504.88	0.58	T_1	15744			

ligand. S₆ has a very similar character π - π * LC transition with larger MLCT character which involves charge flow toward both the ligands.

In the low energy region of band M, the main features are represented by g10 and g8. The latter corresponds to an electronic transition toward S₃. It is assigned by our computations to a π - π^* -symmetry MLCT from an orbital containing both the central metal and acac to the cyclometallated ligand and it is computed at 29156 cm⁻¹ (343 nm). S₄ results from a d-d transition (from the d₂² * to d_{x²-y²}*). The TD-DFT result, 30368 cm⁻¹ (329 nm), compares very well with the fitting g10 at 30430 cm⁻¹ (329 nm). Its computed oscillator strength is not as large as the LC π - π^* toward S₆ and the other LC transitions we have encountered in this complex.

Band L presents two main peaks at 25974 cm⁻¹ (384 nm) and 24691 cm⁻¹ (406 nm). In the decomposed spectrum they correspond to Gaussian functions g2-g6; g5 (25996 cm⁻¹, 385 nm) and g6 (27241 cm⁻¹, 367 nm) can be easily assigned to S_1 (26024 cm⁻¹, 384 nm). A further Gaussian function (g7) can be assigned to S_2 (27267 cm⁻¹, 367 nm). S_2 is an almost pure MLCT characterized by a HOMO – 1 to LUMO mono-electronic transition. The broadness of the band suggests that this transition is enhanced by vibronic coupling in spite of a very low computed intensity. In particular from the computed vibrational spectrum, low energy vibrations, *e.g.*, at 39, 154, 255, 293 cm⁻¹, involve the central metal and the first coordination sphere. In fact, the puckering of the Pd(II) atom out of plane by 0.1 Å, within 2*RT* at room temperature increases the oscillator strength of this transition more than fivefold.

As far as it concerns g2–g4, they give rise to the 24691 cm⁻¹ (406 nm) peak. In this case it is not possible to assign this peak and the corresponding Gaussian functions to any of singlet transitions. It is worth noting that using less than three Gaussian functions prevents any attempt to achieve a satisfactory fit of the spectrum in this region. On the other hand, the computed triplet manifold shows a pattern which closely resemble that one described by the set of Gaussian functions. In particular, the triplet manifold shows four transitions, T_4-T_7 , which have energies (23474, 25656, 25657, 26144 and 26465 cm⁻¹) that are close to the fitting Gaussian functions 24137, 24604, 24983 and 26657 cm⁻¹. Furthermore, the same perturbation that increases the intensity of

 S_2 modifies the pattern of the triplet state moving them toward red to 23327, 25092, 25511, 25889 and 26326 cm^{-1}. The analysis of the composition of the triplet states (see Table S19 in ESI) indicates that only T_5-T_7 include monoelectronic transitions with significant metal contribution. Hence, we suggest that g2 takes into account for T_5 and g3 for the set T_4-T_7 respectively. This trend suggests that triplet states up to T_7 lie below S_1 .

Two further very low intensity Gaussians g6 (26657 cm⁻¹) and g10 (29449 cm⁻¹) take into account T_8 (26465 cm⁻¹), the triplet corresponding to S_2 , and T_{10} . This last state contains two monoelectronic excitation from HOMO – 5 and HOMO – 6 toward the ML d_{xy} – σ * LUMO + 3 (see Fig. S18 in ESI).

We can conclude that, in 1c, the more evident experimental features can be assigned to LC transitions. Band L is principally associated to the BzQ ligand, and band M has a similar character, but it shows a relatively larger participation of the acac ligand. This computational result is in line with the observed low solvatochromism of bands M and L of the spectrum that has been discussed before. The d–d transitions and MLCT pure transitions are computed to be weaker bands than the π - π * LC transitions.

