Supporting Information

Functionalisation of ligands through click chemistry: long-lived NIR emission from organic Er(III) complexes with a perfluorinated core and a hydrogen-containing shell

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**Preparation of ligands and erbium complexes**

**Experimental Procedures**

*General procedures* Unless otherwise stated, all commercially available solvents and reagents were used without further purification. UV-Vis diffuse reflectance spectra in the liquids and solid were measured using a Hitachi U-3010 spectrometer with an integrating sphere. NMR spectra were determined at 400 MHz for $^1$H, 376 MHz for $^{19}$F and 162 MHz for $^{31}$P with a Bruker AVIII 400 spectrometer. Mass spectra were obtained by the EPSRC NMSF, Swansea. CHN elemental analyses were performed by MEDAC Ltd, Egham, Surrey or Exeter Analytical (UK) Ltd. X-ray powder diffraction was performed using the PANalytical X’Pert X-ray diffractometer, at Queen Mary University of London.

![Structures of the ligands](image)

**Figure S1.** Structures of the ligands

1. Bis(4-azido-2,3,5,6-tetrafluorophenyl)phosphinic acid (BAPA, 2) NaN$_3$ (608 mg, 9.35 mmol) was added to a solution of tris(pentafluorophenyl)phosphine oxide (I) (1.627 g, 2.97 mmol) in acetone (30 mL) and H$_2$O (10 mL) and the mixture was heated at 56 °C overnight. Then acetone was evaporated. The mixture was acidified using 2 M hydrochloric acid (10 mL). Ether (30 mL) and 1,4-dioxane (1 mL) were added for extraction. The organic phase was dried (Na$_2$SO$_4$), evaporated and recrystallized from ether-hexane to give the bis(4-azido-2,3,5,6-tetrafluorophenyl)phosphinic acid (2) (967 mg, 73%) as a white solid, mp >77 °C (decomp). $\nu_{\text{max}}/\text{cm}^{-1}$ >2500 (br, OH), 2243, 2131 (vs, N$_3$), 1637, 1469, 1391, 1227. $\delta_p$ (162 MHz, CDCl$_3$) 9.3 (s). $\delta_p$ (376 MHz, CDCl$_3$)
−135.8 (br s, F-o), −153.8 (br s F-m). δ_H (400 MHz, CDCl₃) 11.03 (s, POOH). m/z (APCI) Calcd. for C₁₂F₈N₆O₂P ([M-H]⁻) 442.9698; found 442.9691.

2. \([iPr₂EtNH]^+PL_A^{-}\) (3) Bis(4-azido-2,3,5,6-tetrafluorophenyl)phosphinic acid (BAPA, 2) (44.4 mg, 0.10 mmol) and 1-hexyne (32.9 mg, 0.40 mmol) were mixed in DCM (1 mL). Hüning’s base (0.087 mL, 0.50 mmol) was added and the mixture was stirred for 5 min before the addition of CuI (9.53 mg, 0.069 mmol). After 24 h, DCM was evaporated, acetone (1 mL) was added to the residue, followed by 6 M HCl (1 mL). DCM (30 mL) and water (20 mL) were added and the phases were separated. The organic phase was dried (Na₂SO₄) and evaporated to give \([iPr₂EtNH]^+PL_A^{-}\) (3) (67.2 mg, 91%) as a pale yellow gel. ν_max/cm⁻¹ 2921 (br, C-H), 1645, 1466, 1258. δ_P (162 MHz, CDCl₃) −10.4 (s). δ_F (376 MHz, CDCl₃) −132.2 (br s, F-o), −146.7 (br s, F-m). δ_H (400 MHz, CDCl₃) 0.5-2.9 (m, 33H, C₄H₉ and CH₃ of the cation), 3.03 (m, 2H, CH₂ in the cation), 3.59 (m, 2H, CH in the cation), 7.55 (s, 2H, triazole-H), 10.65 (s, 1H, NH). m/z (APCI) Calcd. for C₂₄H₂₀F₈N₆O₂P ([PL_A⁻]) 607.1263; found 607.1252.

