SUPPORTING INFORMATION

Luminescent bpy-Ln^{3+}-based hybrid coatings

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Figure Captions

Scheme S1. Detailed synthesis of **P4**.

Table S1. $^5D_0$ lifetimes (τ) and absolute emission quantum yield (ϕ) of the films **F4-Eu-MeOH**, **F4-Eu-EtOH** and **F4-Eu** deposited from different solvents.

Figure S1. Structural model of the hybrid thin films used for ellipsometric data analysis. W represents the thickness of the organic-inorganic hybrid layer.

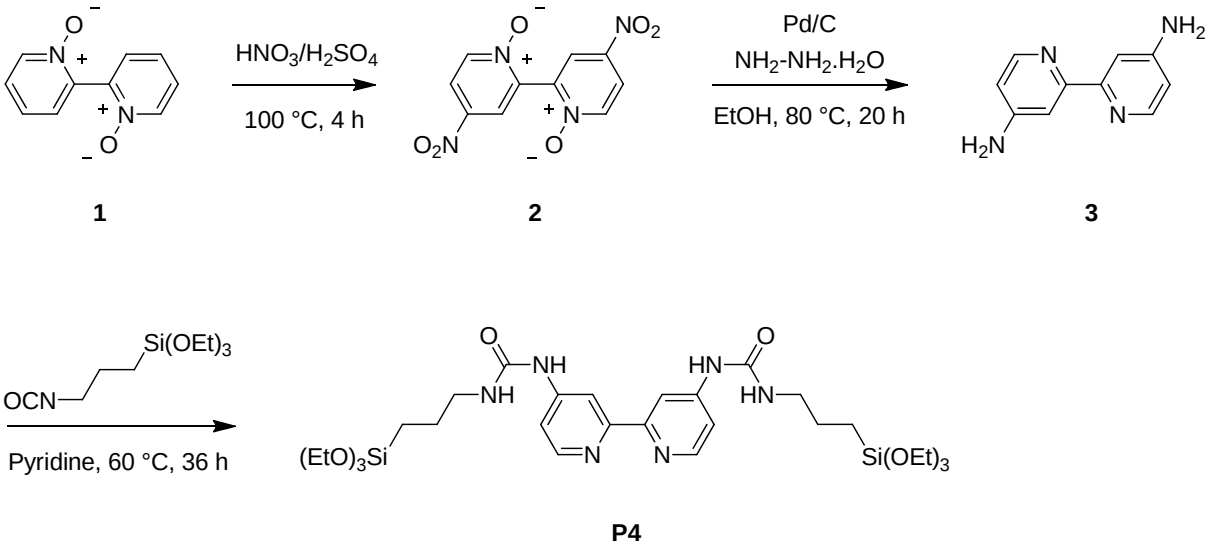
Figure S2. Ellipsometric parameters *Is* (open circles) and *Ic* (open triangles) for selected Eu^{3+}-containing organic-inorganic hybrid thin films (**F4-Eu$_1$** and **F4-Eu$_{36}$**). The solid lines correspond to the data fit for *Is* and the dashed lines for *Ic*. The MSE values are 1.22×10-3 and 1.06×10^{-3} for **F4-Eu$_1$** and **F4-Eu$_{36}$**, respectively.

Figure S3. Emission spectra of **F4-Eu** (**F4-Eu$_1$** (black line), **F4-Eu$_{36}$** (red line), **F4-Eu-MeOH** (green line) and **F4-Eu-EtOH** (blue line)) excited at 320 nm.

Figure S4. Excitation spectra of **F4-Eu** (black line), **F4-Eu-MeOH** (green line) and **F4-Eu-EtOH** (blue line)) monitored at 612 nm.

Figure S5. $^5D_0$ emission decay curves (300 K) monitored at 544 and 612 nm, and excited at 290 nm of **F4-Tb$_1$** and **F4-Eu$_1$** respectively.

Scheme S1.



