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Photophysical properties of an unusual bichromophoric species constructed from a cyclometalated Pt(II) chromophore and a blue Bodipy-acetylacetonate species

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Abstract

A Bodipy species bearing an acetyl-acetonate (acac) group, **3**, has been prepared from a blue absorbing borondipyrromethene core bearing gallate substituted paraffin chains. Compound **3** chelates a Pt(II) center having an orthometalated 2-phenyl-pyridine anion (ppy) as additional ligand, giving rise to a new bichromophoric Pt(II)-Bodipy species. **1**. The absorption spectra, redox behavior and photophysical properties of **1**, **3** and of the neutral Pt(II) compound **2**, containing ppy and an acac derivative as ligands, have been studied. Compounds **3** and **2** are used as models for the Bodipy-based and the metal-based subunits of **1**, respectively. The ^3LC emission of **2** is fully quenched in **1**, whereas the Bodipy fluorescence is only weakly reduced in **1** compared to **3**, indicating weak interaction between the subunits. Two different charge-separated (CS) states have a role in the intercomponent excited state decays of **1**. Notably, whereas in all the previously investigated bichromophoric metal(polypyridine)-Bodipy compounds the light absorbed by the metal-based unit leads to population of the lowest-energy triplet Bodipy-based level, in **1** it contributes with high efficiency (>99%) to the Bodipy fluorescence. An efficient and formally forbidden ^3LC -to- $^1\text{Bodipy}$ energy transfer occurring by Förster mechanism is, unprecedentedly, the dominant ^3LC decay process in **1**.

Introduction

Multichromophoric species are extensively investigated from both fundamental and applicative perspectives. For example, the study of photoinduced intercomponent energy and electron transfer processes occurring in such systems can give useful information for the preparation of artificial systems for the photochemical conversion of solar energy.^{1,2} Pt(II) polypyridine and/or cyclometalated compounds are very attractive chromophores, in virtue of their luminescent properties,³⁻⁵ and boron dipyrromethene (Bodipy) species are playing quite important roles as components of photo-active species:⁶⁻⁸ as a consequence, it is not surprising that multichromophoric species made of Bodipy and Pt(II) polypyridine subunits have been recently investigated.⁹⁻¹³ In all the reported species, the metal-based emissive state, usually a ³MLCT (metal-to-ligand charge transfer) level, was always fully quenched by various mechanisms, all of them ultimately leading to population of the lower-lying, Bodipy-based triplet state, so that overall energy transfer to the Bodipy triplet state was occurring. In fluid solution at room temperature, in most cases the energy transfer process was mediated by a two-step electron transfer involving a charge-separated (CS) state, in which the Pt(LL) unit (LL stands for the polypyridine ligand) played the role of the acceptor and the Bodipy unit acted as the donor (formally, a Bodipy⁺/Pt(LL⁻) CS state). At 77 K, triplet-triplet energy transfer by the Förster mechanism was held responsible for the MLCT quenching.¹⁰ In some Pt(II)-Bodipy systems, the rarely seen triplet Bodipy phosphorescence, firstly reported by our team in mixed Ru(II)-Bodipy species,¹⁴ and successively evidenced also in Ir(III) cyclometalated species,¹⁵ was also recorded.¹⁰

It should be noted that the MLCT emission quenching – leading to population of the lowest-lying Bodipy-centered triplet state - was not peculiar to the mixed Pt(II)-Bodipy species, since the same process was also recorded for other metal-Bodipy species, including the ones investigated by ourselves.^{14,15} On the contrary, the fate of the Bodipy-based fluorescence

in the multicomponent species was not identical for all the studied multichromophoric compounds, but appeared to be dependent on the specific cases. In fact, whereas in Ru(II)-Bodipy as well as in Ir(III)-Bodipy species the Bodipy-based fluorescence was fully quenched - like the $^3\text{MLCT}$ emission - both a room temperature and at 77 K, with population of the Bodipy-based triplet state,^{14,15} in Pt(II)-Bodipy compounds it was only partly quenched.^{9,10} Either complete or partial, the fluorescence quenching was attributed to enhanced intra-Bodipy intersystem crossing (isc), where an important role was played by the above-mentioned CS state, which was energetically intermediate between singlet and triplet Bodipy-based states. In fact, it was proposed¹⁰ that enhanced spin-orbit coupling, needed to accelerate the intra-Bodipy isc, was promoted by coupling of the Bodipy-based singlet states with the closely-lying CS state (and, in some cases, also with the $^3\text{MLCT}$ level), in which the effective presence of the heavy transition metal atom alleviated the spin forbiddenness. A role of the CS as a real intermediate for the intersystem crossing process could also not be excluded. Since electronic interaction between the fluorescent state and the CS state, according to non-adiabatic theory of electron transfer, depends on structural arrangements, different structures can determine different fluorescence quenching.

Here we report the synthesis, characterization, and photophysical properties, of a new Pt(II)-Bodipy species (**1**) and of its model compounds, the Pt(II) cyclometalated species **2** and the Bodipy species **3** (see Fig. 1 for the structural formulae). Beside other factors, compound **1** also differs from formerly-studied, similar Pt(II)-Bodipy bichromophoric species (see Fig. 2 for the structural formulae of representative compounds) as far as the size of the molecular fragment bridging the Bodipy and the metal-containing chromophore is concerned. Actually, the size of the bridging unit is larger in **1** - where it is represented by a roughly linear phenyl-ethynyl-phenyl fragment - with respect to the bridging units which are present in formerly

studied species (compare **1** in Fig. 1 with **4-7** in Fig. 2).^{9,10} The different size of the bridging unit in **1** compared to previously studied systems allows to investigate in detail the effect of geometrical factors on interchromophoric excited-state decays. Noteworthy, in the multichromophoric species **1** the Pt-based emission is practically fully quenched, whereas the Bodipy-based fluorescence is only very weakly quenched. Moreover, the light absorbed by the metal-based chromophore does not populate the Bodipy triplet state, but contributes to the Bodipy-based singlet emission. This last result is unprecedented as far as the photophysical properties of multichromophoric metal-Bodipy systems are concerned (in formerly studied species, the light absorbed by the metal-based unit does not contribute to Bodipy fluorescence, but rather led to population of the Bodipy triplet state).

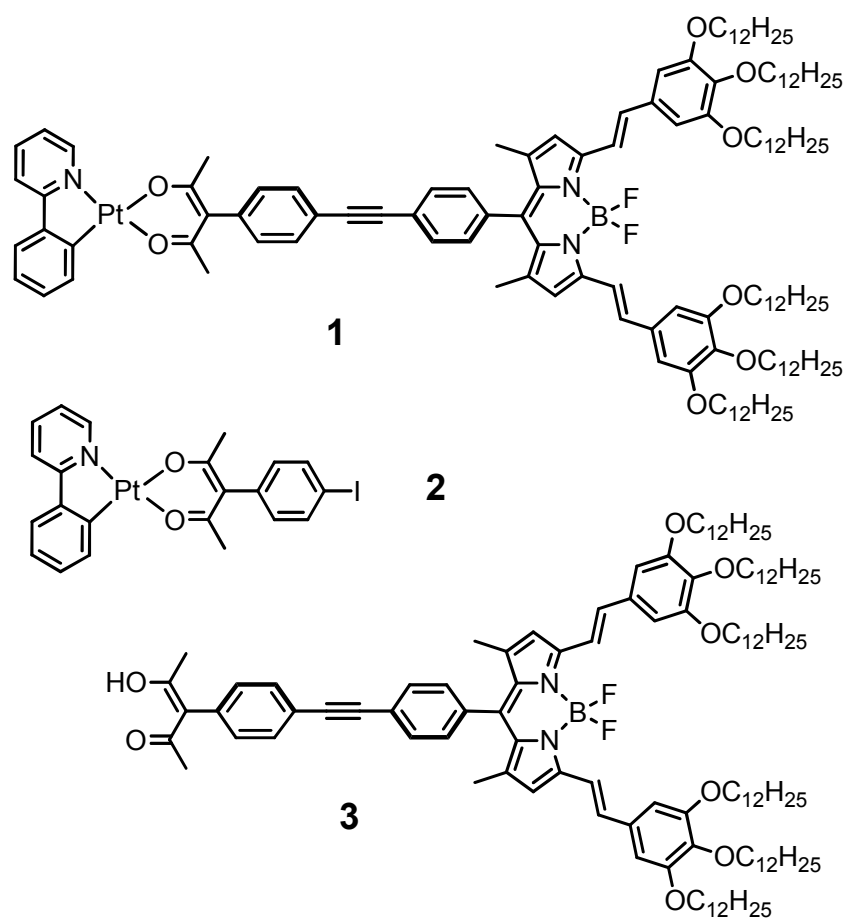


Fig. 1. Structural formulae of the studied compounds.

