Perfluorinated nitrosopyrazolone-based erbium chelates: efficient, non hygroscopic and solution processable 1550 nm emitting compounds.

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Supporting Information

1) Figure S1. Comparison of derivative **2** and **8** FT-IR spectra.
2) Synthetic procedures and characterization for new ligands and complexes.
3) Details on photophysical studies.

1) Figure S1. Comparison of derivative **2** and **8** FT-IR spectra.

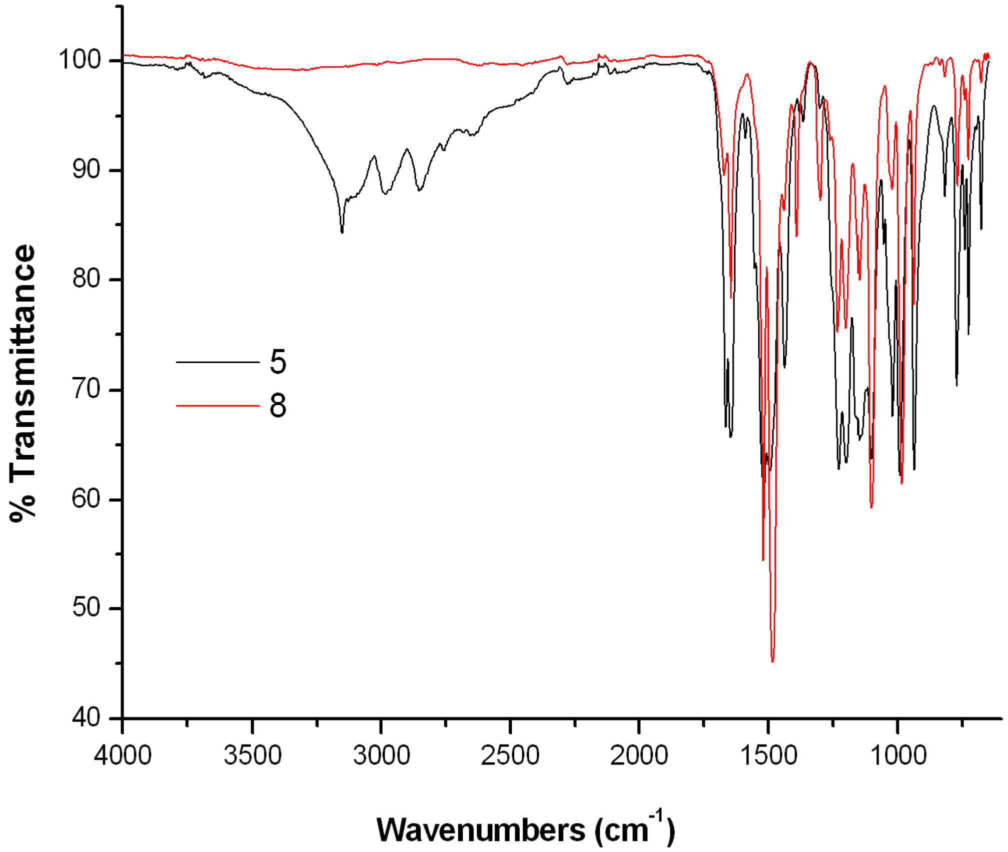


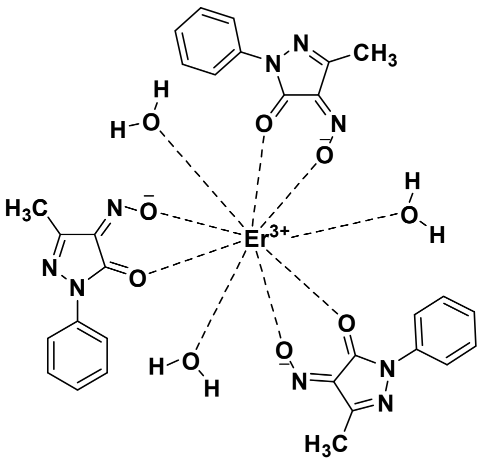
Figure S1. IR (ATR mode) spectra of the hydrated chelate **5** and of the anhydrous chelate **8**

1. Synthetic procedures and characterization for new ligands and complexes.

General Procedures. ^1H and ^{13}C NMR spectra were recorded using a Bruker AMX-500 spectrometer operating at 500 and 125.70 MHz, respectively. ^{19}F spectra were recorded on a Bruker AMX-300. Coupling constants are presented in Hz. Absorption spectrometry was performed using a Jasco V570 spectrophotometer. FT-IR spectra were recorded on a Perkin Elmer 100-TF Infrared operating in Universal ATR configuration. Microwave enhanced reactions were performed in a CEM discover focused oven. Pentafluorophenylhydrazine was purchased from Alfa Aesar, all other commercially available chemicals and solvents were purchased from Sigma Aldrich ad used without further purification. Dry solvents were dried overnight on Na_2SO_4 and filtered immediately before use. Melting points are uncorrected.

