## **Electronic Supplementary Information**

for

# Self-assembling a neutral platinum(II) complex into highly emitting microcrystalline fibers through metallophilic interactions<sup>†</sup>

## by

# Matteo Mauro,\*,*a,b* Alessandro Aliprandi,*a* Cristina Cebrián,*a,c* Di Wang,*d* Christian Kübel,*d* and Luisa De Cola\*,*a,d*

<sup>*a*</sup> ISIS & icFRC, Université de Strasbourg & CNRS, 8 rue Gaspard Monge, 67000 Strasbourg, France Fax: +33 (0) 3 6885 5242; Tel: +33 (0) 3 6885 5220; E-mail: <u>mauro@unistra.fr</u>, <u>decola@unistra.fr</u>.

<sup>b</sup> University of Strasbourg Institute for Advanced Study (USIAS), 5 allée du Général Rouvillois, 67083 Strasbourg, France

<sup>c</sup> Current address: Laboratoire de Structure et Réactivité des Systèmes Moléculaire Complexes (SRSMC) – UMR 7565, Institut de Chimie, Physique et Materiaux (ICPM), Universitè de Lorraine, 1 Boulevard Arago, 57070 Metz, France.

<sup>*d*</sup> Institute of Nanotechnology and Karlsruhe Nano Micro Facility, Karlsruhe Institute of Technology (KIT), Hermann-von-Helmholtz Platz 1, 76344, Eggenstein-Leopoldshafen, Germany.

#### Materials and Methods.

Synthesis and Characterization. All the reactions were carried out under inert atmosphere (Schlenk technique). All the solvents were used as received from Aldrich or Fluka without any further purification. 4-pentylpyridine was bought from TCI Europe. All the chemicals were purchased and used as received. The compounds were purified by column chromatography by using silica gel 60 (230–400 mesh) as stationary phase. <sup>1</sup>H, <sup>13</sup>C and <sup>19</sup>F NMR spectra were recorded on a Bruker Avance 400 spectrometer. The <sup>1</sup>H NMR chemical shifts ( $\delta$ ) are given in ppm and referred to residual protons on the corresponding deuterated solvent. All deuterated solvents were used as received without any further purification. All coupling constants (*J*) are given in Hertz (Hz). Electrospray ionization mass (ESI-MS) spectra were recorded on a Bruker Daltonics (Bremen, Germany) MicroTof with loop injection. Elemental analyses were recorder at the Department of Chemistry, University of Milano (Italy).

Photophysics. Room temperature in solution. Absorption spectra were measured on a Shimadzu UV-3600 spectrophotometer double-beam UV-VIS-NIR spectrometer and baseline corrected. Steady-state emission spectra were recorded on a Horiba Jobin-Yvon IBH FL-322 Fluorolog 3 spectrometer equipped with a 450 W xenon arc lamp, double-grating excitation, and emission monochromators (2.1 nm mm<sup>-1</sup> of dispersion; 1200 grooves mm<sup>-1</sup>) and a TBX-04 single photoncounting detector. Emission and excitation spectra were corrected for source intensity (lamp and grating) and emission spectral response (detector and grating) by standard correction curves. Timeresolved measurements were performed using either the time-correlated single-photon counting (TCSPC) electronics PicoHarp300 or the Multi Channel Scaling (MCS) electronics NanoHarp 250 of the PicoQuant FluoTime 300 (PicoQuant GmbH, Germany), equipped with a PDL 820 laser pulse driver. A pulsed laser diode LDH-P-C-375 ( $\lambda = 375$  nm, pulse FWHM <70 ps, repetition rate 200 kHz - 40 MHz) was used to excite the sample and mounted directly on the sample chamber at 90°. The photons were collected by a PMA-C-192 photomultiplier (PMT) single-photon-counting detector. The data were acquired by using the commercially available software EasyTau (PicoQuant GmbH, Germany), while data analysis was performed using the commercially available software FluoFit (PicoQuant GmbH, Germany).