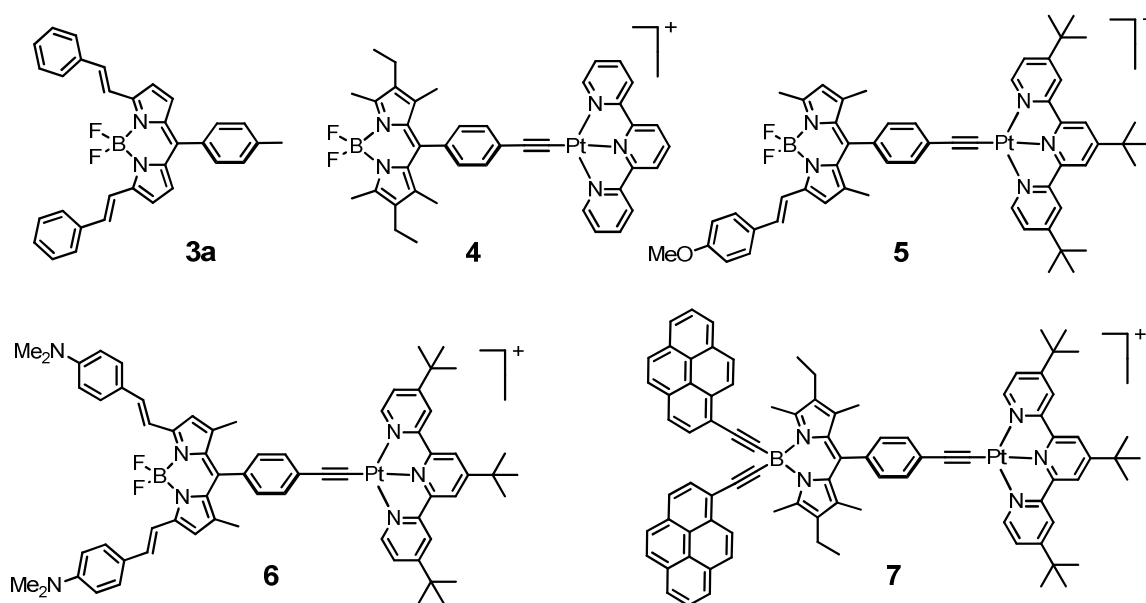
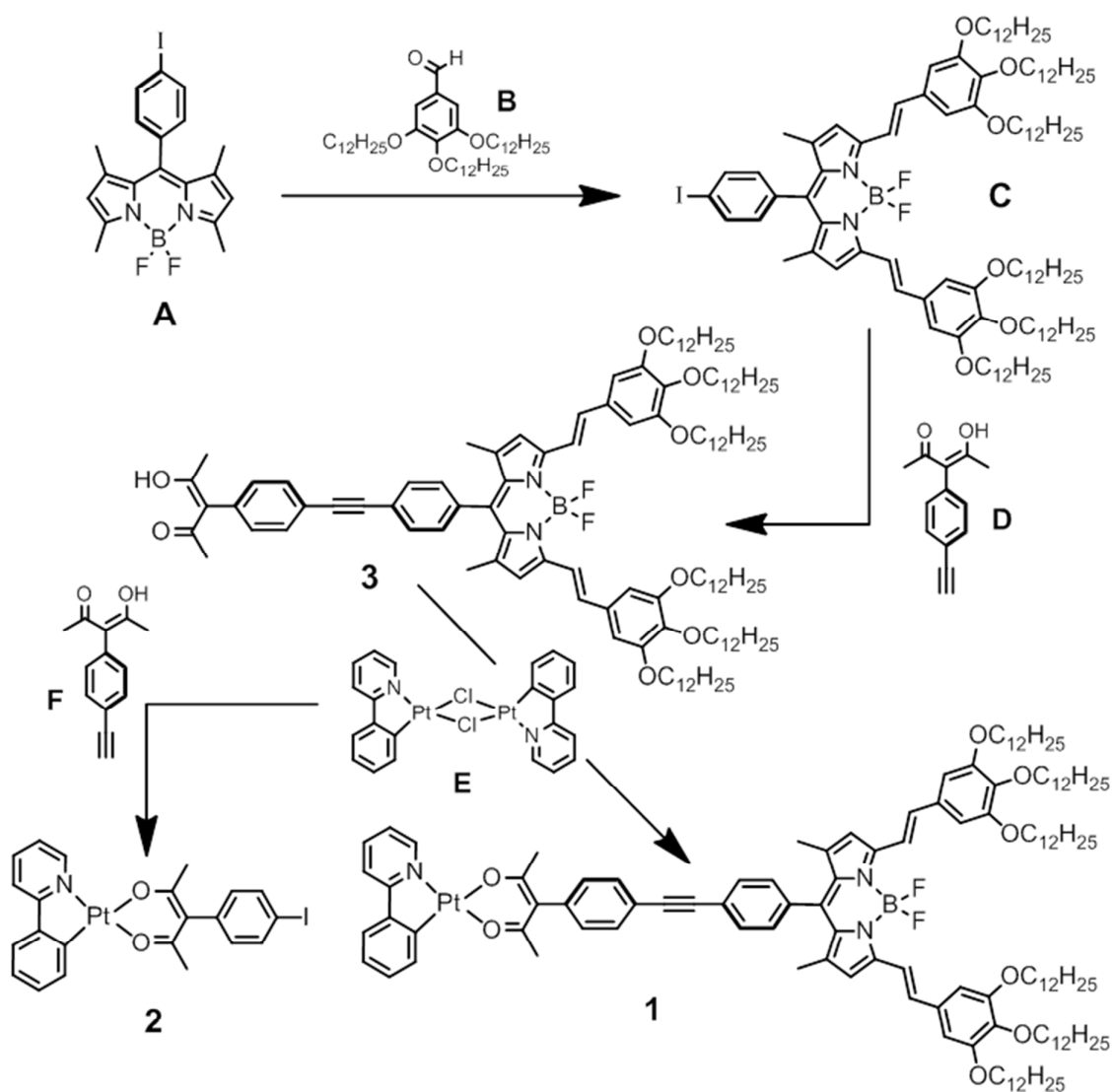


Fig. 2. Structural formulae of formerly investigated compounds cited in the text.

Results and discussion

Synthetic approach. The roadmap for the preparation of the key compounds is sketched in **Scheme 1**. The synthesis starts with the preparation of the blue divinyl-Bodipy **C** obtained by a Knoevenagel condensation of the red Bodipy **A**¹⁶ with 3,4,5-tridodecylalkoxybenzaldehyde **B**¹⁷ under standard conditions, affording **C** in 53% isolated yields.¹⁸ The next step consists in a cross-coupling reaction between **C** and 3-[4-ethynylphenyl]pentane-2,4-dione,¹⁹ catalyzed by low valent palladium(0). The target ligand **3** was isolated pure in 70% by column chromatography and adequate crystallization from standard solvents. Complexation of the acetyl-acetonate (acac) fragment in ligand **3** is obtained in two steps by first deprotonation of the acac with t-BuOK and then complexation with orthometalated- μ -dichloroplatinum(II) complex **E**.²⁰ After purification, the target complex **1** was isolated pure in 32% yield. In a similar manner complex **2** was produced using the μ -dichlorodimer with 3-[4-iodophenyl]pentane-2,4-dione **F**.¹⁹ The molecular structures of all

ligands and complexes were unambiguously assigned by NMR spectroscopy techniques, mass spectra and elemental analysis.



Scheme 1. Synthetic routes for the preparation of the target compounds **1**, **2** and **3**.

Absorption spectra and photophysical properties of the model species 2 and 3. The absorption spectra and luminescence properties of the model compounds **2** and **3** (Table 1) are in line with those of other Pt(II) cyclometalated species^{3,4} and of Bodipy dyes with appended ethenyl substituents.^{6,7,21} The absorption spectrum of compound **2**, in toluene solution, exhibits moderately intense absorption in the UV region, mainly attributed to spin-allowed ligand-

centered (LC) transitions,^{3,4} with a less intense, broad bands at lower energies, attributed to MLCT transitions (see Fig. 3). The emission spectra of **2**, both at room temperature and at 77 K, are structured and lifetimes are in the microsecond time range (see Fig. 4 and Table 1). The slight blue shift of the emission spectrum on passing from fluid solution at room temperature to rigid matrix at 77 K (from 488 to 478 nm, Table 1), along with the structured emission and lifetime, suggests that the emission of **2** can be mainly assigned to a triplet LC state, with small contribution from a triplet MLCT state.^{4,22} The luminescence properties are independent of excitation wavelength, and are in line with those reported for similar Pt(II) compounds.^{22,23} The pump-probe transient absorption spectrum of **2** in toluene at room temperature - performed on exciting at 400 nm, as for all the pump-probe experiments discussed in this work - is shown in Fig. 5: it shows an intense absorption in the range 420 – 500 nm, followed by a broad absorption extending to 720 nm, which is probably due to absorption of the radical 2-phenylpyridine anion. The transient spectrum does not show any significant change in the investigated time window (100 fs – 3.3 ns), however within 5 ps from laser pulse the transient absorption at 430-490 nm grows up whereas the low-energy absorption decays (Fig. 5, top panel). This could be due to a localization of the excited state on specific ligand frameworks (a sort of charge shift within the chromophore); this process should also include intersystem crossing from the initially-prepared singlet (mixed) LC/MLCT state to the emissive and long-lived ³LC, which is expected to be complete within 1 ps.²⁴ At longer times, other spectral changes take place, most likely due to vibrational cooling (Fig. 5, bottom and middle panels). Because of the long emission lifetime of **2** (Table 1), decay of the emissive state is not appreciable in the time window investigated.

Table 1. Absorption spectra and luminescence properties of the studied compounds. All the data are in deaerated toluene.

Compounds	Absorption λ_{\max} [nm] (ϵ [$\text{m}^{-1}\text{cm}^{-1}$])	Luminescence				
		λ_{\max} [nm] 298 K	τ [ns] 298 K ^a	Φ 298 K	λ_{\max} [nm] 77 K	τ [ns] 77 K
1	650 (126000)	670	4.68 (λ , 670)	0.45	665	3.90
	600 (46500)					
	382 (66000)	488 ^{b,c}	0.12 (λ , 486)			
	321 (62500)					
404sh (7000)	488 ^b	1370	0.15	478 ^b	6970	
374 (14500)						
330 (19700)						
3	318 (21000)	670	5.64	0.55		
	650 (126000)					
	600 (46500)					
	382 (53500)					
	321 (43500)					

[a] Emission wavelength, λ , reported in parenthesis; Where not reported, λ is the emission maximum. [b] High-energy feature of a structured emission spectrum. [c] This emission is only visible on exciting at wavelengths shorter than 380 nm, and is extremely weak (see text).