Derivatives 3-methyl-1-phenyl-1H-pyrazol-5-one[1] (**3**) and perfluorotriphenylphosphineoxide[2] (**6**) were prepared according to literature procedure.

Complex 4. A suspension on derivative **3** (0.260 g, 1.28 mmol) and K_2CO_3 (0.088 g, 0.64 mmol) in deionized water (50 ml) was stirred till complete dissolution of the ligand. The yellow solution was added dropwise to a solution of $ErCl_3{\cdot}6H_2O$ (0.114 g, 0.43 mmol) in 8.5 ml of deionized water. The suddenly formed yellow precipitate was immediately filtered under reduced pressure and purified by Soxlet extraction ($CHCl_3$) to remove inorganic impurities. The organic solution was concentrated till about 30 ml and diluted with 20 ml of acetonitrile. The resulting solution was slowly evaporated over a period of 36 h to give the product as an orange solid. (0.13 mmol, 0.108 g, 30 % yield). Mp > 200 °C (dec). Anal. Calcd for $C_{30}H_{24}ErN_9O_6{\cdot}3H_2O$: 43.52% C, 3.65% H, 15.23% N. Found: 43.82% C, 3.59% H, 14.99 % N.



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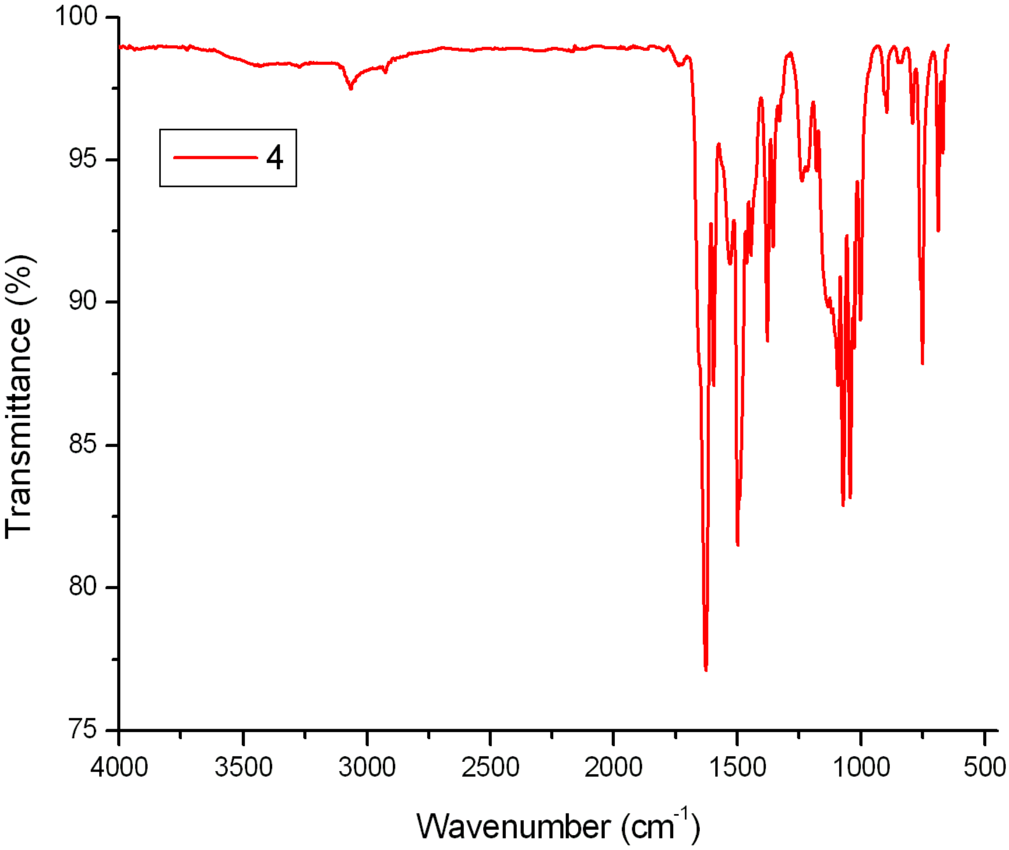
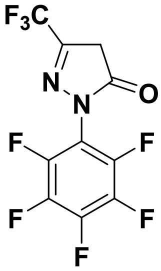
FT-IR (ATR mode, pure compound)



