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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1. 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 ¹H, 376 MHz for ¹⁹F and 162 MHz for ³¹P 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.



Figure S1. Structures of the ligands

Bis(4-azido-2,3,5,6-tetrafluorophenyl)phosphinic acid (BAPA, 2) NaN₃ (608 mg, 9.35 mmol) was added to a solution of tris(pentafluorophenyl)phosphine oxide (1) (1.627 g, 2.97 mmol) in acetone (30 mL) and H₂O (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 (Na₂SO₄), 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). v_{max}/cm⁻¹ >2500 (br, OH), 2243, 2131 (vs, N₃), 1637, 1469, 1391, 1227. δ_P (162 MHz, CDCl₃) 9.3 (s). δ_F (376 MHz, CDCl₃)

-135.8 (br s, F-*o*), -153.8 (br s F-*m*). $\delta_{\rm H}$ (400 MHz, CDCl₃) 11.03 (s, POOH). *m/z* (APCI) Calcd. for C₁₂F₈N₆O₂P ([M-H]⁻) 442.9698; found 442.9691.

- [*iPr₂EtNHJ⁺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). 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 and the phases were separated. The organic phase was dried (Na₂SO₄) and evaporated to give [*i*Pr₂EtNH]⁺PL_A⁻ (3) (67.2 mg, 91%) as a pale yellow gel. *v*_{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. $[iPr_2EtNH]^+PL_B^-$ (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). Hünig'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 (30mL) 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 $[iPr_2EtNH]^+PL_B^-$ (4) (318 mg, 82%) as a pale yellow solid. mp >170 °C (decomp). v_{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). $\delta_{\rm C}$ (101 MHz, CDCl₃) 12.0 (s, CH₂*C*H₃), 17.3 (s, CH(*C*H₃)₂), 18.5 (s, CH(*C*H₃)₂), 42.2 (s, *C*H₂CH₃), 53.8 (s, *C*H(CH₃)₂), 118.5 (m, C-*p*), 118.8-120.5 (m, Ar *C*P), 121.9 (s, Ar *C*H), 126.0 (s, Ar *C*H), 128.8 (s, Ar *C*H), 129.0 (s, Ar *C*), 129.4 (s, triazole *C*H), 141.2 (dm, ${}^{1}J_{\rm C-F}$ 260 Hz, Ar *C*F), 147.0 (dm, ${}^{1}J_{\rm C-F}$ 250 Hz, Ar *C*F), 148.1 (triazole *C*-Ph). *m/z* (APCI) Calcd. for C₂₈H₁₂F₈N₆O₂P (PL_B⁻) 647.0637; found 647.0635.

- 4. [*iPr₂EtNH*]⁺*PL_C⁻* (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 [*i*Pr₂EtNH]⁺PL_C⁻ (5) (57.8 mg, 60%) as a pale yellow solid, mp 101-105 °C. *v*_{max}/cm⁻¹ 2997 (br, C-H), 2677, 1645, 1514, 1499, 1470, 1257, 1233. *δ*_P (162 MHz, CDCl₃) -8.81 (s). *δ*_F (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). *δ*_H (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 C₂₈H₂F₁₈N₆O₂P (PL_C⁻) 826.9695; found 826.9707.
- 5. HPL_D (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). v_{max}/cm^{-1} 3143 (br, CH), 1645, 1472, 1459, 1324, 1270, 1241. δ_P (162 MHz, DMSO- d_6) -13.5 (s). δ_F (376 MHz, DMSO- d_6) -133.6 (m, F-o), -148.0 (m, F-m). δ_H (400 MHz, DMSO- d_6) 5.83 (s, 4H), 7.22 (t, 4H, J 7.4 Hz), 7.47 (t, 4H, J 7.8 Hz), 7.80 (d, 4H, J 8 Hz), 8.15 (d, 4H, J 8 Hz), 8.60 (s, 2H, triazole-H). δ_C (101 MHz, DMSO- d_6) 37.7 (s, CH₂), 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, ${}^{1}J_{C-F}$ 260 Hz, Ar CF), 144.3 (triazole C-CH₂), 146.4 (dm, ${}^{1}J_{C-F}$ 245 Hz, Ar CF). m/z(APCI) Calcd. for C₄₂H₂₂F₈N₈O₂P ([M-H]⁻) 853.1481; found 853.1469.

