Electronic Supplementary Material (ESI) for Dalton Transactions.

Electronic Supplementary Information

Lanthano phosphomolybdate-decorated silica nanoparticles: novel hybrid materials with photochromic properties

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Table S1. Core-level binding energy (BE) and area of each component for C18-SiO_2, C18-SiO_2@PMo_{11}, C18-SiO_2@$Sm(PMo_{11})_2$ and C18-SiO_2@$Eu(PMo_{11})_2$ obtained by curve fitting of XPS spectra

Material	C 1s		N 1s[c]		O 1s		Si $2p_{3/2}$		P $2p_{3/2}$		Mo $3d_{5/2}$		Ln^{III} 3d/4d	
	BE[a] (eV)	Area[b] (%)	BE[a] (eV)	Area[b] (%)	BE[a] (eV)	Area[b] (%)	BE[a] (eV)	Area[b] (%)	BE[a] (eV)	Area[b] (%)	BE[a] (eV)	Area[b] (%)	BE[a] (eV)	Area[b] (%)
C18-SiO_2	284.6 (1.3)	66.0	399.3 (1.5)	6.5	532.2 (1.5)	95.3	102.7 (1.6)	41.2						
	285.7 (1.3)	23.9	402.1 (1.5)	93.5	533.8 (1.5)	4.7	104.0 (1.6)	25.4						
	286.8 (1.3)	8.0												
	288.5 (1.3)	2.1												
C18-SiO_2 @PMo_{11}	284.6 (1.4)	58.3	402.3 (1.8)	100.0	530.0 (1.6)	8.3	102.7 (1.7)	61.0	n.d.[d]		232.0 (2.6)	60.0		
	285.8 (1.4)	24.9			532.2 (1.6)	71.5	104.9 (1.7)	5.7						
	286.9 (1.4)	11.3			533.4 (1.6)	16.3								
	288.7 (1.4)	5.5			534.7 (1.6)	3.9								
C18-SiO_2 @$Sm(PMo_{11})_2$	284.6 (1.2)	71.9	402.0 (1.5)	100.0	529.9 (1.7)	41.9	102.0 (1.8)	64.2	132.5 (2.0)	66.7	230.8 (1.4)	10.4	1082.7 (4.4)	60.0
	285.8 (1.2)	17.4			531.8 (1.7)	43.1	104.6 (1.8)	2.5			231.9 (1.4)	49.6	1109.7 (4.4)	40.0
	286.7 (1.2)	6.3			534.0 (1.7)	8.6								
	287.8 (1.2)	4.4			535.5 (1.7)	6.4								
C18-SiO_2 @$Eu(PMo_{11})_2$	284.6 (1.4)	57.9	402.2 (1.6)	100.0	530.2 (1.7)	39.7	102.5 (1.9)	55.8	133.1 (0.5)	66.7	232.3 (1.5)	49.6	136.9[e] (3.4)	60.0
	286.0 (1.4)	27.3			532.1 (1.7)	46.4	104.8 (1.9)	10.8			234.2 (1.5)	10.4	142.5[e] (3.4)	40.0
	287.1 (1.4)	12.2			533.5 (1.7)	10.8							1134.2 (5.2)	
	288.7 (1.4)	2.6			534.9 (1.7)	3.1							1163.5 (5.2)	

[a] The values between brackets refer to the full width at half-maximum (FWHM) of the bands. [b] Relative area of each component in the different core-level regions. [c] N 1s surface atomic percentage estimated through modulation, which includes the N 1s band and two sets of Mo 3p bands. [d] n.d. – not detected. [e] Surface atomic percentage estimated by curve fitting of the Eu 4d high-resolution spectrum.