1-pentafluorophenyl-3-trifluoromethyl-pirazol-5-one (1). Ethyl 4,4,4-trifluoroacetoacetate (3.9 ml, 30.28 mmol) was added dropwise to a solution of pentafluorophenylhydrazine (6.00 g, 30.28 mmol) in 32 ml of 95 % acetic acid. The brown mixture was refluxed for 8 h in a focused microwave oven. The solution was cooled at ambient temperature and diluted with 70 ml of water. The resulting yellow precipitate was filtered and purified by column chromatography (AcOEt:ETP 3:1) to give the pure product as a pale yellow solid. (5.25 g, 16.65 mmol, 54.5 % yield). Mp 189-190°C. ^{1}H NMR (DMSO-d_6) δ 6.00 (2H, s); ^{13}C (DMSO-d_6) 84.8 (s), 112.4 (t, $^{2}J_{C\text{-}F}$=15.0 Hz), 121.3 (q, $^{1}J_{C\text{-}F}$=269.0 Hz), 138.0 (d, $^{1}J_{C\text{-}F}$=252.0 Hz), 142.3 (d, $^{1}J_{C\text{-}F}$=255.0 Hz), 143.6 (d, $^{1}J_{C\text{-}F}$=251.0 Hz), 144.0 (q, $^{2}J_{C\text{-}F}$=37.5 Hz), 156.4; ^{19}F (DMSO-d_6) δ 64.3 (3F, s), -141.8 (2F, d), -151.5 (1F, t), -161.6 (2F, t). Anal Calcd. for $C_{10}H_2N_2F_8O$: C, 37.76 %; H, 0.63 %; N, 8.81 %. Found: C, 37.71 %; H, 0.56 %; N, 8.94 %.



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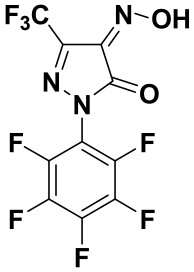
3-trifluoromethyl-4-hydroxyimino-1-perfluorophenyl-1H-pyrazol-5-one(2). 1.5 ml of conc HCl (37 % solution in water) was added dropwise to a solution of derivative **1** (2.50 g, 7.90 mmol) in THF (80 ml) at 0°C. The almost colorless solution gradually turns yellow. Isoamylnitrite (1.07 ml, 0.930 g, 7.9 mmol) was added dropwise. The solution was gradually allowed to reach the ambient temperature and stirred overnight. The solution was evaporated at reduced pressure and the yellow viscous residue taken up with water (100 ml) and extracted with AcOEt (3 x 50 ml). Combined organic phase was dried over Na_2SO_4 and evaporated. The yellow oil residue was taken up with 50 ml of light petroleum ether and sonicated till precipitation of a white solid that was filtered under reduced pressure and dried till constant weight. (1.50 g, 4.35 mmol, 55 % yield). p 118-119°C.
^{13}C (DMSO-d_6) δ 111.1 (t, $^2J_{C\text{-}F}$=13.0 Hz), 119.5 (q, $^1J_{C\text{-}F}$=270.6 Hz), 138.2 (d, $^1J_{C\text{-}F}$=250.6 Hz), 140.2 (q, $^2J_{C\text{-}F}$=38.3 Hz), 142.0 (d, $^1J_{C\text{-}F}$=255.4 Hz), 143.5 (d, $^1J_{C\text{-}F}$=256.5 Hz), 150.2 (s), 160.0 (s); ^{19}F (DMSO-d_6) δ -64.6/-66.2 (3F, s), -144.6 (2F, m), -152.2 (1F, m), -161.7 (2F, m). UV-Vis (EtOH), λ(nm)/ε(cm mol^{-1} l^{-1}): 344/3521, 264/12625. Anal Calcd. for $C_{10}HN_3F_8O_2$: C, 34.60 %; H, 0.29 %; N, 12.11 %. Found: C, 34.99 %; H, 0.48 %; N, 11.68 %.