2c. The two main features of **2c** (bottom of Fig. 5) are band M (peak at 30864 cm⁻¹, 322 nm) as for **1c** and band L (peak at 26525 cm⁻¹, 377 nm).

The high energy part of the band M is described by Gaussians g13, g14 and g16, which can be assigned to the most intense transitions due to S_7 , S_8 and S_{12} . In addition, the low energy part is mostly produced by electronic transitions toward S_4 (29324 cm⁻¹) and S_5 (303641 cm⁻¹) (g10 and g12 respectively), which substantially parallel the **1c** transitions toward S_6 and S_{10} .

Gaussians g4–g8 belong to band L that, in the low energy part, shows a similar shape to **1c**, albeit of different origin. The broad Gaussian g8 can be assigned, as in case of **1c**, to S_2 (27083 cm⁻¹), a low intensity MLCT σ – π * transition from the metal d_{z^2} *, HOMO – 1, to the LUMO orbital localized on BzQ with some contribution from a tail of the S₃.

The energy of S_2 transition is substantially unmodified in the two complexes, **1c** and **2c**, as is also shown by the difference in the (HOMO – 1)-LUMO gap that moves the transition of only 6 nm. Also in this case metal puckering increases the intensity of the transition by a factor of three.



Fig. 5 Absorption spectra of 1c (top) and 2c (bottom) recorded in cyclohexane solution and TD-DFT computations. Black circles represent the experimental data and the line the fitted spectrum by the reported Gaussian functions. The computed S_n electronic vertical transitions are reported as a vertical line, whose length is the associated oscillator strength and, with a rhombus on top. Computed triplet transitions are reported with a vertical line of fixed length and with a circle on top. The position of λ_{max} of the Gaussian function is indicated by a heavy line with a triangle on top. The absorption spectrum of 1c; the absorption spectrum of 2c.

Taking as reference **1c** and the CV results it is possible to evaluate the energy of the first transition, which is almost a pure HOMO–LUMO mono electronic excitation. Being 0.17 eV, the experimental difference between the HOMO–LUMO gaps of **1c** and **2c**, it is fair to assume that in the latter case the S₁ energy should be moved by 1371 cm⁻¹ toward red, *i.e.*, to 24626 cm⁻¹, in good agreement with the computed S₁ energy at 24233 cm⁻¹. This results suggests that the S₁ transition, mostly a π - π *-symmetry



Fig. 6 Absorption spectra of 1f (top) and 2f (bottom) recorded in cyclohexane solution and TD-DFT computations. Black circles represent the experimental data and the line the fitted spectrum by the reported Gaussian functions. The computed S_n electronic vertical transitions are reported as a vertical line, whose length is the associated oscillator strength and, with a rhombus on top. Computed triplet transitions are reported with a vertical line of fixed length and with a circle on top. The position of λ_{max} of the Gaussian function is indicated by a heavy line with a triangle on top.

MLCT from one metal d_{ij}^* to the LUMO (see Fig. 3 for a graphical description of the orbitals), should be assigned to g4 (24016 cm⁻¹, 416 nm).

The feature at 25907 cm⁻¹ (386 nm), is due to the tail of g8 and g4 overlapped to a group of Gaussians g7–g5 and g3 whose origin can be tracked back to the same SO vibronic enhanced ground state to triplet transitions due to the computed out-of-plane vibrations from 29 to 457 cm⁻¹ involving the heavy atom as in case of **1c**.

We can conclude that the electronic spectrum of 2c is very similar to that of 1c: the two main bands considered have to be mostly assigned to $\pi - \pi^*$ of the cyclometallated ring, with minor intervention of the ancillary ligand on band M. On the other hand, it is worth noting that S_1 moves below T_5 .

1f. Fig. 6 shows the experimental spectrum of 1f.