- 6. Complex Er(PL_A)₃ (7) [iPr₂EtNH]⁺PL_A⁻ (3) (50 mg, 0.068 mmol) was dissolved in hot methanol. A solution of ErCl₃·6H₂O (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). v_{max}/cm⁻¹ 2932 (br, C-H), 1647, 1524, 1470, 1268, 1206, 1120, 1085. Anal. Calcd. (Found) for C₇₂H₆₀ErF₂₄N₁₈O₆P₃: C, 43.47 (42.23); H, 3.04 (2.77); N, 12.67 (12.05).
- 7. Complex Er(PL_B)₃ (8) [iPr₂EtNH]⁺PL_B⁻ (4) (30 mg, 0.039 mmol) was dissolved in hot methanol. A solution of ErCl₃·6H₂O (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). v_{max}/cm⁻¹ 3142 (br, C-H), 1646, 1525, 1468, 1409, 1278, 1206, 1141, 1088. *m/z* (MALDI–) Calcd. for C₁₁₂H₄₈ErF₃₂N₂₄O₈P₄ ([Er(PL_B)₄]⁻) 2756.2; found 2756.2. Anal.

Calcd. (Found) for $C_{84}H_{36}ErF_{24}N_{18}O_6P_3$: C, 47.83 (44.64); H, 1.72 (1.89); N, 11.95 (10.93).

- 8. Complex Er(PL_C)₃ (9) [iPr₂EtNH]⁺PL_C⁻ (5) (50 mg, 0.052 mmol) was dissolved in hot methanol. A solution of ErCl₃·6H₂O (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_C)₃ (9) (30 mg, 70%) as a white solid, mp >115 °C (decomp). v_{max}/cm⁻¹ 3171 (br, C-H), 1646, 1516, 1499, 1470, 1304, 1265, 1229, 1211. *m/z* (MALDI–) Peaks for [Er(PL_C)₄]⁻ and (PL_C⁻) were not observed. Anal. Calcd. (Found) for C₈₄H₆ErF₅₄N₁₈O₆P₃: C, 38.08 (36.25); H, 0.23 (0.94); N, 9.51 (12.64).
- 9. *Complex* $Er(PL_D)_3$ (10) HPL_D (6) (38 mg, 0.044 mmol) was dissolved in boiling acetonitrile. A solution of ErCl₃·6H₂O (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 $Er(PL_D)_3$ (10) (33.7 mg, 83%) as a white solid, mp > 220 °C (decomp). v_{max}/cm^{-1} 3050 (br, C-H), 1645, 1599, 1523, 1469, 1324, 1269, 1209, 1119, 1087. *m/z* (NSI+) Calcd. for C₄₂H₂₄F₈N₈O₂P (H₂PL_D)⁺) 855.1627; found 855.1625. Peaks for $Er(PL_D)_3$ were not observed. Anal. Calcd. (Found) for C₁₂₆H₆₆ErF₂₄N₂₄O₆P₃: 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

Figure S2. Diffuse reflectance spectra of Er(PL_{A-D})₃ powders, RT

NIR emission of erbium complexes



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 $Er(PL_{A-D})_3$ and $Y(PL_{A-D})_3$

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:

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

 I_0 is the offset intensity, I_1 is the initial intensity, τ is the lifetime and β 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:



Figure S5. Photoluminescence of Er(PL_B)₃

Variable	Value	
I_0	9.5×10^{-6}	
t_0/s	1.55×10^{-7}	
I_1	9.2×10^{-2}	
τ/s	5.73×10^{-5}	
β	0.73	
$\langle \tau \rangle / \mu s$	69.8	