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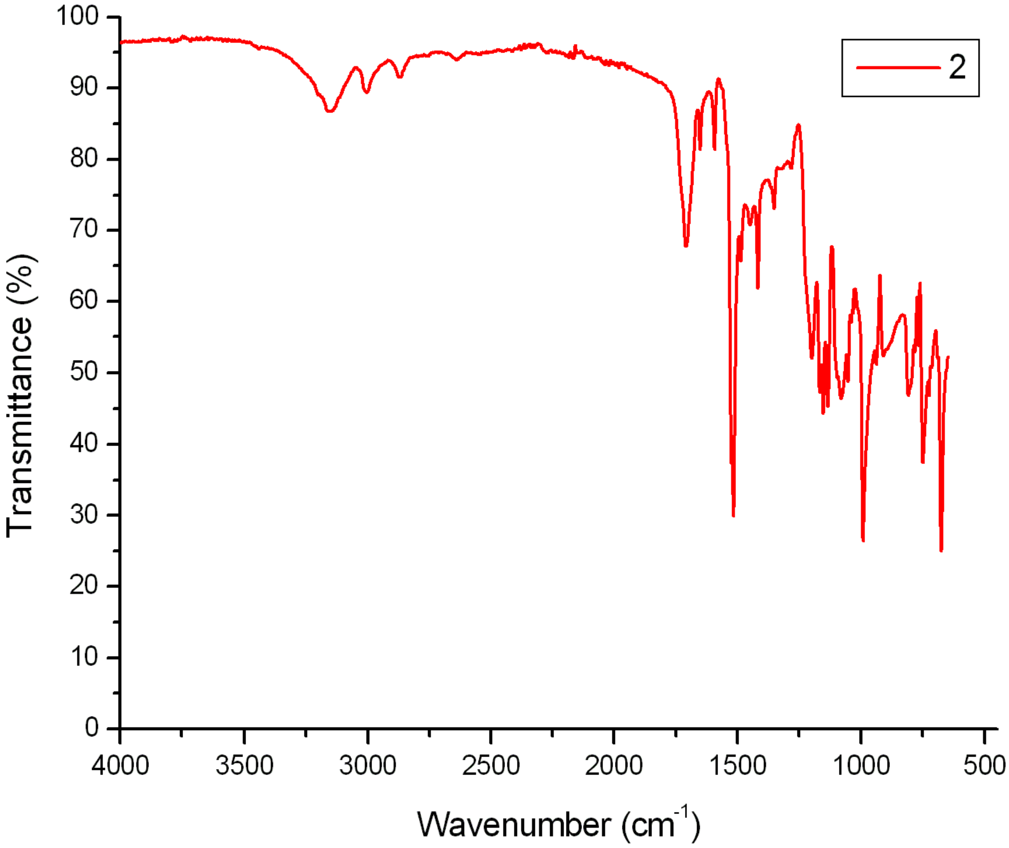
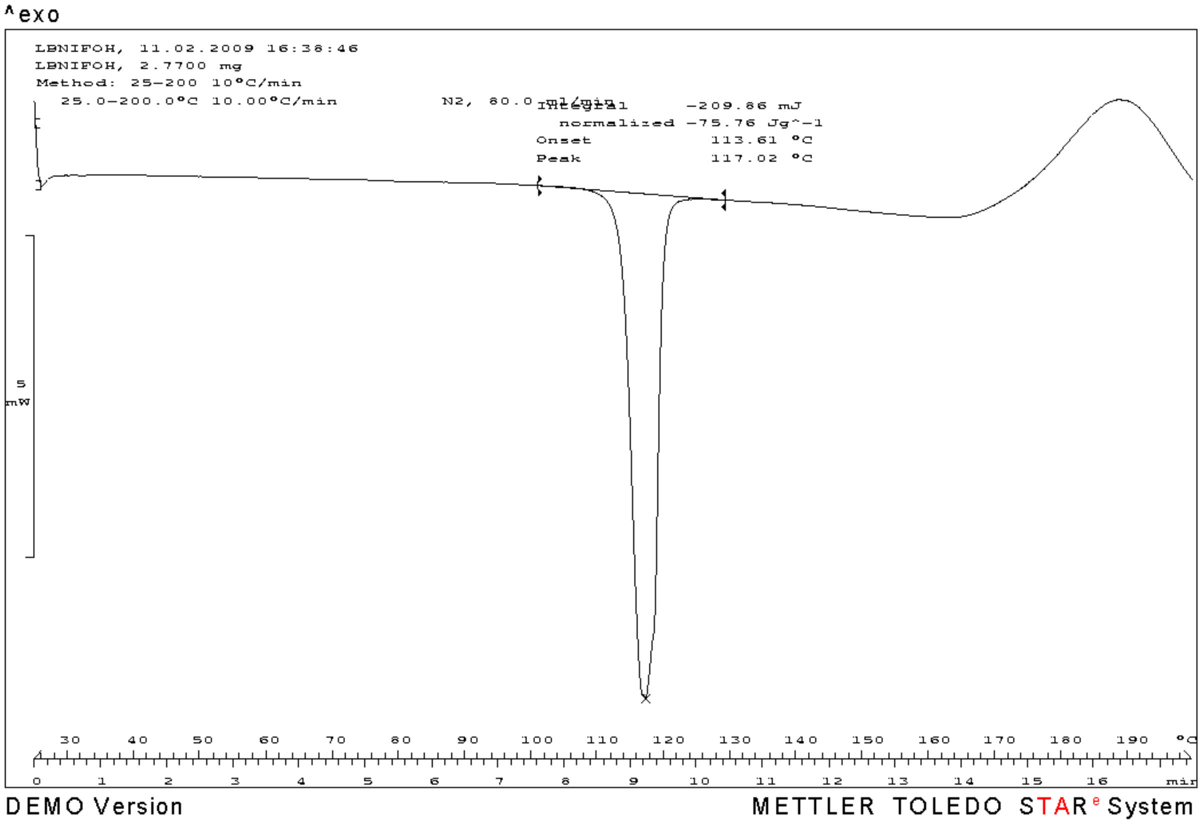
FT-IR(ATR mode, pure compound)

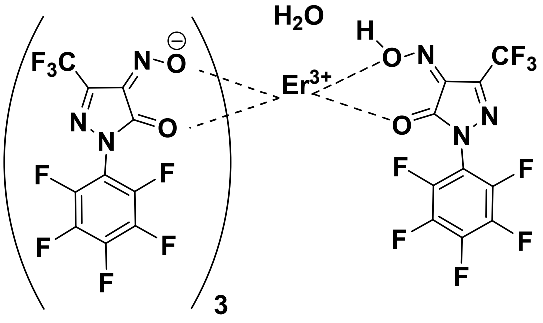


DSC trace.