Table 2. Redox data.^a

Compounds	E_{ox} (V vs SCE)	E_{red} (V vs SCE)
1	+ 0.82 ^b + 1.04	- 0.78
2	+ 0.87	
3	+ 0.83 + 1.04	- 0.91

(a) All the data are in 1,2-dichloroethane. The potentials refer to the peak values obtained from DPV experiments. All the processes are irreversible. (b) The process involves the exchange of two electrons.

Cyclic and differential pulse voltammetries (CV and DPV) of **2** in 1,2-dichloroethane indicate that the compound undergoes an oxidation process, irreversible, whose DPV peak is at +0.87 V vs SCE (see Table 2). According to the LC assignment for the emission of **2**, this oxidation process is tentatively assigned to a one-electron oxidation mainly involving the 2-phenylpyridine ligand, with some contribution from the metal-centered orbital.⁴ In our

experimental conditions no reduction process takes place for potentials less negative than -1.30 V vs SCE.

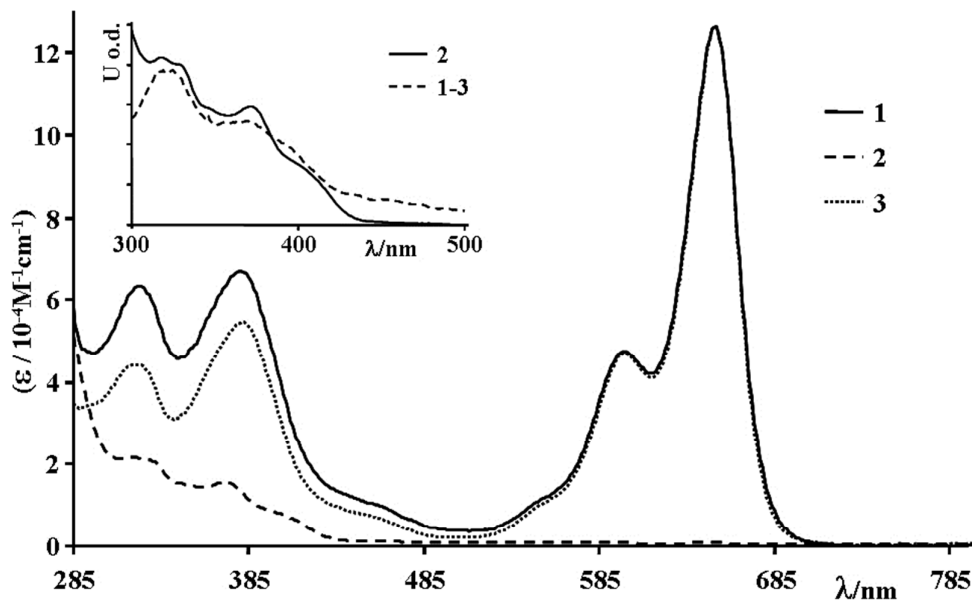


Fig. 3. Absorption spectra of the studied compounds in toluene solutions. Experiments have been made using concentrations in the range $8 \times 10^{-7} - 8 \times 10^{-6}$ M for **1** and **3** and of $8 \times 10^{-6} - 5 \times 10^{-6}$ M for **2**. The inset shows the absorption of **2** and the theoretical spectrum obtained by subtracting the spectrum of **3** from that of **1** (**1-3**); for details, see text.

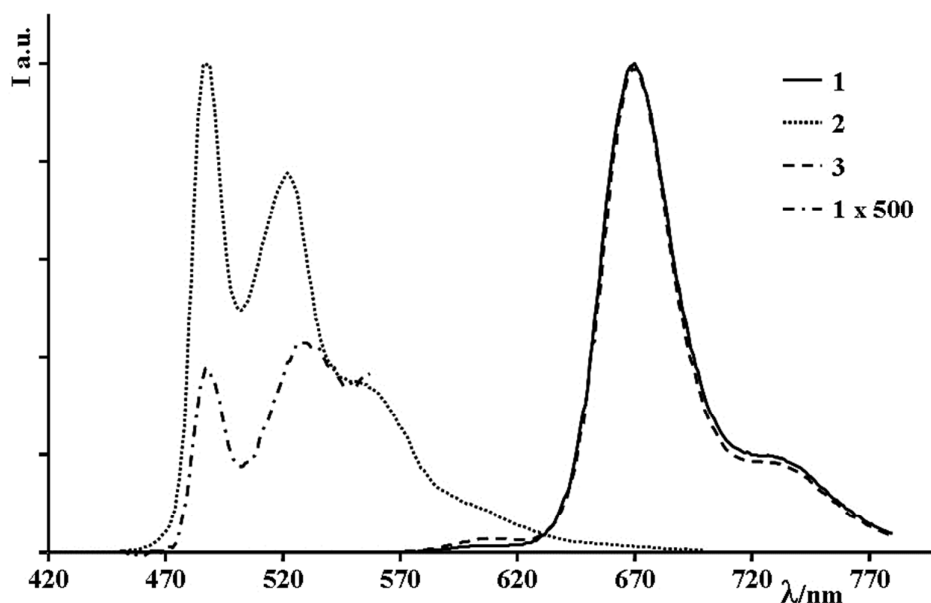


Fig. 4. Emission spectra of **1-3** in toluene solution at room temperature. Typical optical density used is < 0.1 at the excitation wavelength. The dashed-dotted spectrum is a detail of the emission of **1** upon excitation at 317 nm.

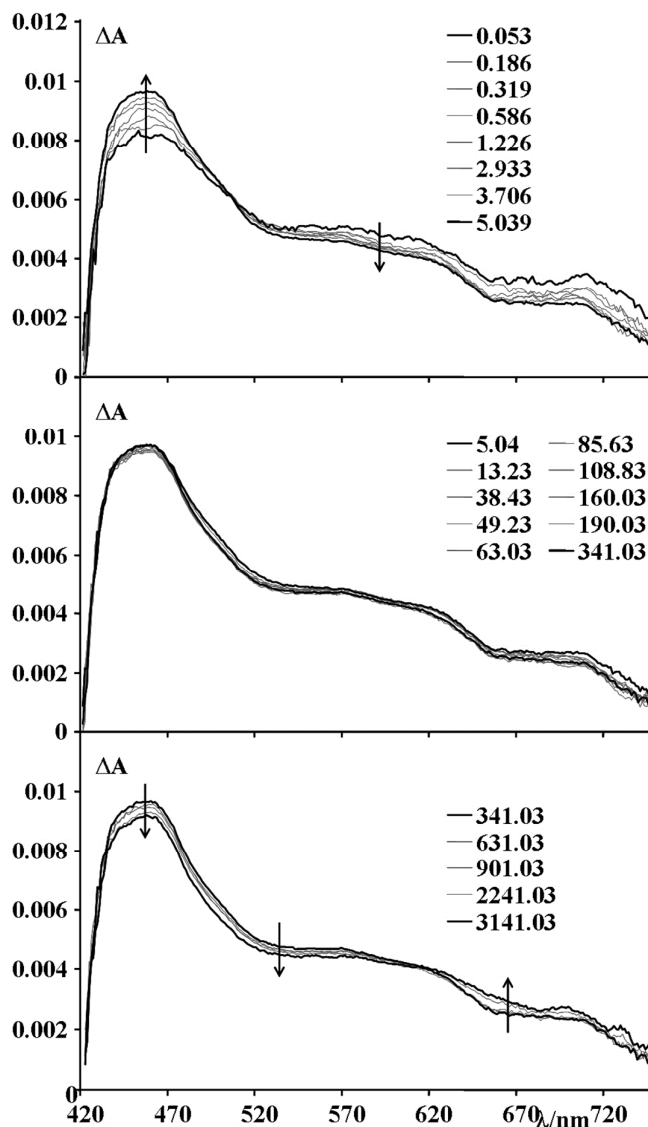


Fig. 5. Transient absorption spectra of **2** in toluene, excitation wavelength, 400 nm. Absorbance at the excitation wavelength, 0.4. Time delays (in ps) are shown in the figure. For further details, see text.