*Solid state measurements*. Steady-state measurements on solid state samples were recorded on a Horiba Jobin–Yvon IBH FL-322 Fluorolog 3 spectrometer as described before. Time-resolved measurements were performed using the time-correlated single-photon-counting option on the Fluorolog 3. NanoLEDs (402 nm; fwhm <200 ns) with repetition rates between 10 kHz and 1 MHz was used to excite the sample. The excitation sources were mounted directly on the sample chamber at 90° to a double-grating emission monochromator (2.1 nm mm<sup>-1</sup> of dispersion; 1200 grooves

mm<sup>-1</sup>) and collected by a TBX-04 single-photon-counting detector. The photons collected at the detector are correlated by a time-to-amplitude converter to the excitation pulse. Signals were collected using an IBH DataStation Hub photon-counting module and data analysis was performed using the commercially available DAS6 software (Horiba Jobin-Yvon IBH).

*Methods.* The quality of the fit was assessed by minimizing the reduced  $\chi^2$  function and by visual inspection of the weighted residuals. For multi-exponential decays, the intensity, namely I(*t*), has been assumed to decay as the sum of individual single exponential decays (Eqn. 1):

$$I(t) = \sum_{i=1}^{n} a_i e^{-\frac{t}{\tau_i}}$$
(1)

where  $\tau_i$  are the decay times and  $a_i$  are the amplitude of the component at t = 0. The percentages to the pre-exponential factors,  $a_i$ , are listed upon normalization. The quantum yield measurements were performed by using an absolute photoluminescence quantum yield spectrometer Quantaurus C11347 (Hamamatsu, Japan) exciting the sample at  $\lambda_{exc} = 300$  and 350 nm. All solvents were spectrometric grade. Deaerated samples were prepared by the freeze-pump-thaw technique.

Cyclic Voltammetry (CV). The electrochemical characterization (cyclic voltammetry) for the metal complexes herein reported was performed in methylene chloride (dichloromethane, DCM)/0.1 M tetrabutylammonium hexafluorophosphate (TBAPF<sub>6</sub>). The concentration of the samples was 1 mM. A 3 mm glassy carbon disk electrode was employed as the working electrode, platinum wire as the counter electrode, and silver wire as the quasi- reference electrode (QRE). DCM (Acros Organics, 99.8%, extra dry over molecular sieves) was used as received without any further purification. TBAPF<sub>6</sub> (electrochemical grade, >99%, Fluka) was used as the supporting electrolyte, which was recrystallized from a 1:1 ethanol/ water solution and dried at 60 °C under vacuum. For the electrochemical experiments, a CHI750C electrochemical workstation (CH Instruments, Inc., Austin, TX) was used. The electro-chemical experiments were performed in a glass cell under argon atmosphere. To minimize the ohmic drop between the working and the reference electrodes, the feedback correction was employed. The working electrodes were stored in ethanol and before the experiments were polished with a 0.05 µm diamond suspension (Metadi Supreme Diamond Suspension, Buehler) and ultrasonically rinsed with ethanol for 5 min. The electrode was electrochemically activated in the background solution by means of several voltammetric cycles at 0.5 V s<sup>-1</sup> between the anodic and cathodic solvent/electrolyte discharges until the same quality features were obtained. The reference electrode was calibrated at the end of each experiment against the ferricenium/ferrocene ( $Fc^+|Fc$ ) couple. All potential values are reported against the ( $Fc^+|Fc$ ) couple.