Band M shows a very intense peak at 34014 cm⁻¹ (293 nm) and comprises Gaussians g10–g17. All the λ_{max} values of the fitting Gaussian functions agree quite well with the computed transitions. Table 3 reports the association of each Gaussian fitting function to groups of computed transitions. In particular, excitations toward S₁₁, S₁₄, S₁₆, S₁₇ and S₁₉ seems to be responsible for the features of the high energy part of this band. The computed value of S₁₄ energy (34567 cm⁻¹, 289 nm) is larger than the g14 λ_{max} (33921 cm⁻¹, 295 nm) value, and this transition appears to be the main feature of the M band.

 S_{11} (32567 cm⁻¹, 307 nm) mostly results from CT from the cyclometallated ring to hfacac, whereas S_{14} is a LC transition of the cyclometallated ring. S_{16} and S_{17} have MLCT character, the former involving both ligands whereas the latter has an intraligand character and only one monoelectronic transition with a full MLCT which contributes 33% (see Table S25 in ESI). S_{19} is an IL transition localized on the hfacac ligand, with a small MLCT contribution from the metal to the hfacac ligand.

The lower energy part of the band M is characterized by two main Gaussian functions, g10 and g11. These can be associated to a group of transitions within the singlet manifold, S_5-S_{10} , which are vibronic-enhanced, and possibly have some contribution from triplets $T_{11}-T_{17}$. In particular, T_{12} is pure metal d- σ to ligand- π vibrationally enhanced transition.

The band L shape apparently shows a high similarity to the same band of 1c and can be fitted by five Gaussian functions, g5-g9.

Unlike 1c, the most relevant computed transitions are singlet S_3 and S_4 , assigned to g8 and g9, although these last two are less close in energy then the computed transitions. S_3 is described as a CT from the cyclometallated ring to the hfacac ligand. It is predominantly a monoelectronic excitation from the HOMO – 1 to the LUMO. It has not a clear corresponding feature in 1c (S_6 of 1c is more indicated as a reference feature); however, its location in the low energy part of the spectrum has to be associated to the LUMO energy stabilisation induced by the fluorine atoms and consequent energy gap reduction between occupied orbitals and the LUMO as shown by CV data (Table 1 and Fig. 1).

Interestingly, the S_4 composition, in terms of monoelectronic transitions, corresponds to the S_1 excitation of **1c** (see Table S11 in ESI). It mostly involves a mono-electronic excitation from the HOMO to the LUMO + 1 (as shown in Fig. 3 or ESI for a graphical description in the case of **2c**). The experimental band associated with this LC transition of the cyclometallated ring (with small MLCT) is only marginally displaced (blue shifted of 8 nm, as mentioned above) and shows the same shape as for **1c**.

The lowest energy peak at 25062 cm⁻¹ shows a behaviour akin to that in **1c**, as can be also seen by the decomposition of the spectrum. In fact, three Gaussian functions are necessary for an accurate description of this feature. They can be assigned to a group of triplet states, T_7 - T_{10} .

In fact, the same perturbation of the geometry of the complex previously described shows that they gain a large contribution of configurations characterized by monoelectronic transitions from metal d_{z^2} (HOMO – 2) to M–BzQ π^* ligand orbitals or from M–BzQ π -ligand orbital to metal d_{xy} (LUMO + 3).

Furthermore, the fitting function g4, giving rise to the low energy feature of 1c band L, is split into two fitting functions g5 and g6 in the case of 1f; this effect can also be traced back to the larger separation between T_7 and T_8 from T_9 and T_{10} induced by the same perturbation.

2f. Fig. 6 shows the experimental and computed electronic spectrum of **2f**.

Band M is produced by excitations in the range S_7 - S_{18} . Excitation toward S_9 and S_{11} give the more relevant contribution in the low energy region. S_9 is a CT from the metal and the cyclometallated ligand to hfacac. In addition, S_{11} is a LC transition on the cyclometallated ligand and analogue to the excitations toward S_4 and S_5 in 1c; thus band M assignment in terms of molecular moieties involved is akin to 1c.

