Redox behaviour, electrochromic properties and photoluminescence of potassium lanthano phosphomolybdate sandwich-type compounds

Supporting Information

Captions to Figures

Figure S1. Infrared spectra in the range: A) 4000-500 cm\(^{-1}\) and B) 1300-600 cm\(^{-1}\) for potassium salts: (a) Sm(PMo\(_{11}\))\(_2\), (b) Eu(PMo\(_{11}\))\(_2\), (c) Gd(PMo\(_{11}\))\(_2\), (d) Tb(PMo\(_{11}\))\(_2\) and (e) Dy(PMo\(_{11}\))\(_2\).

Figure S2. \(^{31}\)P NMR spectra in D\(_2\)O of: (A) Sm(PMo\(_{11}\))\(_2\), (B) Eu(PMo\(_{11}\))\(_2\), (C) Gd(PMo\(_{11}\))\(_2\), (D) Tb(PMo\(_{11}\))\(_2\) and (E) Dy(PMo\(_{11}\))\(_2\).

Figure S3. A) Cyclic voltammograms of K\(^+\) salt of Eu(PMo\(_{11}\))\(_2\) (5 × 10\(^{-4}\) mol dm\(^{-3}\)) in pH 3.0 H\(_2\)SO\(_4\)/Na\(_2\)SO\(_4\) buffer solution at scan rates of 0.02, 0.04, 0.06, 0.08, 0.1, 0.15, 0.2, 0.25, 0.3, 0.35, 0.4, 0.45 and 0.5 V s\(^{-1}\).

B) Cyclic voltammograms of K\(^+\) salt of Gd(PMo\(_{11}\))\(_2\) (5 × 10\(^{-4}\) mol dm\(^{-3}\)) in pH 3.0 H\(_2\)SO\(_4\)/Na\(_2\)SO\(_4\) buffer solution at scan rates of 0.02, 0.04, 0.06, 0.08, 0.1, 0.15, 0.2, 0.25, 0.3, 0.35, 0.4, 0.45 and 0.5 V s\(^{-1}\).

C) Cyclic voltammograms of K\(^+\) salt of Tb(PMo\(_{11}\))\(_2\) (5 × 10\(^{-4}\) mol dm\(^{-3}\)) in pH 3.0 H\(_2\)SO\(_4\)/Na\(_2\)SO\(_4\) buffer solution at scan rates of 0.02, 0.04, 0.06, 0.08, 0.1, 0.15, 0.2, 0.25, 0.3, 0.35, 0.4, 0.45 and 0.5 V s\(^{-1}\).

D) Cyclic voltammograms of K\(^+\) salt of Dy(PMo\(_{11}\))\(_2\) (5 × 10\(^{-4}\) mol dm\(^{-3}\)) in pH 3.0 H\(_2\)SO\(_4\)/Na\(_2\)SO\(_4\) buffer solution at scan rates of 0.02, 0.04, 0.06, 0.08, 0.1, 0.15, 0.2, 0.25, 0.3, 0.35, 0.4, 0.45 and 0.5 V s\(^{-1}\).

Figure S4. UV-visible spectra of Sm(PMo\(_{11}\))\(_2\) (A), Eu(PMo\(_{11}\))\(_2\) (C), Gd(PMo\(_{11}\))\(_2\) (E) and Dy(PMo\(_{11}\))\(_2\) salts (G) in pH 3.0 H\(_2\)SO\(_4\)/Na\(_2\)SO\(_4\) buffer solution before
(a) and after reduction at 0.1 V for 30 min to 6.0 h (b to i); Absorbance evolution versus reduction time (B, D, F and H).

**Figure S5.** Emission decay curves acquired at (A) 10 K and (B) 300 K of EuPOM monitored at 614 nm and excited at 465 nm. The solid lines correspond to the data best fit using a single exponential function. The insets show the respective regular residual plots and the $\chi^2_{\text{red}}$ values for a better judgment of the fit quality.
Figure S1.

(A)

(B)
Figure S2.
Figure S3.

(A)

(B)

(C)

Electrochemical data for different potential ranges and electrolytes. The diagrams illustrate the changes in current (i) with potential (E) vs. Ag/AgCl (3 mol dm$^{-3}$ KCl) for different conditions.
Figure S4.
Figure S5.