Table S2. Core-level binding energy (BE) and area of each component for C18-SiO_2@Gd(PMo_{11})$_2$, C18-SiO_2@Tb(PMo_{11})$_2$ and C18-SiO_2@Dy(PMo_{11})$_2$ obtained by curve fitting of XPS spectra

Material	C 1s		N 1s[c]		O 1s		Si $2p_{3/2}$		P $2p_{3/2}$		Mo $3d_{5/2}$		Ln^{III} 3d/4d	
	BE[a] (eV)	Area[b] (%)	BE[a] (eV)	Area[b] (%)	BE[a] (eV)	Area[b] (%)	BE[a] (eV)	Area[b] (%)	BE[a] (eV)	Area[b] (%)	BE[a] (eV)	Area[b] (%)	BE[a] (eV)	Area[b] (%)
C18-SiO_2 @Gd(PMo_{11})$_2$	284.6 (1.3)	73.4	402.0 (1.5)	100.0	530.0 (1.6)	24.2	102.4 (1.7)	64.7	132.7 (1.8)	66.7	230.8 (1.4)	17.1	1188.3[d] (5.0)	100.0
	285.9 (1.3)	18.0			532.0 (1.6)	65.0	105.8 (1.7)	2.0			232.1 (1.4)	42.9		
	286.8 (1.3)	5.4			533.7 (1.6)	8.1								
	288.4 (1.3)	3.2			535.7 (1.6)	2.7								
C18-SiO_2 @Tb(PMo_{11})$_2$	284.6 (1.3)	67.8	402.0 (1.3)	100.0	530.1 (1.6)	37.3	102.4 (1.8)	64.7	132.9 (2.2)	66.7	231.1 (1.3)	15.3	149.1[e] (5.4)	3.6
	285.9 (1.3)	19.4			532.1 (1.6)	49.4	104.6 (1.8)	1.9			232.4 (1.3)	44.7	1243.2[f] (11.8)	n.d.[g]
	286.9 (1.3)	8.1			534.2 (1.6)	8.6							1277.2[f] (11.8)	n.d.[g]
	288.2 (1.3)	4.7			536.1 (1.6)	4.7								
C18-SiO_2 @Dy(PMo_{11})$_2$	284.6 (1.3)	69.5	402.0 (1.4)	100.0	529.9 (1.6)	23.6	102.4 (1.7)	65.5	132.9 (2.4)	66.7	230.8 (1.5)	17.0	1303.8 [h] (1.7)	n.d.[i]
	285.9 (1.3)	19.1			532.0 (1.6)	63.0	105.4 (1.7)	1.2			232.0 (1.5)	43.0		
	287.3 (1.3)	6.7			534.0 (1.6)	7.3								
	288.5 (1.3)	4.7			535.7 (1.6)	6.1								

[a] The values between brackets refer to the FWHM of the bands. [b] Relative area of each component in the different core-level regions. [c] N 1s surface atomic percentage estimated through modulation, which includes the N 1s band and two sets of Mo 3p bands. [d] BE of the Gd $3d_{5/2}$ component; the second component (Gd $3d_{3/2}$) is overlapped with the carbon KLL Auger lines at ~1223 eV. [e] BE of the Tb 4d band used to estimate the Tb surface atomic percentage, since the RSF of Tb 3d is not reported in the literature or XPS libraries. [f] BEs of the Tb 3d components. [g] n.d. – not determined. [h] BE of the Dy $3d_{5/2}$ component. [i] Dy 3d surface atomic percentage not calculated due to the lack of the RSF of Dy 3d.