As in **1f**, **2f** band L is due to two close-in-energy electronic transitions toward S_3 and S_4 and a transition toward S_5 (g10) that in **1f** belonged to band M. Also in this case, the excitation toward S_3 is a π - π *-symmetry LLCT from the cyclometallated ring to hfacac, and excitation toward S_4 is the LC transition of the cyclometallated ring. S_5 is a MLCT due to excitation from HOMO – 3 (mainly a π d_{ij}* metal orbital) to the LUMO, which is now localised on the hfacac ligand (Fig. 3).

Band T: a comparison between 1c, 2c, 1f and 2f. A detailed analysis of band T in the complexes studied shows that it has many features that can be tracked back to the effect on the electronic structure by the substitution of the coordinating metal and the peripheral substitution of H by F as well.

Furthermore, whereas in 1c and $2c S_1$ belonged to band M (even in the case of 2c it is bathochromically shifted), this is no more true in the case of the last two molecules 1f and 2f, where this transition is moved to band T and becomes more evident in 2f (Fig. 6 and inset). This result is suggested by the TD-DFT computations and is strongly supported by the CV data.

The reduction of the HOMO–LUMO gaps between 1c-f and 2cf, related to the discussed effect of the fluorine substitution in the acac ligand, as evaluated by CV measurements (Table 1) amount to 0.45 eV for the former and 0.48 eV in the latter case (Table 1). Furthermore, the S₁ state is an almost pure monoelectronic HOMO \rightarrow LUMO transition in all the studied molecules as shown by TD-DFT computations. Hence it is possible to evaluate the shift of the S₁ in case of 1f and 2f from the S₁ energies of 1c and 2c that amount to 3629 and 3870 cm⁻¹ respectively. These data locate the S₁ state well inside band T at 22367 (447 nm) and 20361 cm⁻¹ (491 nm) respectively and compare well with the computed TD-DFT values of 21807 (459 nm) and 19486 cm⁻¹ (513 nm). Furthermore, TD-DFT results suggest that the oscillator strength of these transitions are much smaller in case of 1f and 2f than in case of their non fluorinated counterpart 1c and 2c.

On the other hand, we can then suggest that band T in the case of **1c** and **2c** is associated to low-absorbing triplet states (Fig. 5 and Table 3).

This band is (Fig. 5 and inset) very broad and of low intensity and can be ascribed to T_2 and T_1 . Excitations related to T_2 involve only 22% of contribution coming from a mono-electronic one characterized by pure metal d_{z^2} to d_{xy} orbitals and 32% of a HOMO to LUMO + 3 of π - π type whose contribution is 50% in T_2 , suggesting a vibronic contribution to the intensity of these transitions. In fact, the puckering of the Pd atom out of plane reduces the T_2 energy and adds some mono-electronic excitation between pseudo a' (σ -type) and a" (π -type) orbitals switching on the SO interaction. Further contribution can be given by $T_{\rm 3}$ and $T_{\rm 4}.$

This assignment is more clearly evident in case of 2c (Fig. 5 and inset) where this band is mainly due to the same Gaussian functions assigned to T_1 and T_2 .

In addition, in the case of **1f** and **2f**, the very low intensity band T is due to a combination of low-absorbing singlets, S_1 and S_2 , and to the three triplets T_3-T_5 . In particular, we suggest, by comparison with the **1c** spectrum, that S_1 is assigned to the Gaussian g3 (20944 cm⁻¹) and that g4 and g5 could be assigned to T_4 and vibronically enhanced S_2 whereas g2 and g1 take account of T_1 and T_2 . The higher electronegativity of the hfacac ligand leads to some changes in the band shape, but induces a drastic change in the spectral position and nature of S_1 . This behaviour can be observed even in the PhPy-based complexes (see ESI for more information).