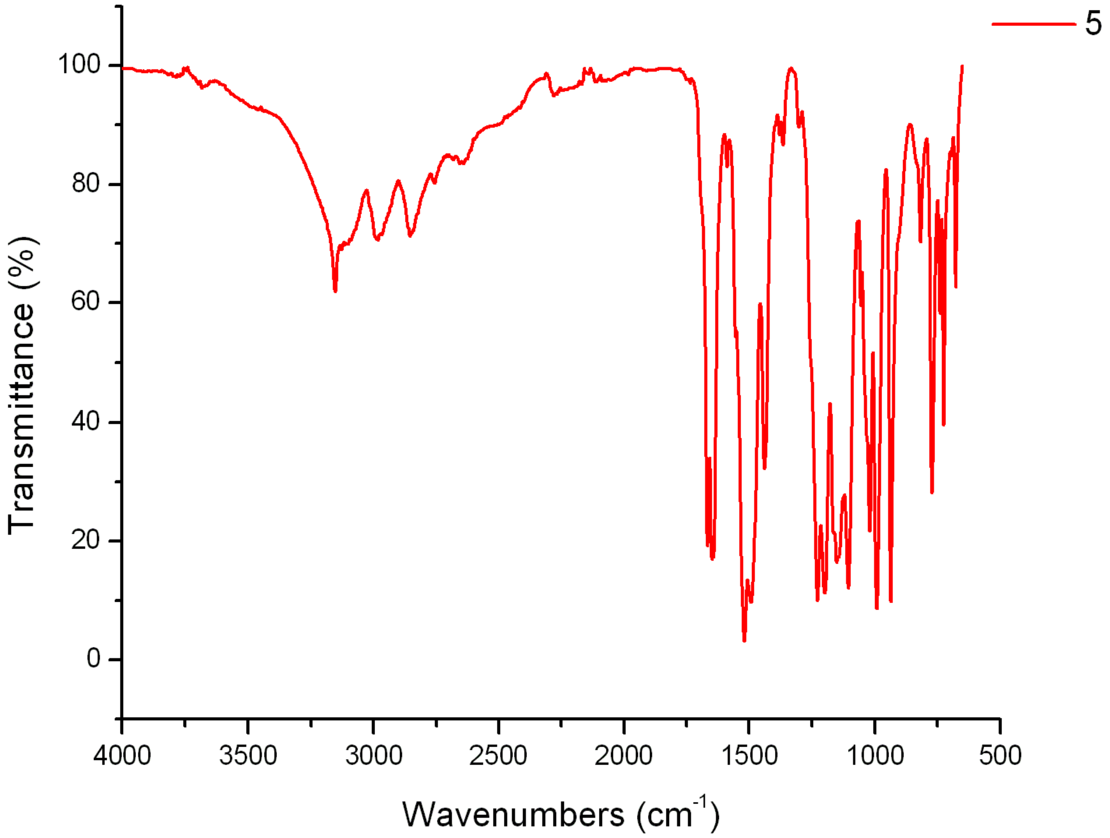
Derivative 2 DSC trace.

Complex 5. Compound **2** (0.500 g, 1.44 mmol) was suspended in 50 ml of deionized water. Potassium carbonate (0.200 g, 1.44 mmol) was added directly as a solid to the suspension and mixture was stirred till complete dissolution of the ligand. Chloroform (100 ml) was added to the cloudless yellow solution and the biphasic mixture was vigorously stirred. $ErCl_3 \cdot 6H_2O$ (0.381 g, 1.00 mmol) was added directly as a solid and the reaction mixture was transferred to a separatory funnel. The yellow organic phase was separated and dried overnight over Na_2SO_4. The solution was concentrated till about 10 ml and layered with 50 ml of light petroleum ether. After 5 days the product was filtered as small yellow-orange crystals. (0.350 g, 0.22 mmol, 61.1 % yield). Mp = 150-153 °C (dec). UV-Vis ($CHCl_3$), λ(nm)/ε(cm mol^{-1} l^{-1}): 356/14700. Anal Calcd. for $C_{40}H_3ErF_{32}N_{12}O_9$: C, 30.59 %; H, 0.19 %; N, 10.70 %; Found: C, 30.51 %; H, 0.41 %; N, 10.99 %.