The absorption spectrum of the Bodipy dye **3** (Fig. 3) exhibits a quite intense band peaking at 650 nm, due to a singlet π - π^* transition involving orbitals which extend over the C=C double bonds of the appended substituents, as also reported in similar ethenyl-appended Bodipy species.^{6,7,21} Luminescence is intense (Table 1 and Fig. 4) and can be assigned to

fluorescence from the lowest-lying singlet $\pi-\pi^*$ state, on the basis of emission energy, lifetime, and quantum yield.⁶ The luminescence properties are independent of

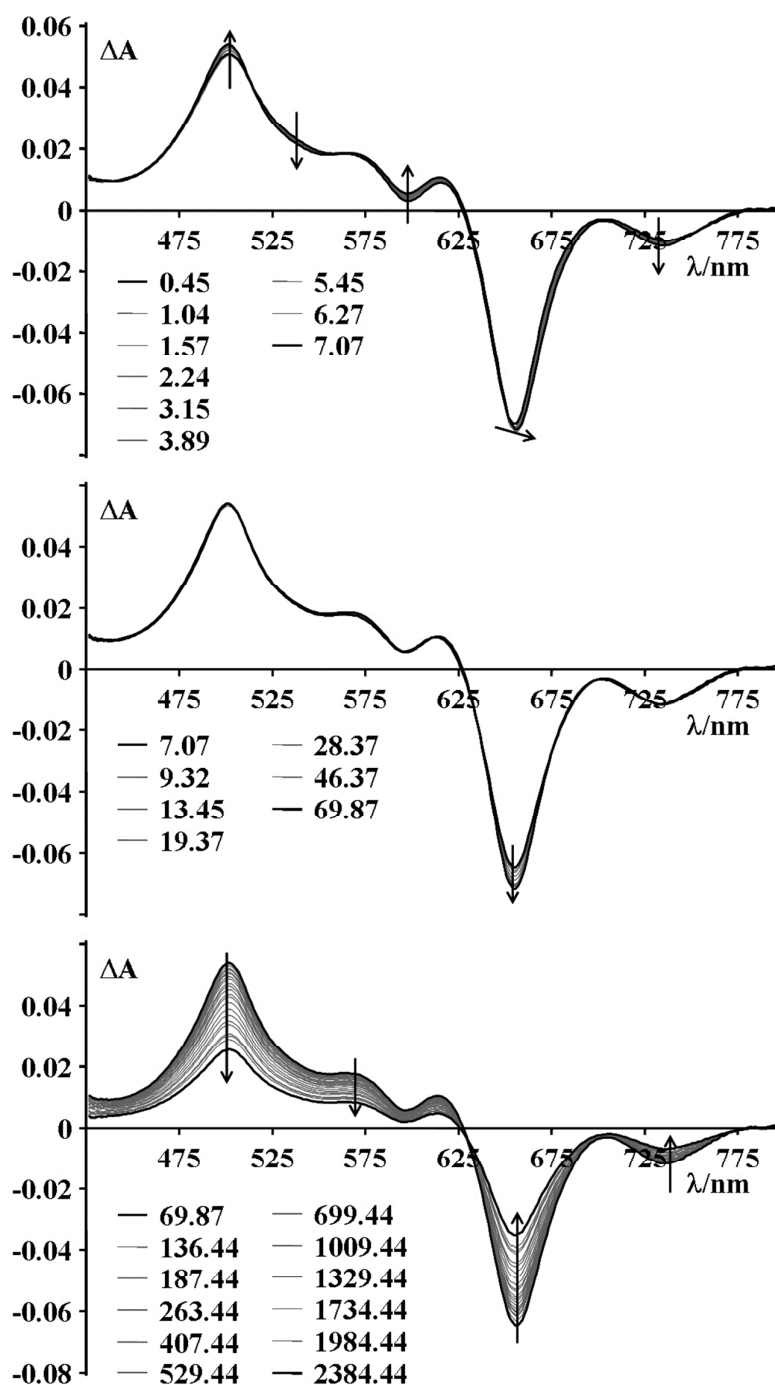


Fig. 6. Transient absorption spectra of **3** in toluene, excitation wavelength, 400 nm; time delays, in ps, are shown in the panels. Absorbance at the excitation wavelength, 0.2. For more details, see text.

excitation wavelength. Time-resolved transient absorption spectrum of **3** (Fig. 6) is characterized by an apparent bleaching peaking at 665 nm, corresponding to the combination of the bleaching of the low-energy absorption band of **3**, peaking at 650 nm (see Fig. 3), and of the σ - σ^* transition in the 630-775 nm range (see Fig. 4). A structured transient absorption is also present in the 450-620 nm range. The excited state decay of the initially prepared **3** exhibits three processes: a first one, within a few ps, characterized by a small red shift in the apparent bleaching at 665 nm and a series of small changes in the ratio between the various transient absorption peaks (Fig. 6, top panel); successively, within a few tens of ps, the apparent bleaching a 665 nm increases (Fig. 6, middle). The first two processes described above can be tentatively attributed to vibrational cooling, including solvent dynamics. Finally, decay to the ground state occurs (Fig. 6, bottom).

Cyclic and differential pulse voltammetries of **3** in 1,2-dichloroethane indicate that it undergoes two oxidation processes, irreversible, whose DPV peaks are at +0.83 and +1.04 V vs SCE. Although the irreversibility of the processes makes difficult to carefully calculate the number of electrons involved, the DPV areas of the two peaks are very similar each other, so suggesting that the processes involve the same number of electrons. It can be noted that the Bodipy species **3a** (see Fig. 2),²⁵ missing the electron donor alkoxy moieties, exhibits a single one-electron, *reversible* oxidation at +1.02 V vs Ag/AgCl (corresponding to about +0.98 V vs SCE), in dichloromethane,²⁵ assigned to the oxidation of the Bodipy main framework. Comparison between the oxidation patterns of **3** and **3a** suggests that the two *irreversible* oxidation processes shown by **3** are due to two one-electron, successive processes involving the two trialkoxyphenyls, electron-rich groups. The separation between the two oxidation potentials would therefore be due to electronic coupling between the two equivalent redox sites. Clearly, the Bodipy-based reversible oxidation, that in **3a** occurs at +1.02 V vs Ag/AgCl, would not occur in the potential window studied here (+1.30 / -1.30 V vs SCE) since the first,

alkoxyphenyl-based oxidation would move the Bodipy-based oxidation to more positive potentials (and, of course, the second alkoxyphenyl-based process would further move the Bodipy-based oxidation to even more positive potentials). On reduction, **3** exhibits an irreversible process, with the DPV peak at -0.91 V. This process is assigned to the reduction involving a Bodipy orbital also extending over the ethenyl groups. Compound **3a** exhibits a reduction process at quite similar potential in dichloromethane, -0.85 V vs Ag/AgCl (corresponding to -0.89 V vs SCE).²⁵

Absorption spectrum and photophysical properties of the bichromophoric species 1.

The absorption spectrum of the mixed multichromophoric species **1** (Fig. 3, Table 1) closely recalls that of its Bodipy-based subunit **3**; the contribution of the absorption spectrum of **2** is evident at wavelengths shorter than 500 nm, as also indicated by the simulated spectrum obtained by subtracting the spectrum of **3** from that of **1**, and comparing the resulting spectrum with that of **2** (see Fig. 3, inset). Interestingly, the spectrum obtained by subtracting that of **3** from that of **1** shows a broad absorption tail at wavelengths longer than 430 nm, which suggests the presence of an interchromophoric CT transition. Apart from such, weak new absorption band, the absorption features of **2** and **3** are roughly identical in **1** (this is particularly true for the absorption band involving the lowest-energy π - π^* spin-allowed transition of the Bodipy subunit around 650 nm; small changes occur for the spin-allowed LC and MLCT bands of the metal-based subunit, see Fig. 3).

The luminescence spectrum of **1** (Fig. 4) is very similar to that of **3**, exhibiting an intense band peaking at 670 nm, at any excitation wavelength, which is assigned to fluorescence of the Bodipy subunit. However, emission lifetime of **1** is slightly shorter than that of **3** (4.7 ns vs 5.6 ns for **1** and **3**, respectively, see Table 1) and emission quantum yield is slightly smaller (0.45 vs 0.55, Table 1). On assuming that the radiative and radiationless decay

rate constants from the singlet Bodipy excited state to the ground state remain identical on passing from **3** to **1**, it appears that a fluorescence quenching takes place, due to an additional decay route, with a rate constant of $3.5 \times 10^7 \text{ s}^{-1}$, based on the emission lifetime data. A close value, $4.0 \times 10^7 \text{ s}^{-1}$, is obtained by using the quantum yield data; the discrepancy is acceptable, considering the experimental uncertainties (10% for lifetimes and 15% for quantum yields, see experimental section). This result, apparently straightforward, differs from that found for all the previously studied Pt-Bodipy species, in which fluorescence quenching calculated by emission lifetimes and quantum yield data gave significantly different values, indicating that both radiative and radiationless decay rate constants of the individual components were modified in the bichromophoric species compared to their isolated components. Noteworthy, this would suggest that intercomponent electronic coupling is weaker in **1** than in any of the similar, formerly studied species **4-7**: indeed, the structural separation among the two chromophores is larger in **1**, so weaker electronic coupling is justified (compare structures in Figs. 1 and 2: the distance between the Pt atom and the boron atom, which can be taken as roughly informative of interchromophoric separation, is clearly larger in **1** than in **4-7**). Beside the constancy of the rate constants for direct decays from the emissive singlet state to the ground state on passing from **3** to **1**, as discussed above, the reduced intercomponent interactions between the two chromophoric subunits of **1** compared to **4-7** makes the fluorescence of the Bodipy subunit less affected by the Pt(II) subunit(s) in **1** than in **4-7**. For example, the fluorescence quantum yield of the isolated Bodipy subunit – that is, missing the Pt-based chromophore - of **6**, 0.18, is reduced to 0.015 in **6**^{9,10}.

Weak interaction between the Pt(II) subunit and the Bodipy component of **1** at the ground state is also evidenced by oxidation results: in fact, cyclic and differential pulse voltammetries indicate that **1** undergoes two oxidation processes, with peaks at +0.82 and

+1.04 V vs SCE (Table 2). Although both processes are irreversible, so that precise calculation of electrons involved in each process cannot be made, internal comparison tends to suggest that the process peaking at +0.82 V should involve two one-electron exchanges, whereas the process at more positive values would involve a single one-electron process. Comparison with the oxidation processes of **2** and **3** (see Table 2) suggests that the process at +0.82 V deals with quasi-simultaneous oxidation of the Pt(II) unit and of one of the trialkoxo-phenyl groups of the Bodipy unit, and the peak at +1.04 V deals with oxidation of the other, not yet reduced trialkyloxo-phenyl group. In other words, oxidation of specific subunits of **2** and **3** occur at about the same potentials in **1**, without any significant mutual perturbation.