Phenyl pyridine and azobenzene complexes. The computational assignment of UV-Vis spectra of PhPy-based complexes can be traced back to the previous discussion about BzQ-based complexes. The interested reader can achieve more information from the ESI; here we only underline some main points of similarity between 1b, 2b, 1e and 2e and, respectively, the analogues 1c, 1f, 2c and 2f:

(a) The low-energy part of the spectrum ($\lambda > 300$ nm) in cyclohexane solution is characterised by two main absorption bands (referred to as band L and band M as above).

(b) In **1b** and **2b**, band L is clearly assigned to the HOMO– LUMO transition, which is a LC transition on the cyclometallated ligand with small perturbation due to CT from the central metal to the cyclometallated ligand.

(c) In **1e** and **2e**, band L results from an overlap of the same electronic transition of point (b) and a new transition involving a LLCT from the cyclometallated ring to the hfacac ligand.

(d) In **1e** and **2e** the HOMO–LUMO transition is a low-intensity CT from the cyclometallated ring to the hfacac ligand which is redshifted in comparison to band L and visible as a long tail of the same band.

(e) Band M is mainly due to LC transitions of the cyclometallated ring and the ancillary ligand. Also in this case a MLCT is present as a perturbation.

In addition, our computations allow an easy explanation of the lack of solvatochromism of the main features. Furthermore, a neat change of energy and characteristics of S_1 is present when acac is replaced by hfacac.

As already pointed out, according to our computations, Azobased complexes do not show the neat change in LUMO energy passing from the acac-based **1a** and **2a** to the hfacac-based **1d** and **2d**. Accordingly, no long tails of the first intense band (band L) have been observed when hfacac replaces acac in **1a** and **2a**. This fact confirms the previously discussed assignment of band T tail at longer wavelengths, and is in good agreement with the CV experimental results.

Apart from this difference, the basic assignment discussed for BzQ-based and PhPy-based complexes can be extended to the Azo-based ones. Fig. 7 reports the UV-Vis spectra of **1a** and **1d** recorded in cyclohexane. In these complexes, a low-energy band is present that clearly corresponds to the discussed band L. In all the Azo-based compounds, this band can be assigned to a LC



Fig. 7 Absorption spectra of (a) 1a and (b) 1d recorded in cyclohexane solution and TD-DFT computations. The computed electronic vertical transition wavelengths are reported as a vertical line whose length is the associated oscillator strength and the numeric label indicates the excited (S_n) state.

transition on the cyclometallated ligand, with a small perturbation of MLCT involving the same ligand as acceptor. The most intense computed transition consists of the excitation toward S_5 in **1a** and toward S_6 in **1d** (Fig. 7). Also in this case, the main contribution to such a transition is a LC excitation on the cyclometallated ring.

The interested reader is referred to the ESI for a detailed description of the computed spectra in these complexes and for the analogues **2a** and **2d**. Here, we only note that the considerations regarding **1a** and **1d** can be extended to **2a** and **2d**.

Luminescence properties. The luminescence properties, as observed at 77 K in dichloromethane (Table 2), provide some useful hints about the nature of the low-lying emitting levels. On general grounds, it is known that for Pd(II) and Pt(II) cyclometallated complexes, ³LC emissions observed at 77 K exhibit narrow and resolved emission spectra and, by contrast, ³MLCT ones are broader and less resolved.2a,3a In addition, luminescence lifetimes are usually much longer for ³LC emissions than for ³MLCT cases. From Table 2, one can notice that the luminescence lifetimes of the Pd(II) complexes exhibit systematically longer lifetimes than the analogous complexes of Pt(II). This is likely due to a sum of different effects. Firstly, the emitting states for the Pd(II) cases are likely to display a purer triplet character than for the Pt(II) counterparts, owing to the difference in spin-orbit coupling constant for the two metal centers, $\xi_{Pd} = 1504 \text{ cm}^{-1} \text{ vs.}$ $\xi_{Pt} = 4481 \text{ cm}^{-1.9}$ Secondly, for the Pt(II) complexes, the emission includes a larger degree of ³MLCT (and ³ILCT) contributions against ³LC contributions. In fact, as already discussed, the metalligand interaction is of an antibonding character (see ESI and the "Electrochemical study" section) and thus, a larger metal contribution means higher-energy orbitals and easier oxidation processes.