5

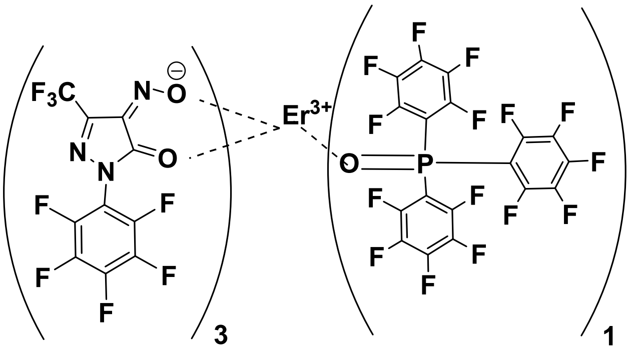
FT-IR (ATR mode, pure compound)



Complexes 7 and 8. A solution of complex **5** (200 mg, 0.13 mmol) was suspended in n-hexane (100 ml). The yellow suspension was refluxed under a Dean-Stark trap for 30 min to remove traces of water. A suspension of **6** (0.419 g, 0.76 mmol) in 15 ml of dry n-hexane was added directly to the refluxing suspension. Colour suddenly turned pale orange and the suspension turned in a cloudless solution. After 15 min a light orange precipitate was formed. The suspension was immediately hot-filtered to give a light yellow solid.

a) Treatment of the solid residue (preparation of 7).

The solid was suspended in a fresh portion of n-hexane (150 ml) and refluxed again for 2 h. The solid did not completely dissolved. The solid residue was again hot filtered to give derivative **7** as a light yellow powder insoluble in hot hexane. (0.060 mg, 0.034 mmol, 26 % yield). Mp > 180 °C. Anal Calcd for $C_{48}ErF_{39}N_9O_7P$: C, 32.87 %; H, 0.00 %; N, 7.19 %. Found C, 33.28 %; H, 0.27 %; N, 7.25 %.



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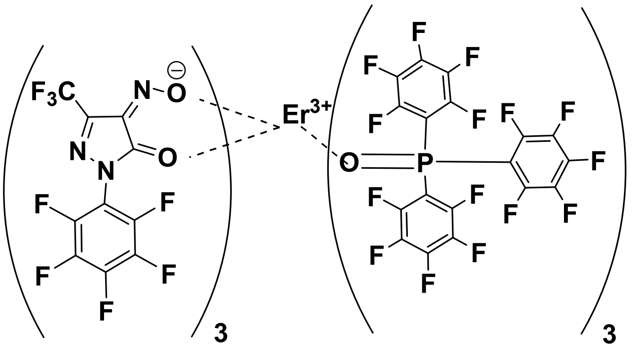
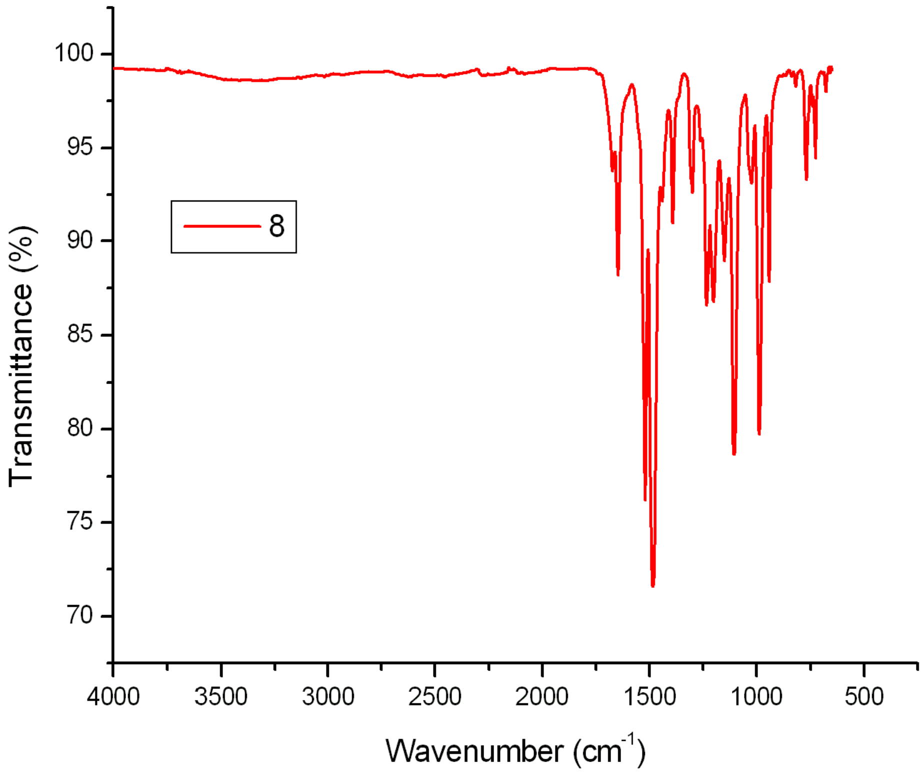
b) Treatment of the filtrate (preparation of 8).