**Computational Details.** Ground-state  $(S_0)$  electronic state geometry was optimized by means of density functional theory (DFT). The parameter-free hybrid functional Perdew-Burke-Ernzerhof PBE0 (called PBE1PBE in Gaussian09)[(a) J. P. Perdew, K. Burke, M. Ernzerhof, Phys. Rev. Lett., 1996, 77, 3865; (b) J. P. Perdew, K. Burke, M. Ernzerhof, Phys. Rev. Lett., 1997, 78, 1396; (c) C. Adamo, V. Barone, J. Chem. Phys., 1999, 110, 6158.] was employed along with the standard valence double- $\zeta$  polarized basis set 6-31G(d,p)[M. M. Francl, W. J. Pietro, W. J. Hehre, J. S. Binkley, M. S. Gordon, D. J. De Frees, J. A. Pople, J. Chem. Phys., 1982, 77, 3654.] for C, H, F, and N. For Pt, the Stuttgart-Dresden (SDD) effective core potentials were employed along with the corresponding valence triple- $\zeta$  basis set. All the calculations were done without symmetry constrain and the lowest energy geometry possesses  $C_s$  symmetry. The nature of all the stationary points was checked by computing vibrational frequencies. The stationary point was found to be true potential energy minima, as no imaginary frequency was obtained. All the optimizations were performed in vacuum. To simulate the absorption electronic spectrum down to 250 nm, for each complex the lowest 30 singlet  $(S_0 \rightarrow S_n)$  as well as the 3 lowest triplet  $(S_0 \rightarrow T_n)$  excitation energies were computed on the optimized geometry at S<sub>0</sub> by means of time-dependent density functional theory (TD-DFT) calculations[R. E. Stratmann, G. E. Scuseria, M. J. Frisch, J. Chem. Phys., 1998, 109, 8218; (b) M. E. Casida, C. Jamorski, K. C. Casida, D. R. Salahub, J. Chem. Phys., 1998, 108, 4439.] at the same level of theory than the  $S_0$  optimization. TD-DFT energies calculations were performed in both vacuum and chloroform as the solvent. Solvation effect was taken into account by means of the non-equilibrium IEFPCM model.[G. Scalmani and M. J. Frisch, J. Chem. Phys., 2010, 132, 114110-114125] All the calculations were performed with Gaussian09W program package. [Gaussian 09, Revision B.1, M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, B. Mennucci, G. A. Petersson, H. Nakatsuji, M. Caricato, X. Li, H. P. Hratchian, A. F. Izmaylov, J. Bloino, G. Zheng, J. L. Sonnenberg, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, J. A. Montgomery, Jr., J. E. Peralta, F. Ogliaro, M. Bearpark, J. J. Heyd, E. Brothers, K. N. Kudin, V. N. Staroverov, R. Kobayashi, J. Normand, K. Raghavachari, A. Rendell, J. C. Burant, S. S. Iyengar, J. Tomasi, M. Cossi, N. Rega, J. M. Millam, M. Klene, J. E. Knox, J. B. Cross, V. Bakken, C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann, O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J. W. Ochterski, R. L. Martin, K. Morokuma, V. G. Zakrzewski, G. A. Voth,

P. Salvador, J. J. Dannenberg, S. Dapprich, A. D. Daniels, Ö. Farkas, J. B. Foresman, J. V. Ortiz, J. Cioslowski, D. J. Fox, Gaussian, Inc., Wallingford CT, 2009.]

**Emission microscopy.** Fluorescence microscopy was performed with an Olympus BX51 microscope using a  $20 \times$  objective and an Olympus U-MWBV BP 400–440 nm, dichroic 455 nm, and LP 475 nm as excitation and emission filter cubes, respectively; images and movies were recorded with a Olympus XC-10 color camera.

**Small-angle/Wide-angle X-ray Scattering (SAXS/WAXS).** SAXS/WAXS measurements of samples were performed with SAXSess Small-angle X-Ray Scattering instrument (Anton Paar GmbH, Austria). The Kratky type camera is attached to a laboratory X-Ray generator (PW3830, PANalytical), and was operated with a fine focus glass sealed X-Ray tube at 40 kV and 50 mA (Cu K $\alpha$ ,  $\alpha = 0.1542$  nm). Detection was performed with the 2D imaging plate and analyzed by an imaging plate reader Cyclone® (Perkin Elmer). Measurements were performed with standard solid sample holder for 30 min. The two-dimensiosal intensity data were converted to one-dimensional data with SASXQuant software (Anton Paar GmbH, Austria) The scattering intensities were corrected for background noise, detector efficiency, empty cell scattering and sample transmission, and were placed on an absolute scale using bean flux measurements. The samples were prepared by drop-cast technique of an acetone solution of the complex at concentration of 4 mg mL<sup>-1</sup> onto the sample holder. The solution was left aging overnight in order to allow the formation of the self-assembled fibers.

**Scanning electron microscopy (SEM).** The SEM images on the fibers were recorder using a Zeiss 1540 EsB dual beam/field emission SEM with a working distance of 8 mm and an electronic high tension (EHT) of 3kV.