For the sake of comparison, Fig. 8 displays emission profiles for **1b**, **1e**, **2b**, and **2e**. From the figure, one sees that the electronwithdrawing effect of the CF₃ groups (**1e** and **2e**) results in shorter-lived and lower-lying emitting states, exhibiting broader spectra with respect to the unfluorinated counterparts (**1b** and **2b**, respectively). This further suggests that the observed emission of both Pd(II) and Pt(II) fluorinated complexes includes a larger ³CT character than for the unfluorinated ones. In this respect, assuming that the triplet states are mainly represented by monoelectronic excitation from HOMO to LUMO, it is easily seen in the case of **1e** from Fig. 2 and **1b** from Fig. S9 (in the ESI) that the former shows a large contribution of hfacac in LUMO whereas in the case of **1b** both HOMO and LUMO have a large contribution from the cyclometallated moiety with almost missing contribution from



Fig. 8 Luminescence spectra (and lifetimes) of the indicated complexes observed in 77 K dichloromethane, $\lambda_{exc} = 337$ nm.

A possible explanation of the lack of emission in Azo-based complexes might be tracked back to the large geometry deformation in the first singlet excited state. In fact, the N–N elongation, *e.g.* 0.056 Å in the case of **2a**, was the largest geometry deformation evaluated by TD-DFT computations in the case of the S₁ excited state. This behavior can be explained on the ground of monoelectronic excitations, ending (in all cases) mainly into the LUMO, which shows a large N–N antibonding character (see ESI).

Conclusions

A comparison between complexes of Pd(II) and Pt(II) with different cyclometallated ligands and with acac and hfacac, by means of the selective perturbation of different moieties of this kind of complex together with TD-DFT computations, has allowed us to gain a deeper insight into their electronic structures as investigated by CV, UV-Vis emission and measurements of the decay times of the low-energy-emitting electronic states.

Of particular relevance is the effect of the fluorine substitution in hfacac. In fact, the main effect of the substitution is to move to lower energy the MO strongly localized on the hfacac, so that in this series of derivatives the LUMO is localized on this moiety of the molecule. This is different from the acac ligand, where the LUMO is mainly localized on the cyclometallated ligand. (Azo)containing compounds do not show any emission due to the presence of the diazo bond, whereas the benzoquinoline derivatives, with the exception of the **2c** complex, show comparable emission behaviour to the already known phenylpyridine derivatives.

Furthermore, the electron-withdrawing effect of the CF_3 groups results in shorter-lived and lower-lying emitting states, exhibiting broader spectra with respect to the non-fluorinated counterparts.

Experimental

Synthesis

All commercially available chemicals were purchased from Aldrich Chemical Co. and were used without further purification. IR spectra (KBr pellets) were recorded on a Perkin-Elmer Spectrum One FT-IR spectrometer equipped for reflectance measurements. ¹H-NMR spectra were recorded on a Bruker WH-300 spectrometer in CDCl₃ solutions, with TMS as internal standard. Elemental analyses were performed with a Perkin-Elmer 2400 analyzer CHNS/O.