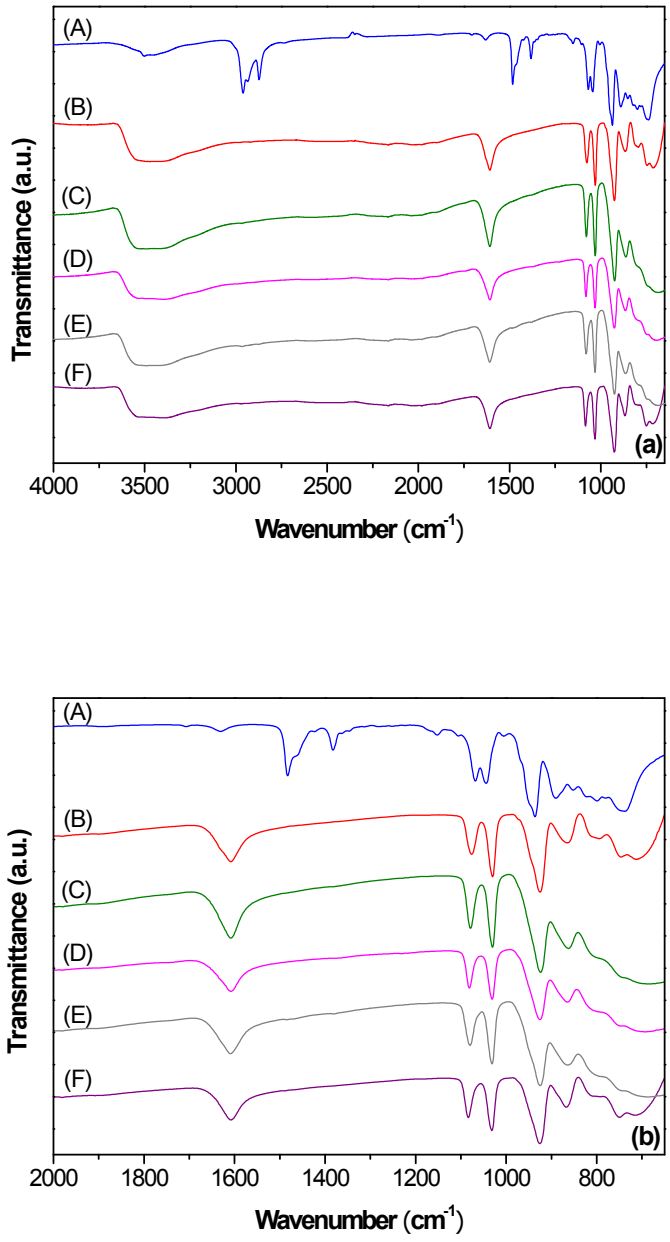

Figure S1. FTIR-ATR spectra of (A) $PMo_{11,}$ (B) $Sm(PMo_{11})_{2,}$ (C) $Eu(PMo_{11})_{2,}$ (D) $Gd(PMo_{11})_{2,}$ (E) $Tb(PMo_{11})_2$ and (F) $Dy(PMo_{11})_2$ in the (a) 4000–650 cm^{-1} and (b) magnified 2000–650 cm^{-1} ranges.