Cooling of the filtrate afforded a light yellow precipitate that was filtered under reduced pressure and dried till constant weight. The solid obtained is soluble in n-hexane at ambient temperature. Crystallization from light petroleum ether afforded the pure derivative 8 as a light yellow solid. (0.085 mg, 0.030 mmol, 23 % yield). Mp. > 170 °C (See DSC trace). Anal Calcd for $C_{84}ErF_{69}N_9O_9P_3$: C, 35.40 %; H, 0.00 %; N, 4.42 %. Found: C, 35.89 %; H, 0.18 %; N, 4.01 %.

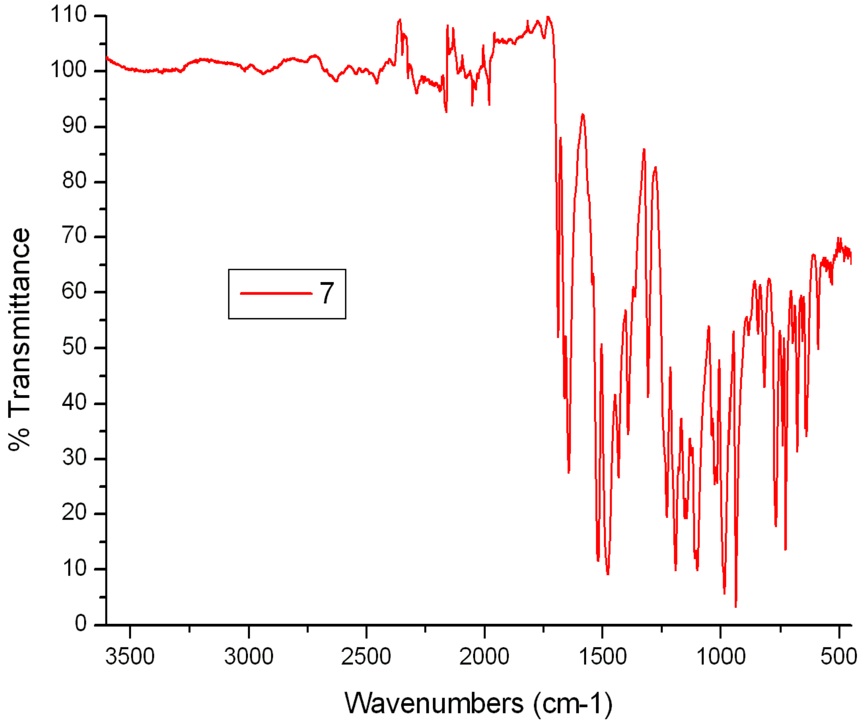


8

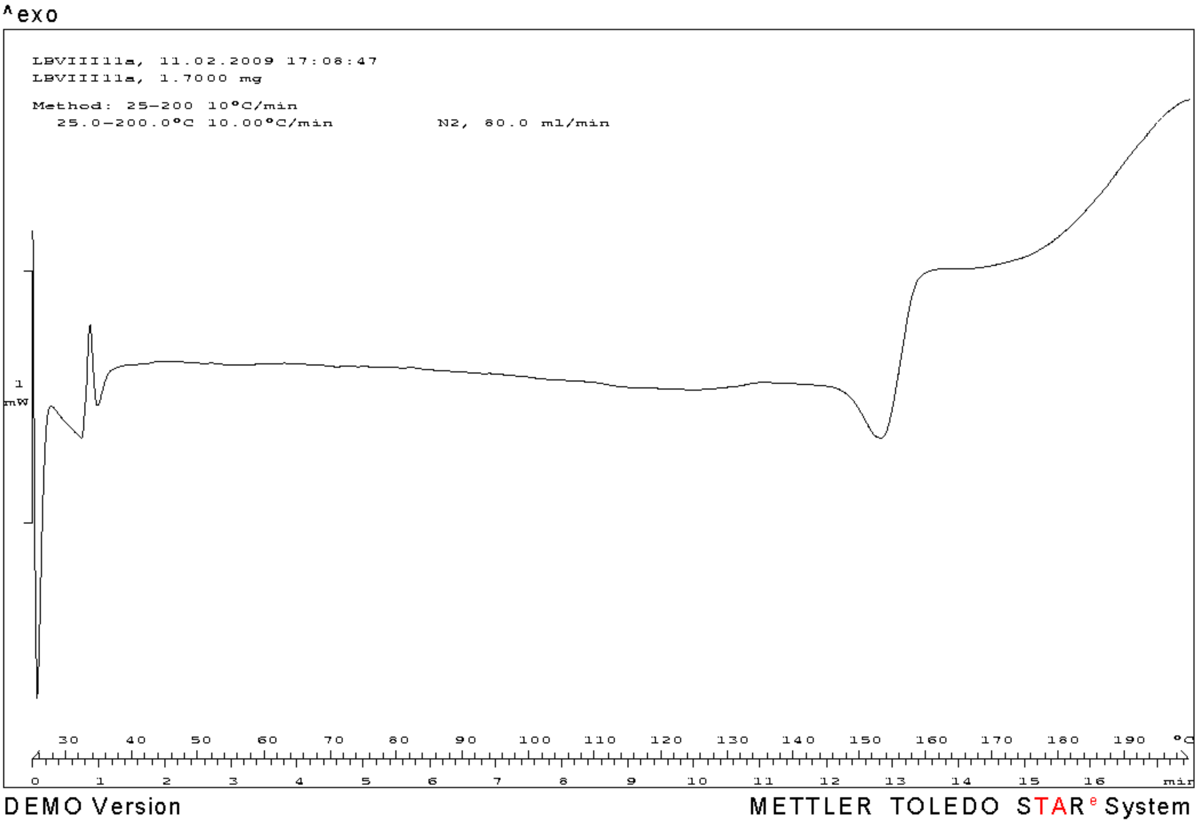
FT-IR (ATR mode, pure compound)