Synthesis of 4,4'-dinitro-2,2'-bipyridine-*N*, *N*'-dioxide (2)[1]

In a two-neck round-bottom flask, 2,2'-bipyridine-N,N'-dioxide (23.0 g, 0.125 mol) was dissolved in a mixture of sulfuric acid (44.5 mL) and oleum (20% SO_3, 34 mL) at 0 °C. Fuming nitric acid (52 mL) was added dropwise over 30 minutes. The solution was heated at 100 °C for 4 hours and then cooled at 0 °C. The precipitation of a yellow solid occurred when the solution was poured onto ice (~400 g). The resulting solid was filtered, washed with water until the filtrates were neutral and then dried. The product was obtained as a yellow-green powder (15.1 g, 54.3 mmol). **Yield:** 61%; **^{1}H NMR** (400 MHz, DMSO-d_6), δ ppm: 8.69 (d, *J* = 3.4 Hz, 2H), 8.60 (d, *J* = 7.2 Hz, 2H), 8.38 (dd, *J* = 3.4 and 7.2 Hz, 2H).

Synthesis of 4,4'-diamino-2,2'-bipyridine (3)[2]

In a two-neck round bottom-flask were introduced (with stirring and under an inert atmosphere) 4,4'-dinitro-2,2'-bipyridine-N,N'-dioxide (10.0 g, 35.9 mmol) and absolute ethanol (280 mL) followed

by palladium on active charcoal (Pd/C 10%, 3.0 g). The suspension was brought to reflux, then a solution of hydrazine monohydrate (9.00 mL, 179 mmol) in absolute ethanol (35 mL) was added dropwise over 1.5 hours. After 20 hours under reflux, the hot solution was filtered through celite which was then washed with hot absolute ethanol (4 × 50 mL). After evaporation of the solvent, water (200 mL) was added and the mixture was kept overnight at 4 °C. Finally, the suspension was filtered and the resulting solid was washed with water (10 mL) and ethyl acetate (2 × 20 mL). The final product (6.29 g, 33.8 mmol) was obtained as a yellow solid. **Yield**: 94%; **^{1}H NMR** (250 MHz, DMSO-d_6), δ ppm: 8.06 (d, *J* = 5.5 Hz, 2H), 7.56 (d, *J* = 2.2 Hz, 2H), 6.49 (dd, *J* = 5.5 and 2.2 Hz, 2H), 6.11 (s, 4H).

Synthesis of P4[3]

Dry 4,4'-diamino-2,2'-bipyridine (previously heated at 80°C under vacuum) (1.50 g, 8.05 mmol), dry pyridine (26 mL) and freshly distilled 3-isocyanatopropyltriethoxysilane (4.26 mL, 17.7 mmol) were introduced into a Schlenk tube. The Schlenk tube was sealed and the mixture was stirred under an inert atmosphere at 60 °C for 2 days. After evaporation of the pyridine under vacuum, the product was washed with pentane (3 × 30 mL). After drying under reduced pressure, **P4** (3.84 g, 5.62 mmol) was obtained as a white powder. **Yield**: 70%; **^{1}H NMR** (400 MHz, DMSO-d_6), δ (ppm): 9.05 (s, 2H), 8.37 (d, *J* = 5.7 Hz, 4H), 8.35 (d, *J* = 1.9 Hz, 2H), 7.48 (dd, *J* = 5.7 and 1.9 Hz, 2H), 6.40 (s, 2H), 3.75 (q, *J* = 7.0 Hz, 12H), 3.09 (m, 4H), 1.51 (m, 4H), 1.15 (t, *J* = 7.0 Hz, 18H), 0,57 (m, 4H). **^{13}C NMR** (100 MHz, DMSO-d_6): δ (ppm): 155.9, 154.5, 149.5, 148.0, 111.7, 108.5, 57.6, 39.5, 23.3, 18.1, 7.2.

References :

1 (Wehman, P.; Dol, G. C.; Morrman, E. R.; Kamer, P. C. J.; van Leeuwen, P. W. N. M. *Organometallics*, **1994**, 13, 4856)

2 (Hilton, A.; Renouard, T.; Maury, O.; Le Bozec, H.; Ledoux, I.; Zyss, J. *Chem. Commun.* **1999**, 2521)

3 S. Benyahya, F. Monnier, M. Taillefer, M. Wong Chi Man, C. Bied and F. Ouazzani, *Adv. Synth. Catal.*, 2008, **350**, 2205-2208.