Reduction of **1** is in a some way surprising, as an irreversible process appears at -0.78 V, a significantly less negative potential than the reduction of **3** (Table 2). If the orbitals involved in the reduction processes of **1** and **3** were the corresponding ones in the two species, and considering that the LUMO orbital of **3** is assumed to be the orbital also involved in the low-energy absorption transition, as well as in the emission process, a red shift in both absorption and emission spectra of **1** in comparison with **3** should occur, but this is not experimentally found (Figs. 3 and 4, Table 1). Therefore, it can be inferred that the reduction processes of **1** and **3** do not involve corresponding orbitals and molecular sites. A possible reduction site which is present in **1** but not in **2** and **3** is the chelating acetylacetonate unit coupled with the phenyl-ethynyl-phenyl moiety. In fact (see structures in Fig. 1), (i) the bridging, "central" phenyl-ethynyl-phenyl moiety which is present in **1** is also present in **3**, where anyway the acetyl-acetonate is not chelating any metal center and is in its acidic form; (ii) the chelating acetyl-acetonate unit is present in **2**, where anyway the phenyl-ethynyl-phenyl group is absent. So we assign the reduction of **1** at -0.78 V to an orbital mainly centered on the phenyl-ethynyl-phenyl unit coupled to the chelating acetylacetonate unit. # This orbital is not one of the orbitals involved in the low-energy absorption and emission transitions centered in

the Bodipy subunit (in such transitions, orbitals centered in the main Bodipy framework are involved), so the presence of this easy-to-reduce orbital in **1** does not modify the Bodipy-based absorption and emission spectroscopic properties in **1** in comparison to **3** (Table 1). Also, the orbital involved in the reduction of **1** at -0.78 V is not directly involved in the metal-perturbed LC excited state. However, it could be the acceptor orbital for the weak CT band which appears in the absorption spectrum of **1** in the 450-500 nm range (see Fig. 3, inset).

Intercomponent excited-state decay processes in 1. To rationalize the reduced fluorescence of **1** with respect to **3**, mentioned above, the presence of a low-lying CS state can be taken into account. On considering the redox data, a low energy Bodipy⁺/(L⁻)Pt(ppy) CS state can be present (ppy is the 2-phenylpyridine anion; L represents a moiety connected to both the Bodipy and the platinum-containing subunit, but not necessarily linked directly to the metal. So, the Bodipy⁺/(L⁻)Pt(ppy) CS state differs from the formerly reported Bodipy⁺/Pt(LL⁻) CS states,^{9,10} where the "excited", odd electron always resided on a polypyridine ligand directly chelating the metal center, the terpyridine ligand in **4-7**). This Bodipy⁺/(L⁻)Pt(ppy) CS state can be formed by photoinduced, oxidative²⁶ electron transfer from the Bodipy singlet excited state to the phenyl-ethynyl-phenyl unit connected to the chelating acetylacetonate moiety, which we proposed to be the site of the LUMO of **1** (see above; the phenyl-ethynyl-phenyl unit would therefore work like a bridge between the peripheral chromophores). The driving force of such a process, ΔG , is approximated by equation 1,²⁷ where: E_{00} is the energy of the Bodipy singlet state, taken as the 77 K emission of **1** (1.86 eV); E_{ox} is the oxidation potential of the Bodipy subunit (+0.83 V); E_{red} is the reduction potential of the acceptor unit (-0.78 V); e is the electron charge. In eq. 1, the work term is neglected and Koopman theorem is assumed as valid. With such simplifications, ΔG is -0.25 eV, so the energy level of the Bodipy⁺/Pt(L⁻) CS state can be approximated to 1.61 eV (see Fig. 7).

$$\Delta G = (eE_{ox} - E_{00}) - eE_{red} \quad (1)$$

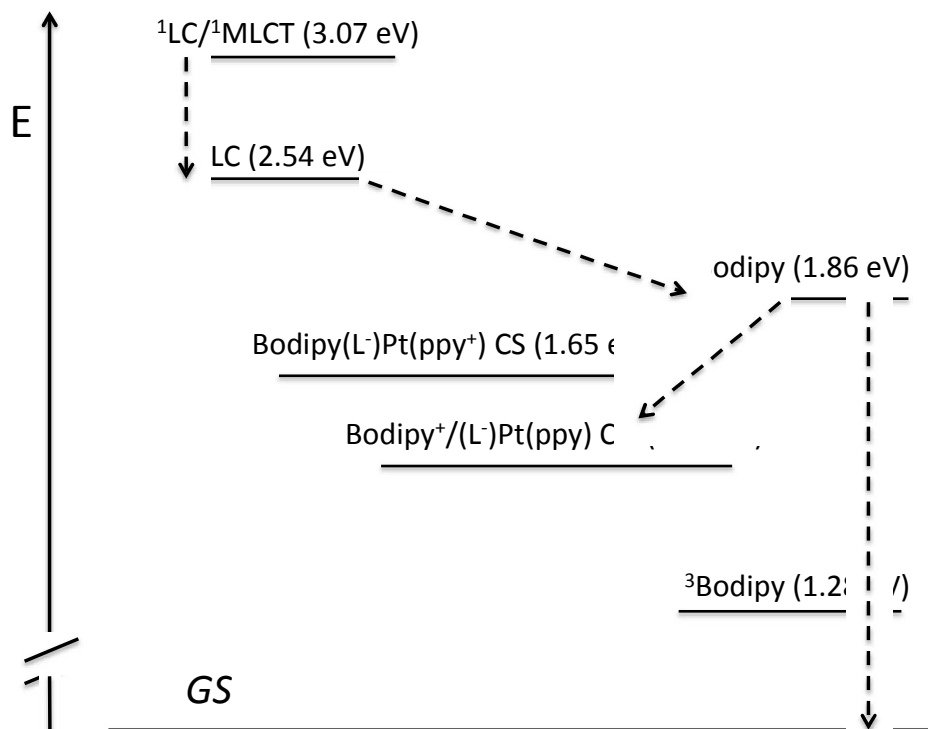


Fig. 7. Excited state energy levels diagram (solid lines) and main excited-state decays (dashed) of **1**. The energy level diagram is not scaled. For clarity, excited states centered on the metal-based unit are shown on the left side, levels involving the Bodipy subunit are on the right and intercomponent, charge-separated states are in the middle. The ^3LC state is a metal-perturbed ^3LC level, with some contribution from a $^3\text{MLCT}$ state. GS means the ground state. The $^1\text{LC}/^1\text{MLCT}$ state is approximated by the low-energy shoulder absorption of **2**. The ^3LC level is approximated by the 77 K emission of **2**. The $^3\text{Bodipy}$ state is approximated by considering the singlet-triplet energy difference in **4** (640 meV)⁹ and the energy of the $^1\text{Bodipy}$ state of **1**, approximated to the 77 K emission of **1**. The energies of the two CS states are calculated as described in the text.

Therefore, the (small) quenching of the Bodipy fluorescence in **1** with respect to **3** is attributed to photoinduced oxidative electron transfer to a lower-lying $\text{Bodipy}^+/\text{(L)}\text{Pt(ppy)}$ CS state, similarly to what proposed in formerly studied metal(polypyridine)/Bodipy bichromophoric species, although the CS state present in **1** differs from previous cases as far as

the localization of the "excited" electron is concerned (see above).^{9,10,14} The slower electron transfer quenching in **1** compared to the other cases (for example, $3.5 \times 10^7 \text{ s}^{-1}$ for **1** vs $1.8 \times 10^8 \text{ s}^{-1}$ for **7**, where anyway driving force of the electron transfer is also larger, -0.41 eV) can be due to a combination of reduced inter-chromophoric interaction and, particularly in some cases, different electron transfer driving force.¥

On exciting **1** at wavelength shorter than 385 nm, where contribution of the Pt(II) subunit to the absorption spectrum is not negligible, a very weak structured emission, almost identical in shape to the emission of **2**, so attributed to a residual ^3LC emission involving the metal-based subunit, is recorded (see Figure 4, inset).§ The lifetime of this emission, recorded at 486 nm, is 120 ps; however, this is very close to the time limit of our time-resolved single-photon-counting spectrometer, so it cannot be considered as a real lifetime, but better as an upper limit. Clearly, the ^3LC state is strongly deactivated in **1** by radiationless decays involving the supramolecular, multicomponent nature of **1**.