3. \([iPr₂EtNH]^+PL_B^{-}\) (4) Bis(4-azido-2,3,5,6-tetrafluorophenyl)phosphinic acid (BAPA, 2) (222.1 mg, 0.5 mmol) and phenylacetylene (204.2 mg, 2.0 mmol) were mixed in DCM (3 mL). Hüning’s base (0.432 mL, 2.5 mmol) was added and the mixture was stirred for 5 min before CuI (47.6 mg, 0.345 mmol) was added. After 24 h, DCM was evaporated. Acetone (1 mL) was added to the residue, followed by 6 M HCl (1 mL). DCM (50 mL) and water (30 mL) were used to separate phases. The organic phase was dried (Na₂SO₄), concentrated and added to boiling hexane dropwise. The precipitate formed was collected by filtration to give \([iPr₂EtNH]^+PL_B^{-}\) (4) (318 mg, 82%) as a pale yellow solid. mp >170 °C (decomp). ν_max/cm⁻¹ 2995 (br, C-H), 1646, 1524, 1469, 1273, 1144, 1075. δ_P (162 MHz, CDCl₃) −10.5 (s). δ_F (376 MHz, CDCl₃) −131.9 (br s, F-o), −146.2 (br s, F-m). δ_H (400 MHz, CDCl₃) 1.40-1.60 (m, 15H, CH₃), 3.15 (m, 2H, CH₂), 3.72 (m, 2H,
CH), 7.43 (m, 2H), 7.50 (m, 4H), 7.95 (d, 4H), 8.19 (s, 2H, triazole-H), 10.68 (s, 1H, NH). δC (101 MHz, CDCl3) 12.0 (s, CH2CH3), 17.3 (s, CH(CH3)2), 18.5 (s, CH(CH3)2), 42.2 (s, CH2CH3), 53.8 (s, CH(CH3)2), 118.5 (m, C-p), 118.8-120.5 (m, Ar CP), 121.9 (s, Ar CH), 126.0 (s, Ar CH), 128.8 (s, Ar CH), 129.0 (s, Ar C), 129.4 (s, triazole CH), 141.2 (dm, 1JCF 260 Hz, Ar CF), 147.0 (dm, 1JCF 250 Hz, Ar CF), 148.1 (triazole C-Ph).

m/z (APCI) Calcd. for C28H12F8N6O2P (PL−) 647.0637; found 647.0635.

4. [iPr2EtNH]**PLC− (5) Bis(4-azido-2,3,5,6-tetrafluorophenyl)phosphinic acid (BAPA, 2) (44.4 mg, 0.10 mmol) and pentafluorophenylacetylene (76.8 mg, 0.40 mmol) were mixed in DCM (1 mL). Hünig’s base (0.087 mL, 0.50 mmol) was added and the mixture was stirred for 5 min before the addition of CuI (9.53 mg, 0.069 mmol). After 24 h, DCM was evaporated, then acetone (1 mL) was added to the residue, followed by 6 M HCl (1 mL). DCM (30 mL) and water (20 mL) were added and the phases were separated. The organic phase was filtered, dried (Na2SO4), concentrated and added to boiling hexane dropwise. The precipitate formed was collected by filtration to give [iPr2EtNH]**PLC− (5) (57.8 mg, 60%) as a pale yellow solid, mp 101-105 °C. νmax/cm−1 2997 (br, C-H), 2677, 1645, 1514, 1499, 1470, 1257, 1233. δp (162 MHz, CDCl3) −8.81 (s). δF (376 MHz, CDCl3) −131.1 (br s, F-o), −139.2 (d, J 15 Hz), −145.6 (br s, F-m), −152.9 (m), −161.2 (m). δH (400 MHz, CDCl3) 1.35-1.65 (m, 15H, CH3), 3.16 (s, 2H, CH2), 3.72 (s, 2H, CH), 8.35 (s, 2H, triazole-H), 10.43 (s, 1H, NH). m/z (APCI) Calcd. for C28H12F8N6O2P (PL−) 826.9695; found 826.9707.

