Electronic Supplementary Information (ESI)

NMR

The proton NMR spectrum of **4** is shown in **Fig.1S**. Both protons in ortho-position of the Pt are slightly deshielded due to the presence of the phenyl ring tethered via the triple bond to the Pt centre. The other protons localized on the terpyridine or the bodipy (methyl and ethyl group) are weakly influenced each other due to the orthogonality imposed by the twisted phenyl ring.
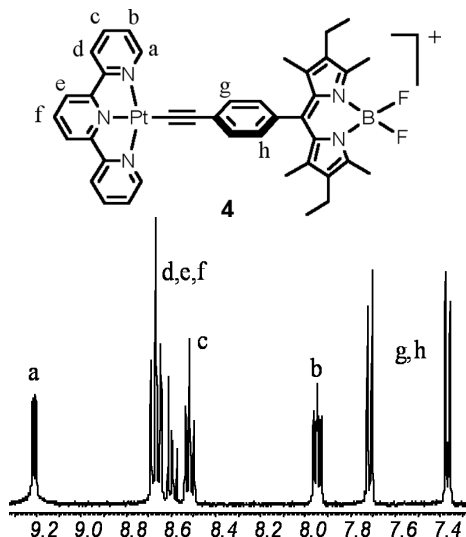

Fig.1S ^{1}H spectra of complex **4** in d_6-DMSO/D_2O. For the sake of clarity only the aromatic portion is shown.

Equipment and methods

Electrochemical studies employed cyclic voltammetry with a conventional 3-electrode system using a BAS CV-50W voltammetric analyser equipped with a Pt microdisk (2 mm^2) working electrode and a silver wire counter-electrode. Ferrocene was used as an internal standard and was calibrated against a saturated calomel reference electrode (SCE) separated from the electrolysis cell by a glass frit presoaked with electrolyte solution. Solutions contained the electro-active substrate in deoxygenated and anhydrous dimethylformamide containing tetra-n-butylammonium hexafluorophosphate (0.1 M) as supporting electrolyte. The quoted half-wave potentials were reproducible within ≈ 15 mV.

Absorption spectra have been recorded with a Jasco 560 spectrophotometer, emission spectra have been performed with a Horiba Jobin-Yvon Fluoromax P spectrofluorimeter equipped with a Hamamatsu R3896 photomultiplier, and were corrected for photomultiplier response using a program purchased with the fluorimeter. Emission lifetimes were measured with an Edinburgh OB-900 single-photon counting spectrometer equipped with a Hamamatsu PLP-2 laser diode (pulse width at 408 nm, 59 ps). The emission decay traces were analyzed by a Marquadt algorithm. Luminescence quantum yields have been calculated by using the optically

dilute method; as the reference, $[Ru(bpy)_3]^{2+}$ in aerated water was used (Φ = 0.028). Experimental uncertainty for absorption spectra maxima is 2 nm, for molar absorption is 10%, for luminescence emission maxima is 4 nm, for lifetime is 10%, and for quantum yields is 20%.

Calculation of the electronic interaction energy between bodipy-based and MLCT triplet states involved in MLCT-to-bodipy energy transfer

The Dexter-type energy-transfer mechanism is described as a double electron exchange between donor and acceptor.[1,2] When the electronic coupling is weak, energy transfer can be considered to occur nonadiabatically, and the rate constant of energy transfer can be expressed as in eq 1;[3] ν_{en} and $\Delta G^{\#}$ can be obtained from eqs 2 and 3, respectively:

$$k_{en} = \nu_{en} e^{\left(-\frac{\Delta G^{\#}}{RT}\right)} \qquad \text{eq. 1}$$

$$\nu_{en} = \left[\frac{2(H_{en})^2}{h}\right] \left(\frac{\pi^3}{\lambda RT}\right)^{\frac{1}{2}} \qquad \text{eq. 2}$$

$$\Delta G^{\#} = \left(\frac{\lambda}{4}\right)\left(1 + \frac{\Delta G^{\circ}}{\lambda}\right)^2 \qquad \text{eq. 3}$$

Following the usual assumptions,[4] the free energy change ΔG° can be expressed as the difference between the spectroscopic energies of the donor and acceptor (estimated from their emission energies at 77 K). In our case, we assume for the reorganization energy λ a value of 3000 cm^{-1} (mainly on the basis of difference in energy emission of model **3** at room and low temperature, **Table 1**). This yields a value of about 0.06 for the exponential term of eq 1. Within this asumption, for the compound **4** ν_{en} is ca. 8.0 x 10^9 s^{-1}, and, as a consequence (eq 2), the electronic interaction energy H_{en} is 3.6 cm^{-1}.

References

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