In the formerly investigated metal(polypyridine)-Bodipy species, decay of the $^3\text{MLCT}$ state led to population of the Bodipy-centered triplet state, mainly via a two-step electron transfer process involving a CS state at room temperature, whereas at 77 K direct energy transfer leading to the same Bodipy-centered triplet state was operative.^{9,10,14,15} In any cases, the light absorbed by the metal-based moiety did not contribute to Bodipy fluorescence. If this was also the case for **1**, the fluorescence quantum yield of the Bodipy-based subunit should depend on the excitation wavelength, decreasing on moving the excitation to higher energy and anyway to wavelengths shorter than 385 nm, where metal-based absorption becomes not negligible. However, considering the small contribution of the Pt(II) subunit to the overall absorption in the UV region (about 20% in the range 400 - 320 nm) and the experimental uncertainty on the emission quantum yield measurements with the optically diluted method (ca. 15%), the slight difference between quantum yield values obtained by exciting at 372 nm ($\Phi =$

0.43), where Pt(II) subunit is not negligible, and at 604 nm ($\Phi = 0.46$), where only the Bodipy subunit absorbs, is not significant. A much more diagnostic experiment was made by exciting the same, diluted solution of **1** at 372 and 610 nm, wavelengths where **1** has the same molar absorption, and comparing the ratio of the relative emission intensities at 670 nm with the emission ratio obtained by exciting a solution of **3** at 372 nm and 608 nm, wavelengths where **3** has the same molar absorption. This experiment gives a direct comparison of emission intensity, unaffected by experimental uncertainties on quantum yield, and allows to eliminate also the errors which can be generated by the different intensity output of the exciting lamp at 370 and in the 608 - 610 nm range.¶ Actually, if the ratio between the emission intensity on exciting at high energy excitation wavelength and the emission intensity on exciting at low energy excitation wavelength is identical for **3** and **1**, the electronic energy directly absorbed by the Pt(II) subunit can be assumed to be transferred to the fluorescent Bodipy state in a roughly quantitative manner. Indeed this is exactly what found: for **3**, the 670 nm emission ratio found on exciting at 372 and 608 nm is 0.6 (so suggesting that the photons emitted by our lamp at 372 nm are 60% than those emitted at 608 nm, assuming that efficiency of population of the fluorescent state of **3** is unitary at any excitation wavelength), and the same is obtained for **1**, on exciting at 372 and 610 nm. This definitely indicates that the light absorbed by the Pt(II) subunit of **1** decays almost quantitatively to the fluorescent ¹Bodipy state.¢

To discuss the mechanism of energy transfer from the metal-based subunit to the fluorescent, singlet Bodipy level, it can be considered that excitation at 372 nm populates the singlet mixed LC/MLCT state of **1**, and this state could deactivate (i) by intersystem crossing to the ³LC state (an *intra*-component process) or (ii) by energy transfer to the singlet Bodipy state (an *inter*-component process). Although case (ii) would easily justify the efficient energy transfer from the Pt(II) unit to the Bodipy singlet state, it appears less probable since intersystem crossing has been proposed to be faster than 1 ps in MLCT or LC manifolds of

Pt(II) polypyridine or cyclometalated complexes.²⁴ Therefore, population of the fluorescent Bodipy-centered singlet state from a Pt-based excited state most likely occurs by energy transfer from the ³LC state. This process would be spin-forbidden, however there is a very good spectral overlap between ³LC emission and Bodipy singlet absorption (compare absorption spectrum of **3** and emission spectrum of **2** in Figs. 3 and 4, respectively): in fact, the presence of the heavy platinum metal alleviates the spin forbiddenness. The above arguments tend to suggest that a somewhat unusual, formally forbidden but highly efficient ³LC-to-¹Bodipy energy transfer takes place in **1**.

The efficient energy transfer from the ³LC state of the metal-based chromophore to the singlet, emissive Bodipy state is a peculiar characteristic of the present compound, since the emissive states centered in the metal-based subunit decay very efficiently to the Bodipy *triplet* state in all the formerly studied similar species (not limited to the cases of Pt(II) compounds), without contributing to Bodipy fluorescence.^{9,10,14,15} So, this peculiar behavior of **1** warrants to be analyzed in more detail, and should be rationalized why the formally forbidden ³LC-to-¹Bodipy energy transfer is the preferred decay of ³LC in **1**.

The Bodipy⁺/(L⁻)Pt(ppy) CS state responsible for Bodipy fluorescence partial quenching could hardly contribute to the excited-state decay of the ³LC state. In fact, the ³LC state is essentially a metal-perturbed π - π^* triplet state involving the ppy ligand, so two electron transfer processes would be requested to populate the Bodipy⁺/(L⁻)Pt(ppy) CS level from the ³LC state (in principle, population of Bodipy⁺/(L⁻)Pt(ppy) CS level from the ³LC state could occur by energy transfer - considering the CT optical nature of the CS state, as evidenced by the absorption spectrum - but evidently the process is inefficient).\$ However, another charge-separated state, which can be formulated as Bodipy(L⁻)Pt(ppy⁺) CS state (see Fig. 7) and is close in energy to the Bodipy⁺/(L⁻)Pt(ppy) CS level, can be present in **1**. This Bodipy(L⁻)Pt(ppy⁺) CS state can be populated from the ³LC state via photoinduced oxidative

electron transfer to the L subunit, that is to the phenyl-ethynyl-phenyl moiety. Such an electron transfer would be endoergic of about 0.9 eV, but it should have a large reorganization energy, since it would require the formal oxidation of the ppy ligand, so it could be relatively slow. According to Fig. 7, another intercomponent process could compete with the (experimentally found) ^3LC -to- $^1\text{Bodipy}$ energy transfer process for ^3LC quenching, that is energy transfer to $^3\text{Bodipy}$. However, such a direct triplet-triplet energy transfer, both via Förster or Dexter mechanisms, is less probable because of negligible spectral overlap.

The above discussion suggests that all the decay processes of the ^3LC state in **1** can be relatively slow, and indicates that the ^3LC -to- $^1\text{Bodipy}$ energy transfer can indeed be the preferred decay route. Assuming Förster energy transfer as the leading mechanism for ^3LC decay, the rate constant can be calculated by equation 2.^{27,28}

$$k_{en}^F = 8.8 \times 10^{-25} \frac{K^2 \Phi}{n^4 r_{AB}^6 \tau} J_F \quad (2)$$

In the simplified equation 2, k_{en}^F is the rate constant of the energy transfer process, K is an orientation factor which accounts for the directional nature of the dipole-dipole interaction, Φ and τ are the luminescence quantum yield and lifetime of the donor model (the emission properties of **2**, in this case), respectively, n is the solvent refractive index, r_{AB} is the distance (in Å) between donor and acceptor. Considering the subunits of **1** as freely rotating along the triple bond axis, the random value for the orientation factor (0.667) is assumed. The donor-acceptor distance r_{AB} is taken as the distance from the platinum atom and the carbon bridging the two pyrrole rings of the Bodipy unit, that is 16.265 Å using computer-optimized structures. The overlap integral J_F for Förster interaction can be calculated according to equation 3.^{27,28}

$$J_F = \frac{\int F(\bar{\nu})\varepsilon(\bar{\nu})/\bar{\nu}^4 d\bar{\nu}}{\int F(\bar{\nu})d\bar{\nu}} \quad (3)$$

In this equation, $F(\bar{\nu})$ is the luminescence spectrum of the donor model (**2**), and $\varepsilon(\bar{\nu})$ is the absorption spectrum of the acceptor (compound **3**), on an energy scale (cm^{-1}). The calculated value of J_F is $7.95 \times 10^{-14} \text{ cm}^{-1}$, so that the theoretical rate constant for $^3\text{LC} - \text{to} - ^1\text{Bodipy}$ energy transfer in **1**, according to Förster mechanism, results to be $7.3 \times 10^7 \text{ s}^{-1}$, enough to allow for a 99% energy transfer efficiency, in agreement with experimental data. As a matter of fact, LC emission is also totally absent in **1** at 77 K (Table 1), indicating that the energy transfer mechanism is also operative at low temperature, again in agreement with the hypothesis of Förster energy transfer, known to be only slightly temperature dependent.

The pump-probe transient spectrum of **1**, unfortunately, is useless to investigate the intercomponent processes: actually, it is roughly identical to that of the Bodipy model **3**, in spite of the fact that at the excitation wavelength of 400 nm, used for the experiment, part of the light is absorbed by the Pt(II)-based subunit (see transient spectrum of **1** in supplementary information and compare it with Fig. 6). In fact, even at about 470 nm, characteristic of the transient absorption of the phenylpyridine reduced anion, there is no significative difference between **1** and **3** transient spectra. This is rationalized when one considers (i) that the extinction coefficient of the transient absorption of the Bodipy unit can be quite larger than that of the phenylpyridine reduced anion, and (ii) that only 20% of the exciting light (at the best) can be absorbed by the metal-based subunit. Under such circumstances, it is not surprising that the features due to excited states centered on the metal-based subunits are totally obscured in the transient spectrum of **1**.

Conclusions

A new bichromophoric species, **1**, made of a Pt(II)(ppy)(acac) subunit and of a blue-absorbing Bodipy has been prepared, together with its model species, **2** and **3**, and the absorption spectra, redox behavior, and photophysical properties of all the compounds have been investigated. The absorption spectrum of the bichromophoric species **1** shows features that can be attributed to individual subunits, plus a very weak absorption assigned to CT transitions. Oxidation processes of **1** are superimposed to those of **2** and **3**, and reduction processes indicate that a new, low energy LUMO is formed in **1**. The bridging unit connecting the Pt-based chromophore and the Bodipy dye subunits, that is the phenyl-ethynyl-phenyl-acac moiety, which is longer than the bridging units connecting the metal-based and Bodipy-based units of any hybrid similar multicomponent system investigated so far,^{9,10,13-15} introduces significant differences in the properties of **1** in comparison to those of formerly-studied compounds. For example, whereas in **4-7** the interchromophoric interactions were strong enough to modify the radiative and radiationless rate decay constants of the individual components, the weaker electronic coupling promoted by the larger bridge in **1** allows the chromophores of the present hybrid species to maintain unaffected their individual intra-chromophoric decay rate constants. Moreover, Bodipy fluorescence is only very weakly reduced in **1** compared to **3**, whereas the quenching of the Bodipy unit fluorescence was much larger in former cases (for example, Bodipy fluorescence quantum yield was reduced from 0.18 to 0.015 in **6** in comparison to the native Bodipy compound missing the Pt-based unit).^{9,10}

Among other differences from formerly-studied, similar hybrid systems, a relevant one is that in **4-7** and similar species, excitation of the metal-based unit mainly led to population of the Bodipy *triplet* state, even via a sequence of electron transfer routes, whereas in **1** the light energy absorbed by the metal-based chromophore is transferred with high efficiency (>99%) to the lowest-energy Bodipy *singlet* state, so contributing to Bodipy fluorescence. Such a process

takes place by an unusual, formally forbidden $^3\text{LC} - \text{to} - ^1\text{Bodipy}$ energy transfer, most likely by Förster mechanism, both at room temperature and at 77 K.