5. HPLD (6) Bis(4-azido-2,3,5,6-tetrafluorophenyl)phosphinic acid (BAPA, 2) (44.4 mg, 0.10 mmol) and 9-(prop-2-ynyl)-9H-carbazole (73) (82.1 mg, 0.40 mmol) were mixed in DCM (1 mL). Hünig’s base (0.087 mL, 0.50 mmol) was added and the mixture was stirred for 5 min before the addition of CuI (9.53 mg, 0.069 mmol). After 24 h, DCM was evaporated, acetone (1 mL) was added to the residue, followed by 6 M HCl (1 mL).
DCM (30 mL) and water (20 mL) were added. The precipitated product was filtered off and washed with DCM and acetone to give HPL-D (6) (58.0 mg, 68%) as a white solid, mp >140 °C (decomp). $\nu_{\text{max}}/\text{cm}^{-1}$ 3143 (br, CH), 1645, 1472, 1459, 1324, 1270, 1241. $\delta_F$ (162 MHz, DMSO-d$_6$) –13.5 (s). $\delta_P$ (101 MHz, DMSO-d$_6$) 37.7 (s, CH$_2$), 110.1 (s, Ar CH), 118.3 (m, C-p), 119.7 (s, Ar CH), 120.7 (s, Ar CH), 122.8 (s, Ar C), 126.3 (s, Ar CH), 126.6 (s, triazole CH), 140.2 (Ar C), 141.4 (dm, $^1J_{C-F}$ 260 Hz, Ar CF), 144.3 (triazole C-CH$_2$), 146.4 (dm, $^1J_{C-F}$ 245 Hz, Ar CF). $m/z$ (APCI) Calcd. for C$_{42}$H$_{22}$F$_8$N$_8$O$_2$P ($[\text{M-H}]^-$) 853.1481; found 853.1469.

6. Complex Er(PL$_A$$)_3$ (7) [iPr$_2$EtNH]$^+$PL$_A^-$ (3) (50 mg, 0.068 mmol) was dissolved in hot methanol. A solution of ErCl$_3$·6H$_2$O (8.62 mg, 0.0226 mmol) in methanol (4 mL) was added slowly. A precipitate formed immediately and the mixture was left overnight. Then the solid was filtered off and washed with hot methanol to give the erbium complex Er(PL$_A$$)_3$ (7) (32.2 mg, 72%) as a yellow solid, mp >160 °C (decomp). $\nu_{\text{max}}/\text{cm}^{-1}$ 2932 (br, C-H), 1647, 1524, 1470, 1268, 1206, 1120, 1085. Anal. Calcd. (Found) for C$_{72}$H$_{60}$ErF$_{32}$N$_{18}$O$_8$P$_3$: C, 43.47 (42.23); H, 3.04 (2.77); N, 12.67 (12.05).

7. Complex Er(PL$_B$$)_3$ (8) [iPr$_2$EtNH]$^+$PL$_B^-$ (4) (30 mg, 0.039 mmol) was dissolved in hot methanol. A solution of ErCl$_3$·6H$_2$O (4.91 mg, 0.0129 mmol) in methanol (4 mL) was added slowly. A precipitate formed immediately and the mixture was left overnight. Then the solid was filtered off and washed with hot methanol to give the erbium complex Er(PL$_B$$)_3$ (8) (26.5 mg, 97%) as a yellow solid, mp >150 °C (decomp). $\nu_{\text{max}}/\text{cm}^{-1}$ 3142 (br, C-H), 1646, 1525, 1468, 1409, 1278, 1206, 1141, 1088. $m/z$ (MALDI–) Calcd. for C$_{112}$H$_{48}$ErF$_{32}$N$_{24}$O$_{8}$P$_4$ ($[\text{Er(PL$_B$)}]^{+}$) 2756.2; found 2756.2. Anal.
Calcd. (Found) for C_{84}H_{36}ErF_{24}N_{18}O_{6}P_{3}: C, 47.83 (44.64); H, 1.72 (1.89); N, 11.95 (10.93).