#### Transmission electron microscopy (TEM).

The TEM analyses were performed using an aberration (image) corrected FEI Titan 80-300 electron microscope at an accelerating voltage of 300 kV, with 50  $\Box$  m C2 condenser aperture and spot size 11 to reach a very low current density (150 *e* nm<sup>-2</sup> s<sup>-1</sup>). TEM and SAED patterns were acquired using a Gatan US1000 slowscan CCD camera. Samples for TEM analysis were prepared by deposition of the needles from organic suspension onto Quantifoil copper grids coated with holey carbon film and removing of the residual solvent after 30 sec. A series of 28 pairs of diffraction spots were also acquired on fibers prepared by using the same method employed for the

photophysically characterized samples, and an average lattice spacing of 3.44  $\pm$  0.02 Å has been found.

#### Synthetic pathway for ligand pyC<sub>5</sub>-CF<sub>3</sub>-tzH<sub>2</sub>.



i) MeOH/MeONa, reflux, NH<sub>4</sub>Cl; ii) CF<sub>3</sub>COOEt, NH<sub>2</sub>NH<sub>2</sub>×H<sub>2</sub>O, THF reflux.

Synthesis of pyridine-2,6-biscarboxamidine dihydrochloride. In a 500 mL round bottom flask 2,6-dicarbonitrile (20.0 g, 154.9 mmol, 1.0 eq.) and MeONa (1.67 g, 30.98 mmol, 0.2 eq) were dissolved in 180 mL of dry methanol. After refluxing for 6 h, ammonium chloride (12.8 g, 340.8 mmol, 2.2 eq.) was added to the reaction mixture and kept overnight under reflux. After cooling, the solid was filtered over a Buchner, washed with Et<sub>2</sub>O, dried and collected as pure compound (30.6 g, 130.2 mmol, yield 84.0%) <sup>1</sup>H NMR (400 MHz, D<sub>2</sub>O)  $\delta$ : 8.43 (m). HR-ESI-MS (*m/z*): [M-2HCl+H]<sup>+</sup> calcd. 164.0933; found 164.0931.

Synthesis of 2,6-bis(3-(trifluoromethyl)-1*H*-1,2,4-triazol-5-yl)pyridine (pyC<sub>5</sub>-CF<sub>3</sub>-tzH<sub>2</sub>). In a 500 mL round-bottom flask, ethyltrifluoroacetate (13.7 mL, 114.4 mmol, 1.8 eq.) was dissolved in 150 mL of THF and hydrazine monohydrate (6.15 mL, 126.7 mmol, 2.0 eq.) was added. The reaction mixture was refluxed for 2 h, followed by the addition of pyridine-2,6-biscarboxamidine dihydrochloride (15.0 g, 63.5 mmol, 1 eq.) and sodium hydroxide (2.54 g, 63.5 mmol, 1 eq.). The reaction mixture was kept overnight refluxing under N<sub>2</sub>. After cooling, the desired product, **pyC<sub>5</sub>-CF<sub>3</sub>-tzH<sub>2</sub>**, was purified from the crude on column chromatography by using silica gel as stationary phase and dichloromethane and acetone 9:1 as eluent (2.04 g, 5.84 mmol, yield 9.2%). <sup>1</sup>H NMR (400 MHz, CD<sub>2</sub>Cl<sub>2</sub>)  $\delta$ : 13.82 (2H), 8.21 (2H), 8.06 (1H); <sup>19</sup>F{<sup>1</sup>H} NMR (CD<sub>2</sub>Cl<sub>2</sub>,  $\delta$ ): -65.61 (1F). HR-ESI-MS (*m/z*): [M+Na]<sup>+</sup> calcd. 372.0395; found 372.0403.

#### Synthetic pathway for complexes Pt-CF<sub>3</sub>tz-pyC<sub>5</sub>



iii) 3:1 2-MeOEtOH:H<sub>2</sub>O, DIPEA, 83°C overnight.