Experimental section

Preparation and characterization of the compounds.

Compound C. To a round bottom flask equipped with a dean stark apparatus, the red Bodipy **A** (200 mg, 0.44 mmol, 1 eq.),¹⁹ 3,4,5-tridodecylalkoxybenzaldehyde **B** (1.2 g, 1.82 mmol, 4 eq.) and p-TsOH (5 mg, 0.03 mmol) were dissolved in 25 mL of toluene and 1 mL of piperidine; the resulting solution was heated at 140°C until all the solvents were collected by the dean stark apparatus. To the solid reaction media was added 25 mL of toluene and 1 mL of piperidine and the dryness protocol was repeated 4 times. Purification by chromatography on silica gel (50:50 to 100:0 dichloromethane:petroleum ether) followed by precipitation ($\text{CH}_2\text{Cl}_2/\text{EtOH}$), afforded **C** as a dark blue solid (400 mg, 0.23 mmol, 53 %).

^1H NMR (300 MHz, C_6D_6): δ 7.88 (d, 2H, $^3J = 15.9$ Hz), 7.11 (d, 2H, $^3J = 15.9$ Hz), 7.04 (AB quartet, 4H, $^{AB}J = 8.1$ Hz, $v\delta_{AB} = 286.08$ Hz), 6.75 (s, 4H), 6.38 (s, 2H), 4.05 (t, 4H, $^3J = 6.3$ Hz), 3.78 (t, 8H, $^3J = 6.30$ Hz), 1.81-1.25 (m, 96H), 0.87 (t, 18H, 6.3 Hz); ^{13}C NMR (75 MHz, C_6D_6): δ 153.8, 153.4, 141.2, 140.5, 138.2, 137.5, 136.9, 135.2, 133.3, 132.1, 130.9, 118.7, 118.3, 106.8, 94.2, 73.4, 69.1, 32.3, 30.2, 30.1, 30.0, 29.8, 26.7, 23.1, 14.4; IR (ATR, cm^{-1}): ν 3071 (w), 2920 (s), 2850 (s), 1615 (m), 1578 (m), 1537 (s), 1485 (s), 1466 (m), 1431 (s), 1417 (m), 1385 (m), 1331 (m), 1300 (m), 1229 (m), 1198 (m), 1160 (s), 1113 (s), 1061 (m), 950 (s), 916 (m), 766 (m), 694 (m); UV-vis (THF): λ nm (ϵ , $\text{M}^{-1}\cdot\text{cm}^{-1}$) 319 (31400), 377 (49200), 598 (50500), 648 (121500); EI-MS m/z (nature of the peak) 1731.19 ([M], 100); Anal. Calcd for $\text{C}_{105}\text{H}_{170}\text{BF}_2\text{IN}_2\text{O}_6$: C, 72.80; H, 9.89; N, 1.62; Found: C, 73.06; H, 9.79; N, 1.42.

Compound 3. To an argon-degassed solution of 3-[4-ethynylphenyl]pentane-2,4-dione **D** (31 mg, 0.15 mmol) and the Bodipy **C** (251 mg, 0.145 mmol) in benzene/triethylamine (50/10 mL) was added $[\text{Pd}(\text{PPh}_3)_4]$ (10 mg, 0.008 mmol) and the resulting mixture was stirred at 60°C during 48 hours. The solution was poured into H_2O (50 mL) and extract with CH_2Cl_2 (3 x 50 ml). The organic phase was washed with water and brine and dried over sodium sulfate. The solvents were removed under vacuum. Purification by chromatography on silica gel (60:37:3 to

60:30:10 dichloromethane:petroleum ether:ethyl acetate) followed by precipitation by adding EtOH to a solution of **3** in CH₂Cl₂ afforded a dark blue solid (183 mg, 0.101 mmol, 70 %).

¹H NMR (400 MHz, C₆D₆): δ 8.39 (d, 2H, ³J = 16.0 Hz), 7.47(4) (d, 2H, ³J = 8 Hz), 7.47(1) (d, 2H, ³J = 8 Hz), 7.33 (d, 2H, ³J = 16.0 Hz), 6.99 (s, 4H), 6.657 (d, 2H, ³J = 8 Hz), 6.652 (d, 2H, ³J = 8 Hz), 6.47 (s, 2H), 4.30 (t, 4H, ³J = 6.8 Hz), 3.82 (t, 8H, ³J = 6.4 Hz), 2.01-1.95 (m, 4H), 1.78-1.66 (m, 12H), 1.63 (s, 6H), 1.52-1.30 (m, 112H), 0.87 (t, 18H, 6.3 Hz); ¹³C NMR (50 MHz, C₆D₆): δ 190.7, 154.1, 153.6, 141.7, 140.8, 138.1, 137.9, 135.9, 133.9, 133.7, 132.4, 132.2, 131.6, 129.4, 124.2, 122.5, 119.1, 118.6, 114.7, 107.0, 90.9, 90.0, 73.7, 69.2, 32.4, 30.4, 30.2, 30.1, 29.9, 26.7, 23.1, 14.4; IR (ATR, cm⁻¹): ν 2916 (s), 2849 (s), 2115 (w), 1613 (m), 1574 (m), 1540 (m), 1485 (s), 1431 (m), 1367 (m), 1331 (m), 1298 (m), 1196 (s), 1161 (s), 1105 (s), 1067 (s), 985 (s), 652 (m), 832 (m), 817 (m), 766 (m), 750 (s), 694 (m); UV-vis (THF): λ nm (ε, M⁻¹.cm⁻¹) 327 (50700), 381 (61000), 598 (43500), 648 (125000); EI-MS m/z (nature of the peak) 1803.1 ([M], 100); Anal. Calcd for C₁₁₈H₁₈₁BF₂N₂O₈ : 78.54; H, 10.11; N, 1.55; Found: C, 78.37; H, 9.82; N, 1.37.

Complex 1. A solution of **3** (150 mg, 0.083 mmol) in 30 mL of THF was cooled to 0°C and *t*-BuOK (10 mg, 0.089 mmol) was added in one portion. The reaction mixture was stirred during 2 hours and warm to room temperature. The platinum dichloride bridged dimer (30 mg, 0.038 mmol) and the resulting solution was heated at 60°C during 18 hours. The solution was poured on 50 mL of saturated NH₄Cl and extracted with CH₂Cl₂ (3 x 20 ml). The organic phase was washed with water and brine and dried over sodium sulfate. The solvents were removed under vacuum. Purification by chromatography on silica gel (60:47:3 to 60:30:10 dichloromethane:petroleum ether:ethyl acetate) followed by precipitation (EtOH/CH₂Cl₂) afforded complex **1** as a blue dark solid (52 mg, 32 %).

¹H NMR (400 MHz, C₆D₆): δ 9.05 (d, 1H, ³J = 5.6 Hz), 8.40 (d, 2H, ³J = 16.0 Hz), 8.33 (d, 1H, ³J = 16.0 Hz), 7.54 (d, 2H, ³J = 8.2 Hz), 7.47 (d, 2H, ³J = 8.0 Hz), 7.36 (d, 1H, ³J = 8.0 Hz), 7.31 (d, 1H, ³J = 8.0 Hz), 7.26-7.21 (m, 2H), 7.03-6.96 (m, 5H), 6.87 (d, 1H, ³J = 8.0 Hz), 6.81-6.77 (m, 3H), 6.65 (d, 2H, ³J = 8.0 Hz), 6.47 (s, 2H), 6.22 (dd, 1H, ³J = 8.0 Hz, ⁴J = 1.2 Hz), 4.30 (t, 4H, ³J = 6.8 Hz), 3.82 (t, 8H, ³J = 7.2 Hz), 2.01-1.95 (m, 4H), 1.78-1.66 (m, 12H), 1.67 (s, 3H), 1.61 (s, 3H), 1.52-1.30 (m, 104H), 0.87 (t, 18H, 6.3 Hz); ¹³C NMR (50 MHz, C₆D₆): δ 205.72, 153.52, 153.19, 141.76, 140.02, 137.51, 137.49, 137.38, 137.30, 136.20, 133.24, 132.59, 132.51, 132.44, 132.46, 132.27, 132.19, 132.15, 132.02, 131.99, 130.53, 129.74, 129.1, 128.93, 126.20, 123.77, 118.23, 106.99, 89.97, 89.15, 73.78, 69.50, 53.55, 32.1,

30.56, 29.91, 29.95, 29.65, 29.54, 26.40, 26.31, 22.85, 14.26; IR (ATR, cm^{-1}): ν 2920 (s), 2851 (s), 1689 (m), 1611 (m), 1566 (m), 1538 (s), 1485 (m), 1465 (m), 1429 (m), 1417 (m), 1366 (m), 1331 (m), 1275 (m), 1198 (s), 1161 (m), 1111 (s), 989 (s), 951 (m), 815 (m), 764 (m), 751 (m), 731 (m), 704 (m); UV-vis (THF): λ nm (ϵ , $\text{M}^{-1}\cdot\text{cm}^{-1}$) 321 (62100), 381 (66650), 598 (42560), 648 (122900); EI-MS m/z (nature of the peak) 2154.3.1 ($[\text{M}+\text{H}^+]$, 100); Anal. Calcd for $\text{C}_{129}\text{H}_{188}\text{BF}_2\text{N}_3\text{O}_8\text{Pt}$: C, 71.97; H, 8.80; N, 1.95; Found: C, 71.67; H, 8.64; N, 1.72.