8. Complex Er(PL\hspace{0.1em}C)_{3} (9) \([iPr_2EtNH]^+\)PL\hspace{0.1em}C\hspace{0.1em}− (5) (50 mg, 0.052 mmol) was dissolved in hot methanol. A solution of ErCl_{3}\cdot6H_2O (6.64 mg, 0.0174 mmol) in methanol (4 mL) was added slowly. A precipitate formed immediately and the mixture was left overnight. Then the solid was filtered off and washed with hot methanol to give the erbium complex Er(PL\hspace{0.1em}C)_{3} (9) (30 mg, 70%) as a white solid, mp >115 °C (decomp). ν_{max}/cm\(^{-1}\) 3171 (br, C-H), 1646, 1516, 1499, 1470, 1304, 1265, 1229, 1211. m/z (MALDI−) Peaks for [Er(PL\hspace{0.1em}C)_{4}]\hspace{0.1em}− and (PL\hspace{0.1em}C\hspace{0.1em}−) were not observed. Anal. Calcd. (Found) for C_{84}H_{66}ErF_{54}N_{18}O_{6}P_{3}: C, 38.08 (36.25); H, 0.23 (0.94); N, 9.51 (12.64).

9. Complex Er(PL\hspace{0.1em}D)_{3} (10) HPL\hspace{0.1em}D (6) (38 mg, 0.044 mmol) was dissolved in boiling acetonitrile. A solution of ErCl_{3}\cdot6H_2O (5.66 mg, 0.0148 mmol) in methanol (1 mL) was added slowly. A precipitate formed immediately, was filtered off and washed by hot MeOH, DCM and acetone to give complex Er(PL\hspace{0.1em}D)_{3} (10) (33.7 mg, 83%) as a white solid, mp > 220 °C (decomp). ν_{max}/cm\(^{-1}\) 3050 (br, C-H), 1645, 1599, 1523, 1469, 1324, 1269, 1209, 1119, 1087. m/z (NSI+) Calcd. for C_{42}H_{24}F_{8}N_{8}O_{2}P (H_{2}PL\hspace{0.1em}D)^{+} 855.1627; found 855.1625. Peaks for Er(PL\hspace{0.1em}D)_{3} were not observed. Anal. Calcd. (Found) for C_{126}H_{66}ErF_{24}N_{24}O_{6}P_{3}: C, 55.47 (53.28); H, 2.44 (2.06); N, 12.32 (11.79).
2. Optical spectra of lanthanide complexes

Diffuse reflectance spectra of erbium complexes

![Diffuse reflectance spectra of Er(PL$_{A,D}$)$_3$ powders, RT](image)

**Figure S2.** Diffuse reflectance spectra of Er(PL$_{A,D}$)$_3$ powders, RT

NIR emission of erbium complexes

![Emission spectra of Er(PL$_{A,D}$)$_3$ powders, RT](image)

**Figure S3.** Emission spectra of Er(PL$_{A,D}$)$_3$ powders, RT
3. XRD powder diffraction of lanthanide complexes

Figure S4. Powder X-ray diffraction data of Er(PL₃-D)₃ and Y(PL₃-D)₃
4. PL lifetimes of ErL₃ and model calculations

The stretched exponential fitting is an empirical fit that is widely used to fit nonexponential decay processes, and is frequently used to describe a superposition of exponential relaxation times:

\[ I = I_0 + I_1 \exp\left[-\left(\frac{t}{\tau}\right)^\beta\right] \]

\(I_0\) is the offset intensity, \(I_1\) is the initial intensity, \(\tau\) is the lifetime and \(\beta\) is the stretching function. The average lifetime is calculated with 

\[ \langle \tau \rangle = \frac{\tau}{\beta} \Gamma\left(\frac{1}{\beta}\right) \]

Example of fitting the decay:

![Graph showing photoluminescence decay](image)

**Figure S5.** Photoluminescence of Er(PL₃)₃

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