Synthesis of Pt-CF<sub>3</sub>tz-pyC<sub>5</sub>. In a 50 mL round-bottom flask, compound  $pyC_5$ -CF<sub>3</sub>-tzH<sub>2</sub> (200.0 mg, 0.573 mmol, 1.5 eq.), PtCl<sub>2</sub>(DMSO)<sub>2</sub> (230.0 mg, 0.546 mmol, 1 eq.), 4-pentylpyridine (90.5 uL, 0.546 mmol, 1.0 eq.) and 100 µL of DIPEA were suspended in 20 mL of a 3:1 2-methoxyethanol and water. The reaction mixture was heated overnight at 83°C under nitrogen atmosphere. A yellowish-green precipitate appeared few minutes after the heating. The desired compound (Pt-CF<sub>3</sub>tz-pyC<sub>5</sub>) was purified on column chromatography using silica gel as stationary phase and 1:1 THF:cyclohexane mixture as eluent, and obtained as greenish-yellow solid (285 mg, 0.412 mmol, yield 75.5%). <sup>1</sup>H NMR (400 MHz, CD<sub>2</sub>Cl<sub>2</sub>)  $\delta$ : 9.38 (2H), 8.04 (1H), 7.75 (2H), 7.40 (2H), 2.76 (2H), 1.73 (2H), 1.38 (4H), 0.92 (3H); <sup>19</sup>F{<sup>1</sup>H} NMR (400 MHz, CH<sub>2</sub>Cl<sub>2</sub>)  $\delta$ : -64.78 (1F); <sup>13</sup>C NMR (75 MHz, CD<sub>2</sub>Cl<sub>2</sub>)  $\delta$ : 164.61 (s), 157.63 (s), 153.08 (s), 149.26 (s), 143.70 (s), 126.93 (s), 118.77 (s), 35.81 (s), 31.77 (s), 29.91 (s), 22.90 (s), 14.21 (s).

HR-ESI-MS (positive scan, m/z): [M+H]<sup>+</sup> calcd. 692.1280; found 692.1376 Elemental analysis calcd. for C<sub>21</sub>H<sub>18</sub>F<sub>6</sub>N<sub>8</sub>Pt C 36.48%, H 2.62%, N 16.20%, found C 36.88%, H 2.93%, N 15.85%.

The chemical characterization is in accordance with the structure of the complex as sketched in Fig. 1 of the manuscript. In particular, the <sup>1</sup>H NMR spectrum shows a proton resonance at 9.38 ppm attributable to the H in *orto*-position with respect to the N heteroatom of the ancillary pyridine ligand, which displays the coupling with the central <sup>195</sup>Pt atom, with <sup>3</sup> $J_{H,Pt} = 25$  Hz, as typical of Pt(II) complexes containing N-coordinated pyridine and cyclometalating ligands.



## <sup>1</sup>H NMR spectrum for $Pt-CF_3tz-pyC_5$ in $CD_2Cl_2$ .

<sup>19</sup>F NMR spectrum for  $Pt-CF_3tz-pyC_5$  in  $CD_2Cl_2$ .





## <sup>13</sup>C NMR spectrum for $Pt-CF_3tz-pyC_5$ in $CD_2Cl_2$ .

### MS spectrum obtained for Pt-CF<sub>3</sub>tz-pyC<sub>5</sub>.



## Mass Spectrum SmartFormula Report

Analysis Info Analysis Name Method Sample Name Comment	C:\Documents and s esi wide pos.m RR01	Settings\Labo\Bureau\micro tof\O27093ML	.d	Acquisition Date Operator Instrument / Ser#	06/03/2014 15:52:54 Administrator micrOTOF 66
Acquisition Parame Source Type Focus Scan Begin Scan End	ESI Not active 50 m/z 3000 m/z	lon Polarity Set Capillary Set End Plate Offset	Positive 4500 ∨ -500 ∨	Set Nebulizer Set Dry Heater Set Dry Gas Set Divert Valve	0.4 Bar 180 °C 4.0 l/min Source
Intens. 300 200 100 0		692,1376 691,1386 693,1449 692,1280	. h		+MS, 1.5-1.6min #(102-106) C 21 H 19 F 6 N 8 Pt ,692.13
300 200 100 0 	5.0 687.5	689.1242 690.0 692.5	695.1310 	697.5 700.0	0 702.5 705.0m/z
Meas. m/z # 692.1376 1	Formula C 21 H 19 F 6 N 8 Pt	Score m/z err [mDa] err [ppm] 100.00 692.1280 -9.5 -13.8	mSigma rdb e <sup>-</sup> C 117.1 13.5 even	onf N-Rule	

11

Figure S1. Optimized geometry of complex  $Pt-CF_3tz-pyC_5$  at its electronic S<sub>0</sub> state. A partial atom labelling is also given.