Complex 2. To a solution of 3-[4-iodobenzene]pentane-2,4-dione **F** (125 mg, 0.41 mmol) and Ag_2O (88 mg, 0.39 mmol) in 30 mL of distilled THF, was added the platinum dichloride bridged dimer (159 mg, 0.20 mmol) and the resulting solution was heated at 80°C under argon overnight. After cooling to ambient temperature, the solution was filtered over a pad of celite and the solvents was removed *in vacuo*. 100 mL of CH_2Cl_2 was added to the residue and this solution was washed with water (2 x 50 mL) and brine (1 x 50 mL). The organic layer was dried over anhydrous Na_2SO_4 , filtered and dried *in vacuo*. The residue was purified by column chromatography on silica gel eluting with 70:30 CH_2Cl_2 :Petroleum Ether to yield complex **2** as yellow powder (187 mg, 0.29 mmol, 70%).

^1H NMR (400 MHz, C_6D_6): δ 9.01 (d, 1H, $^3\text{J} = 6.4$ Hz), 8.27 (d, 1H, $^3\text{J} = 7.6$ Hz), 7.36 (dt, 1H, $^3\text{J} = 7.6$ Hz, $^4\text{J} = 1$ Hz), 7.24 (dd, 1H, $^3\text{J} = 7.6$ Hz, $^3\text{J} = 7.6$ Hz), 6.89 (AB quartet, 4H, $^{AB}\text{J} = 7.2$ Hz, $\nu\delta_{AB} = 411.93$ Hz), 6.86 (d, 1H, $^3\text{J} = 7.6$ Hz), 6.79 (dt, 1H, $^3\text{J} = 7.6$ Hz, $^4\text{J} = 1.2$ Hz), 6.21 (dt, 1H, $^3\text{J} = 7.2$ Hz, $^4\text{J} = 1.0$ Hz), 1.56 (s, 3H), 1.51 (s, 3H); ^{13}C NMR (50 MHz, C_6D_6): 183.9, 182.7, 169.1, 147.1, 145.3, 141.3, 141.0, 138.2, 137.6, 134.2, 134.2, 134.1, 131.8, 129.6, 123.8, 123.4, 120.6, 118.3, 116.5, 92.7, 29.3, 28.5; IR (ATR, cm^{-1}): ν 3043.03 (w), 2997 (w), 1696 (m), 1608 (m), 1560 (s), 1481 (m), 1418 (s), 1362 (m), 1297 (m), 1153 (m), 1112 (w), 1094 (w), 1059 (m), 998 (s), 968 (s), 920 (w), 814 (s), 796 (w), 753 (vs), 729 (s); 680 (s), 650 (s); UV-vis (THF): λ nm (ϵ , $\text{M}^{-1}\cdot\text{cm}^{-1}$) 251 (25300), 280 (21529), 315 (9846), 329 (8979), 402 (2800); MALDI-TOF m/z (nature of the peak, relative intensity) 651.0 ($[\text{M}+\text{H}^+]$, 100); Anal. Calcd for $\text{C}_{22}\text{H}_{18}\text{INO}_2\text{Pt}$: C, 40.63; H, 2.79; N, 2.15 Found: C, 40.78; H, 2.72; N, 2.44.

Equipments and methods

UV/Vis absorption spectra were recorded with a Jasco V-560 spectrophotometer. For steady-state luminescence measurements, a Jobin Yvon-Spex Fluoromax P spectrofluorimeter was used, equipped with a Hamamatsu R3896 photomultiplier. The spectra were corrected for photomultiplier response by using a program purchased with the fluorimeter. For the

luminescence lifetimes, an Edinburgh OB 900 time-correlated single-photon-counting spectrometer was used. A Hamamatsu PLP 2 laser diode (59 ps pulse width at 408 nm) and/or nitrogen discharge (pulse width 2 ns at 337 nm) were employed as excitation sources. Emission quantum yields for deaerated solutions were determined by the optically diluted method²⁹ with $[\text{Ru}(\text{bpy})_3]^{2+}$ (bpy = 2,2-bipyridine) in air-equilibrated aqueous solution as quantum yield standard ($\Phi_{\text{em}} = 0.028$ ³⁰). Time-resolved transient absorption experiments were performed by using a pump-probe setup based on the Spectra-Physics MAI-TAI Ti:sapphire system as the laser source and the Ultrafast Systems Helios spectrometer as the detector. The pump pulse was generated with a Spectra-Physics 800 FP OPA instrument. The probe pulse was obtained by continuum generation on a sapphire plate (spectral range 450–800 nm). The effective time resolution was around 200 fs, and the temporal chirp over the white-light 450–750 nm range around 150 fs; the temporal window of the optical delay stage was 0–3200 ps. The time-resolved data were analyzed with the Ultrafast Systems Surface Explorer Pro software.³¹

Electrochemical measurements were carried out in argon purged 1,2-dichloroethane at room temperature with a Autolab multipurpose equipment interfaced to a PC. The working electrode was a glassy carbon (8mm², Amel) electrode. The counter electrode was a Pt wire, and the reference electrode was an SCE separated with a fine glass frit. The concentration of the complexes was about 5×10^{-4} M. Tetrabutylammonium hexafluorophosphate was used as supporting electrolyte and its concentration was 0.05 M. Differential pulse voltammetry (DPV) were obtained at scan rates of 4, 10, 20 mV/s. Redox potentials were corrected by the internal reference ferrocene (395 mV vs SCE).

Experimental uncertainties are as follows: absorption maxima, 2 nm; molar absorption, 15%; luminescence maxima, 4 nm; luminescence lifetimes, 10%; luminescence quantum yields, 15%; transient absorption decay and rise rates, 10%; DPV peaks, 15 mV.

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REFERENCES AND NOTES

- # The acetyl-acetonate group, chelating a positively-charged subunit (the $\{\text{Pt}(\text{ppy})\}^*$ group) behaves as an electron withdrawing group for the phenyl-ethynyl-phenyl moiety in **1**, so stabilizing its LUMO.
- ¥ There is no indication of the presence of the CS state in the transient absorption spectroscopy of **1** (see later). However, it should be considered that, once formed, the CS state can decay very rapidly to the ground state, directly or via the triplet Bodipy state, so it could not accumulate enough to be visible.
- § This confirms that the contribution of a triplet MLCT state to the emissive state of **2** is minimal, otherwise the residual metal-based emission in **1** should have been different. So emission of **2** (and corresponding excited states, also in **1**) are correctly described as metal-perturbed ^3LC .
- ¶ Using a spectrofluorimeter in which correction for excitation lamp is present (not our case), clearly the ratio between emission of **3** at 670 nm exciting at different, iso-absorbing wavelengths should be 1.
- € The residual ^3LC emission at 480 nm in **1** has a lifetime < 0.12 ns, whereas the unquenched LC emission of **2** has a lifetime of more than 1200 ns (Table 1): This means that the percentage of ^3LC in **1** which decays by radiative process, without contributing to Bodipy fluorescence is less than 10^{-4} . Therefore, energy transfer from metal-based excited states to the Bodipy fluorescent level can be considered quantitative.
- § Differently from ^3LC , electron transfer quenching of the $^1\text{Bodipy}$ state via the $\text{Bodipy}^+/(L^-)\text{Pt}(\text{ppy})$ CS state in Fig. 7 is feasible, since this latter process is a one-electron transfer process. Interestingly, quenching of the $^1\text{Bodipy}$ state via the $\text{Bodipy}(L^-)\text{Pt}(\text{ppy}^+)$ CS state, in principle a suitable decay process for the ^3LC state (see later), would be specularly an impossible electron-transfer decay route for the $^1\text{Bodipy}$ state.
- £ This would suggest that the nature of the lowest-energy excited state of the metal-based unit, i.e. LC, could mainly be responsible for the slow electron transfer, so favoring energy transfer decay routes.

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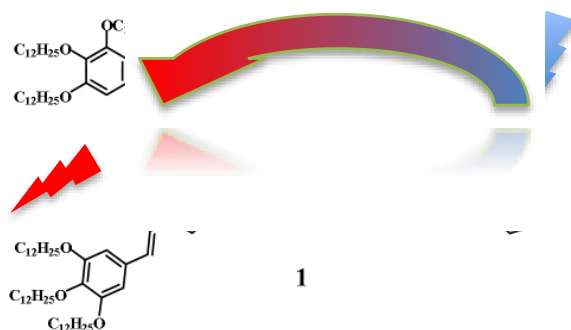
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Photophysical properties of an unusual bichromophoric species constructed from a cyclometalated Pt(II) chromophore and a blue Bodipy-acetylacetonate species

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Table of contents entry



The bichromophoric species **1** made of a Pt(II) cyclometalated unit and a blue Bodipy dye has been prepared. **1** exhibits an unusual, formally-forbidden energy transfer from the triplet ligand-centered state involving the metal-containing subunit to the fluorescent singlet Bodipy-centered level.