The Pd(II) complexes **1a–f** were synthesised as previously reported from their corresponding acetate-bridged complexes,⁴ whereas the Pt(II) analogues **2a–f** were synthesised from the dinuclear chloro-bridged cycloplatinated parents by a reported procedure^{10,11} with the following modifications: the cyclometallated chloride bridged dimer intermediates were prepared using strictly one equivalent of cyclometallating ligand, and the bridge intermediate was, after isolation, treated with Tl(acac)¹² or Na(hfacac)⁵ to yield **2b–c** and **2e–f** respectively, in good overall yield. The previously described procedure is not successful when using azobenzene as the cyclometallated ligand; consequently, for the synthesis of **2a** and **2d**, the chloride-bridged platinum complex intermediate was obtained *via* the corresponding platinum allyl.¹³

Preparation of Pt azobenzene chloride-bridged dimer. Azobenzene (0.60 mmol, 0.11 g) was added to a solution of $[(\eta^3-C_4H_7)Pt(\mu-Cl)]_2$ (0.30 mmol, 0.17 g) in chloroform (15 mL) The mixture was heated at reflux for 35 h, cooled to room temperature and filtered off; the dark-brown solid was dried under vacuum to give the pure product in 72% yield (0.18 mg). Mp. 300 °C. Anal. Calcd. for $C_{24}H_{18}N_4Cl_2Pt_2$ (%): C, 34.97; N, 6.80; H, 2.18. Found (%): C, 34.92; N, 6.84; H, 2.22. IR (KBr, cm⁻¹): 1458, 1360, 1303, 760, 714, 578. ¹H NMR data are not available because of the low solubility in common solvents.

Preparation of Pt 2-phenylpyridine chloride-bridged dimer. 2-Phenylpyridine (1.20 mmol, 0.50 g) in 2-ethoxyethanol (9 mL) was added to a solution of K_2PtCl_4 in water (3 mL). The mixture was heated at 80 °C for 48 h in an inert gas atmosphere. The green solid obtained was filtered, washed with water (5 mL) and methanol (15 mL) and air-dried. Yield 75% (0.96 g). Mp. 280 °C. Anal. Calcd. for $C_{22}H_{16}N_2Cl_2Pt_2$ (%): C, 34.33; N, 3.64; H, 2.80. Found (%): C, 34.00; N, 3.35; H, 2.25. IR (KBr, cm⁻¹): 3102, 3017, 1610, 1491, 746, 690. ¹H NMR (300 MHz, DMSO-d₆, 298 K, TMS), ppm: 9.49 (d, J = 5.7 Hz, $J(^{195}$ Pt–H) = 29 Hz, 2H), 8.30–8.07 (m, 4H), 7.77 (d, J = 7.59 Hz, 2H,), 7.53–7.49 (m, 4H), 7.20–7.11 (m, 4H).

Preparation of Pt benzo[*h*]**quinoline chloride-bridged dimer.** This complex was prepared following a similar procedure to that used for the preparation of 2-phenylpyridine chloride-bridged dimer. Yellow solid, yield 56% (0.77 g). Mp. 280 °C. Anal. Calcd. for $C_{26}H_{16}N_2Cl_2Pt_2$ (%): C, 38.16; N, 3.42; H, 1.97. Found (%): C, 37.99; N, 3.31; H, 1.91. IR (KBr, cm⁻¹): 3048, 1623, 1453, 741, 706. ¹H NMR (300 MHz, DMSO-d₆, 298 K, TMS), ppm: 9.69 (d, with broad ¹⁹⁵Pt satellites, J = 5.8 Hz, 2H), 8.74 (d, J = 8.1 Hz, 2H), 8.39 (d, J = 7.55 Hz, 2H), 7.97–7.86 (m, 6H), 7.81 (d, J =8.78 Hz, 2H), 7.76–7.52 (m, 2H).

Synthesis of 2a. A typical preparation is reported for complex 2a; all analogous complexes, 2b–f, were prepared following the same synthetic procedure. Colour, yield, melting point, elemental analyses, IR and ¹H NMR data are reported in the ESI.