**Figure S2**. Cyclic voltammetry characteristics obtained for the complex  $Pt-CF_3tz-pyC_5$  at a 100 mV s<sup>-1</sup> scan rate, in CH<sub>2</sub>Cl<sub>2</sub>, with 0.1 M tetrabutylammonium hexafluorophosphate (TBAPF<sub>6</sub>) as the supporting electrolyte, at 298 K with ohmic drop compensation.



**Figure S3**. Isodensity surface plots of the molecular orbitals closer to the frontier region and mainly involved into the electronic transitions for the complex  $Pt-CF_3tz-pyC_5$  in the gas phase at its S<sub>0</sub> optimized geometry. Isodensity value 0.04 *e* Bohr<sup>-3</sup>.



Figure S4. Excitation and emission spectra for the complex Pt-CF<sub>3</sub>tz-pyC<sub>5</sub> fibers at concentration of 4 mg mL<sup>-1</sup> in acetone obtained at  $\lambda_{em} = 630$  nm and upon excitation at  $\lambda_{exc} = 300$  nm, respectively. Absorption spectrum for the complex Pt-CF<sub>3</sub>tz-pyC<sub>5</sub> in CHCl<sub>3</sub> (black traces) at room temperature concentration of  $5 \times 10^{-5}$  M is also displayed for comparison.



Figure S5. Emission microscopy images taken on a sample of fibers of complex Pt-CF<sub>3</sub>tz-pyC<sub>5</sub> obtained from acetone at concentration of 4 mg mL<sup>-1</sup>, upon excitation in the range 400–440 nm. Emission LP filter: 476 nm. a) without polarizer; b) and c) with polarizer as indicated by the white arrow.



**Figure S6**. SAXS/WAXS pattern recorded as intensity [cps] *vs*. scattering angle  $2\theta$  [°] on a dropcast sample of fibers of complex **Pt-CF<sub>3</sub>tz-pyC<sub>5</sub>** obtained from acetone solution at concentration of 4 mg mL<sup>-1</sup>.



**Figure S7**. SAXS/WAXS pattern recorded as intensity [cps] *vs*. Bragg spacing [Å] on a drop-cast sample of fibers of complex **Pt-CF<sub>3</sub>tz-pyC<sub>5</sub>** obtained from acetone solution at concentration of 4 mg mL<sup>-1</sup>.



## <u>Tables</u>

**Table S1**. Selected geometrical parameters  $[Å, \circ]$  and energy  $[E_h]^a$  of the ground-state  $(S_0)$  optimized geometry for the complex **Pt-CF<sub>3</sub>tz-pyC<sub>5</sub>**. A partial atom labelling scheme is reported in Fig. S1.

	Bond length		angle	
parameter	[Å]	parameter	[°]	
<i>R</i> (Pt–N(1))	2.027	<(N(1)-Pt-N(4))	79.1	
R(Pt-N(4))	1.998	<(N(1)-Pt-N(5))	100.9	
R(Pt-N(5))	2.052	¢(N(1)−Pt−N(5)−C(5))	-179.7	
R(C(3)-N(3))	1.326	¢(N(4)−Pt−N(5)−C(5))	180.9(5)	
R(C(3)-N(1))	1.357			
R(C(2)-C(4))	1.496			
R(N(5)-C(5))	1.348			
Energy –1965.647806				

<sup>*a*</sup> 1  $E_{\rm h}$  = 2625.500 kJ mol<sup>-1</sup>

**Table S2.** List of selected molecular orbital energies [eV] and HOMO–LUMO energy gap for the complex **Pt-CF<sub>3</sub>tz-pyC<sub>5</sub>**. For each entry, the symmetry of the corresponding orbital is also reported in parenthesis.

orbital	Pt-CF <sub>3</sub> tz-pyC <sub>5</sub>
LUMO + 4 (a')	-0.758
LUMO + 3 (a'')	-0.971
LUMO + 2 (a')	-1.573
LUMO + 1 (a'')	-1.795
LUMO (a')	-2.437
HOMO (a'')	-6.662
HOMO – 1 (a')	-7.537
HOMO – 2 (a')	-7.572
HOMO – 3 (a'')	-7.714
HOMO – 4 (a')	-7.766
HOMO-LUMO	4.226
gap	

**Table S3.** Computed excitation energies and oscillator strengths for the complex  $Pt-CF_3tz-pyC_5$ . Except for S<sub>1</sub> and T<sub>1</sub> transitions, only calculated excitation with  $f \ge 0.07$  are listed. Also, only singly excited configurations mostly contributing are reported, together with the corresponding transition symmetry.