FT-IR (micro ATR mode, pure sample)



DSC trace (derivative 8)



3. Details on photophysical characterization.

Photoluminescence Studies: For NIR PL measurements, the compounds, were excited by a 355 nm (3.49 eV) Nd:YAG laser (Laser Export mod. LCS-DTL-374QT) with excitation power of 2.7 mW and a pulse repetition rate of 10 kHz. NIR luminescence were detected by nitrogen cooled PMT (Hamamatsu R5509-73) coupled with an high speed amplifier (Hamamatsu C5594) and a 74100 Cornestone 2601/4 (ORIEL) monochromator (bandpass 15 nm). For time-resolved measurements, a PCI plug-in multichannel scaler ORTEC 9353 was used in photon counting acquisition mode, with an overall time resolution better than 100 ns.

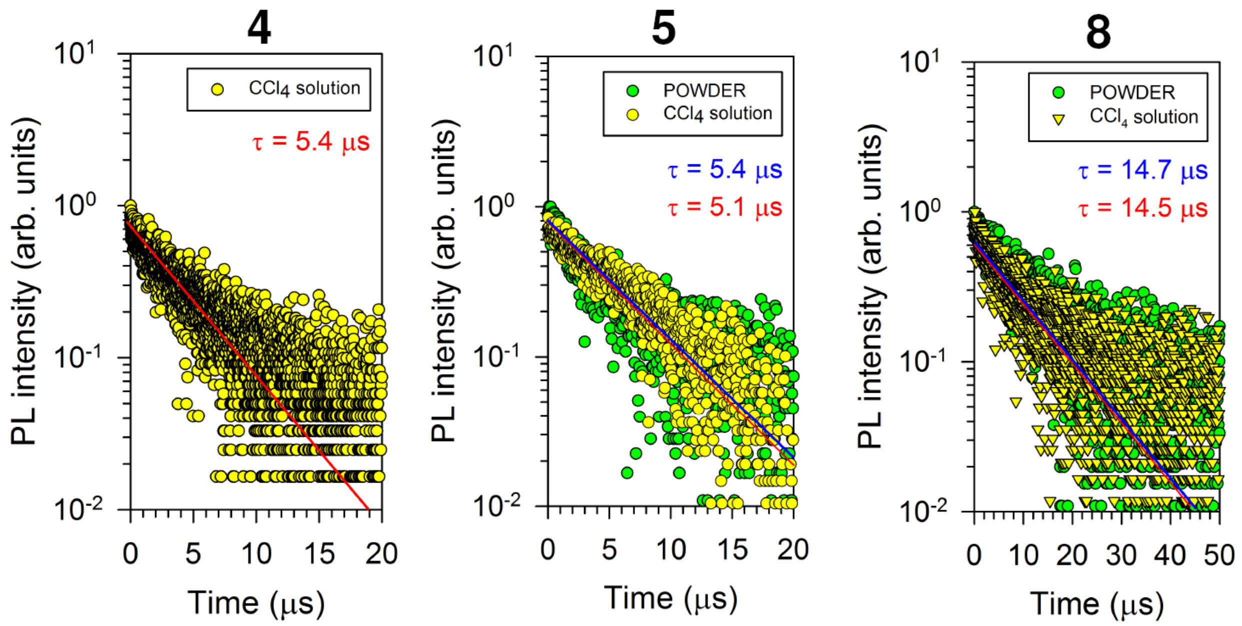


Figure S2. Photoluminescence decay profile at 1530 nm of compounds: **4, 5** and **8**, corresponding to the data reported in Table 1 of the Manuscript (excitation 355 nm).

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[1] M. S. K Youssef,. S. A. M. Metwally, M. A El-Maghraby, M. I. Younes *J. Het. Chem.,*1984, **21**, 1747-52.
[2] L.A. Wall, R.E. Donadio, W.J. Pummer *J. Am. Chem. Soc.*, 1960, **82**, 4846-4848.