Electronic Supplementary Material (ESI) for Journal of Materials Chemistry

Table S1

Films	Solvent	$\tau(\lambda_{ex})$	$\phi(\lambda_{ex})$
F4-Eu-MeOH	MeOH	0.483±0.004 (280) 0.488±0.004 (300)	0.02±0.002 (285) 0.02±0.002 (300)
F4-Eu-EtOH	EtOH	0.403±0.004 (280) 0.381±0.003 (280)	0.03±0.003 (285) 0.03±0.003 (300)
F4-Eu	MeOH-DMF	0.430±0.004 (290)	0.05±0.005 (290)

Figure S1

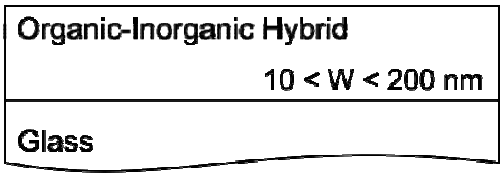


Figure S2.

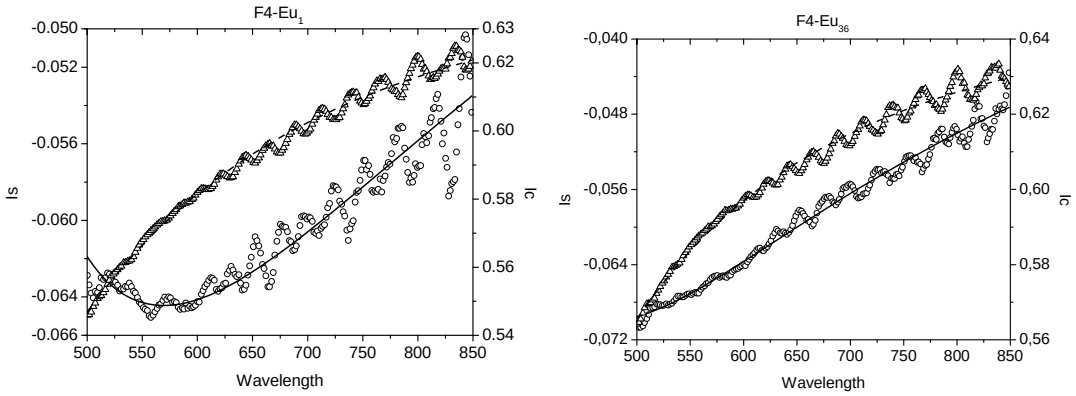


Figure S3.

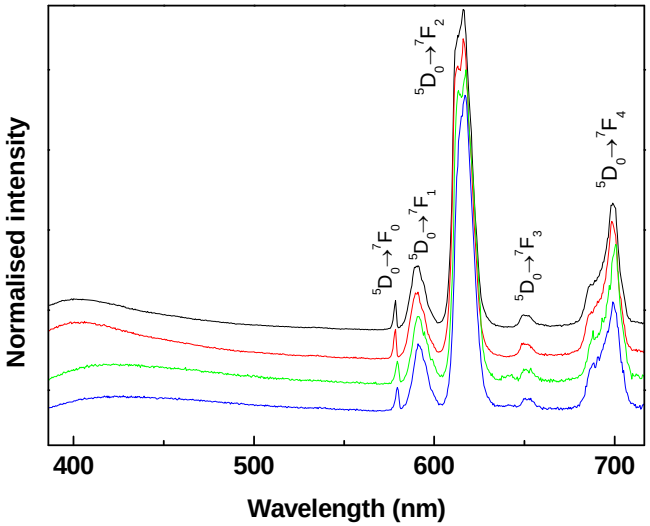


Figure S4.

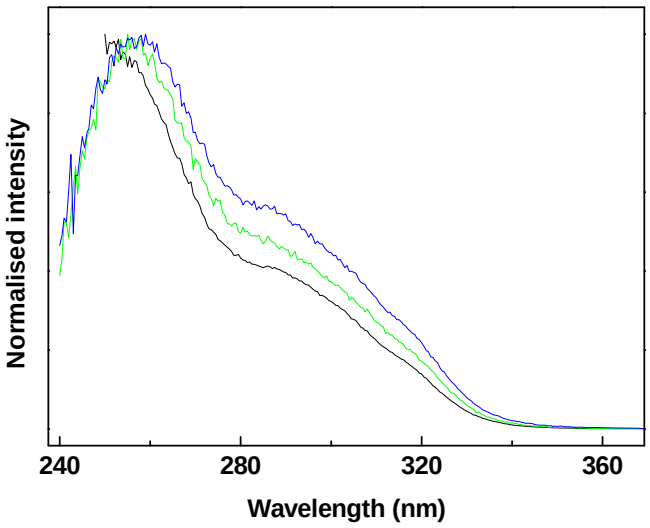


Figure S5.