	$S_0 \rightarrow T_n$	$S_0 \rightarrow S_n$	$S_0 \rightarrow T_n$	$S_0 \rightarrow S_n$	
	<i>vacuum</i>		chloroform		
$\lambda$ [nm, eV] (f)	441, 2.811 (0.000) <sup><i>a</i></sup>	395, 3.140 (0.008)	$\overline{432, 2.872 (0.000)^a}$	386, 3.211 (0.010)	
symmetry	$(^{3}A'') 0.680 \text{ HOMO} \rightarrow \text{LUMO}$	$(^{1}A'')$ HOMO $\rightarrow$ LUMO	$(^{3}A'') 0.682 \text{ HOMO} \rightarrow \text{LUMO}$	$(^{1}A'') 0.700 \text{ HOMO} \rightarrow \text{LUMO}$	
	428, 2.894 $(0.000)^a$ ( <sup>3</sup> A') 0.542 HOMO $\rightarrow$ LUMO + 1	289, 4.290 (0.143) (1A') 0.506 HOMO – 1 $\rightarrow$ LUMO –0.436 HOMO $\rightarrow$ LUMO + 1	424, 2.922 $(0.000)^a$ ( <sup>3</sup> A') 0.528 HOMO $\rightarrow$ LUMO + 1	287, 4.326 (0.436) ( <sup>1</sup> A') 0.519 HOMO → LUMO + 1 $-0.434$ HOMO $-2 \rightarrow$ LUMO	
	350, 3.538 (0.000) <sup><i>a</i></sup> ( <sup>3</sup> A′) 0.491 HOMO – 1 → LUMO	282, 4.392 (0.083) ( <sup>1</sup> A <sup>''</sup> ) 0.648 HOMO − 3 → LUMO	351, 3.534 (0.000) <i><sup>a</sup></i> ( <sup>3</sup> A′) 0.536 HOMO – 2 → LUMO	279, 4.449 (0.116) ( <sup>1</sup> A'') 0.622 HOMO – $3 \rightarrow$ LUMO	
		273, 4.546 (0.167) ( <sup>1</sup> A') 0.572 HOMO − 2 → LUMO + 4		265, 4.686 (0.236) (¹A´) 0.681 HOMO – 4 → LUMO	
		267, 4.617 (0.214) (¹A´) 0.535 HOMO – 4 → LUMO		258, 4.805 (0.226) ( <sup>1</sup> A´´) 0.619 HOMO − 2 → LUMO + 1	
		257, 4.832 (0.173) ( <sup>1</sup> A'') -0.629 HOMO - 1 $\rightarrow$ LUMO + 1		239, 5.187 (0.058) ( <sup>1</sup> A´´) 0.679 HOMO − 4 → LUMO + 1	
		238, 5.208 (0.074) ( <sup>1</sup> A') 0.628 HOMO − 3 → LUMO + 1		236, 5.263 (0.106) ( <sup>1</sup> A´) 0.667 HOMO – 3 → LUMO + 1	
		237, 5.224 (0.126) ( <sup>1</sup> A') $-0.642$ HOMO $-1 \rightarrow$ LUMO $+2$		234, 5.291 (0.196) ( <sup>1</sup> A′) −0.658 HOMO − 2 → LUMO + 2	
		221, 5.620 (0.099) ( <sup>1</sup> A') 0.661 HOMO – 9 → LUMO		229, 5.417 (0.051) ( <sup>1</sup> A'') 0.619 HOMO – 9 $\rightarrow$ LUMO + 4	

<sup>*a*</sup> TD-DFT calculations performed with Gaussian09 neglect intersystem crossing processes, which mix states of the singlet and triplet manifold. For this reason, the computed oscillator strengths for triplet excitation transitions are equal to zero.

Movie S1. Emission microscopy images taken on a sample of fibers of complex  $Pt-CF_3tz-pyC_5$  obtained from acetone at concentration of 4 mg mL<sup>-1</sup>, upon excitation in the range 400–440 nm. Emission LP filter: 476 nm with polarizer inserted. The polarization plane is continuously rotating.