A suspension of thallium acetylacetonate (0.27 mmol, 0.08 g) in dichloromethane (5 mL) was added to a suspension of the dinuclear chloro-bridged Pt(II) complex (0.13 mmol, 0.11 g,) dissolved in dichloromethane (15 mL). The resulting mixture was stirred for 180 h at room temperature. The reaction was monitored by TLC and, after completion, the reaction mixture was filtered through Celite and the solvent was removed under reduced pressure. Recrystallization of the crude product from chloroformmethanol solution afforded **2a** as brown crystalline solid. Yield 70% (0.09 g).

Electrochemical study

Cyclic voltammetry data were measured with IR compensation using an Epsilon electrochemical analyser. The experiments were carried out with 3 mL of a *ca.* 10^{-3} M solution of compound at a scan rate of 100 mV s⁻¹. Potentials were measured using a glassy carbon working electrode, a platinum wire as counterelectrode and a Ag wire as pseudoreference electrode. Potentials were finally corrected *versus* ferrocene/ferrocenium⁺ by adding ferrocene as an internal standard to the studied solution after the experiment. Oxidations and reductions of the complexes were observed in dry *N*,*N*'-dimethyl formamide using tetra(*n*butyl)ammonium hexafluorophosphate (0.1 M) as supporting electrolyte, and under nitrogen atmosphere.

Photophysical characterization

UV-Vis absorption spectra were obtained with a Perkin-Elmer lambda 900 UV/vis spectrometer. Luminescence spectra and lifetimes of the complexes at 77 K were obtained with a Perkin-Elmer LS 50B luminescence spectrometer, equipped with a Hamamatsu R-928 photomultiplier tube. The samples were placed within capillary tubes immersed in liquid nitrogen and the experiments were performed by applying both a temporal delay and gating in order to exclude fast scattering from the apparatus; the excitation source was set at 337 nm in all cases.

Computational methods

The Gaussian98 package (revision A11)^{14a} and Gaussian03 (revision D02)^{14b} have been used for all the computations. Density functional theory was applied using the MPW1PW91 hybrid

xc functional.¹⁵ The geometry optimizations were performed by applying the Stuttgart/Dresden ECP basis set¹⁶ on Pd and Pt atoms, and the Dunning/Huzinaga valence double- ζ (D95V) basis set¹⁷ on C, N, O, F and H atoms (default "SDD" Gaussian98 keyword). Default gradient and displacement thresholds were used for the geometry optimization convergence criteria. All the reported geometries are relative minima of the potential energy surface (electronic energy in the Born–Oppenheimer approximation), as confirmed by the analytical computation of the Hessian matrix at the same level of approximation.

Time-dependent density functional theory (TD-DFT)¹⁸ was applied to compute the excitation wavelengths, oscillator strengths and associated excited state percentage composition in terms of monoelectronic excitations between occupied and virtual Kohn– Sham orbitals. Such percentage values were computed by doubling the squared coefficient associated with the monoelectronic excitation as printed in the Gaussian 98 output file. TD-DFT calculations were performed by using the same level of approximation used in the structure optimization.

According to the updates to the Gaussian03 manual,¹⁹ in Gaussian98: "the original implementation of the mPW exchange functional was not consistent with the equations in the paper:¹⁵ the local scaling factor was applied in computing the non-local correction. The version of mPW in Gaussian03 corrects this error, but since the parameters in the original paper were optimized with the incorrect functional, the correct one cannot reproduce the original results..."

In order to check the effect of this modification, in the case of BzQ-based complexes the computations were also performed with Gaussian03. Geometries were unmodified within 10^{-4} Å. All the reported computations of S₀ and excited states properties (by TD-DFT) have also been confirmed.

Excited-state geometries were obtained by the Turbomole 5.9 suite of programs.²⁰ The Kohn–Sham orbitals were drawn by the program Molekel4.3.²¹

Acknowledgements

This research was supported by the Italian Ministero dell'Istruzione, dell'Università e della Ricerca (MiUR) through FIRB (RBNE01P4JF) and PRIN (2005035277_005) and Centro di Eccellenza CEMIF.CAL (CLAB01TYEF) grants.

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