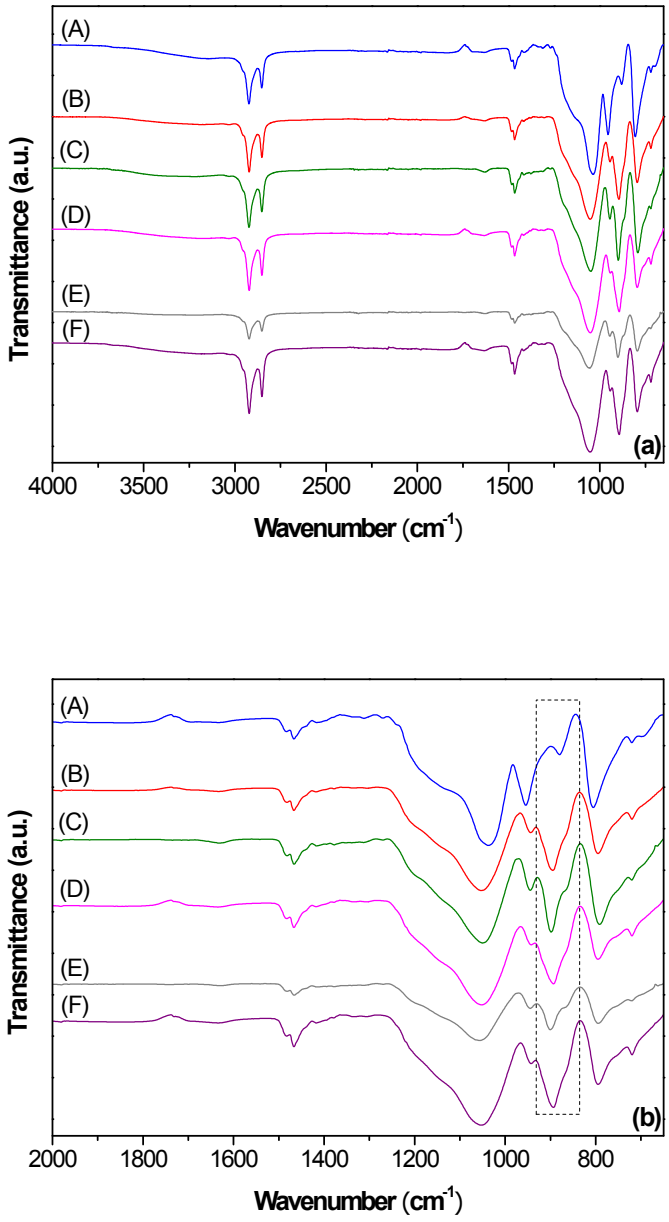

Figure S2. FTIR-ATR spectra of (A) C18-SiO_2@PMo_{11}, (B) C18-SiO_2@$Sm(PMo_{11})_2$, (C) C18-SiO_2@$Eu(PMo_{11})_2$, (D) C18-SiO_2@$Gd(PMo_{11})_2$, (E) C18-SiO_2@$Tb(PMo_{11})_2$ and (F) C18-SiO_2@$Dy(PMo_{11})_2$ in the (a) 4000–650 cm^{-1} and (b) magnified 2000–650 cm^{-1} ranges. Dashed rectangle: characteristic vibrational bands of the lanthano phosphomolybdates.

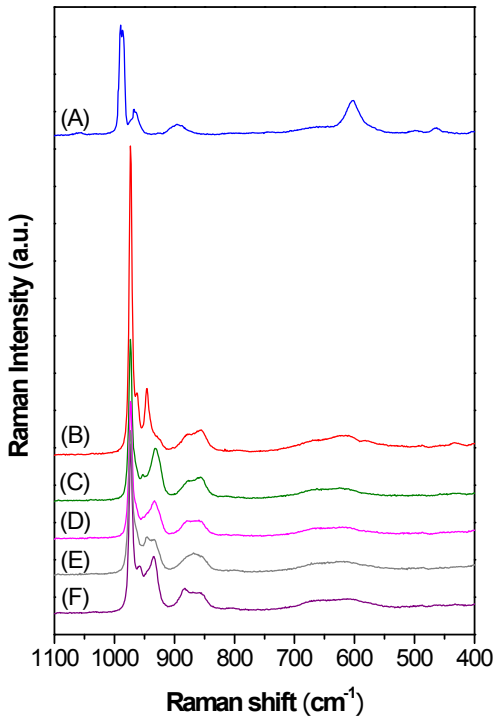

Figure S3. Raman spectra of (A) PMo_{11}, (B) $Sm(PMo_{11})_2$, (C) $Eu(PMo_{11})_2$, (D) $Gd(PMo_{11})_2$, (E) $Tb(PMo_{11})_2$ and (F) $Dy(PMo_{11})_2$ in the 1100–400 cm^{-1} range.

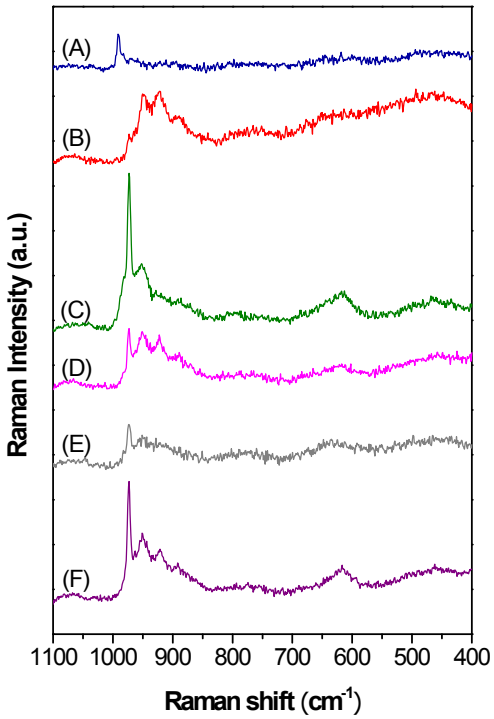

Figure S4. Raman spectra of A) C18-SiO_2@PMo_{11}, (B) C18-SiO_2@$Sm(PMo_{11})_2$, (C) C18-SiO_2@$Eu(PMo_{11})_2$, (D) C18-SiO_2@$Gd(PMo_{11})_2$, (E) C18-SiO_2@$Tb(PMo_{11})_2$ and (F) C18-SiO_2@$Dy(PMo_{11})_2$ in the 1100–400 cm^{-1} range.

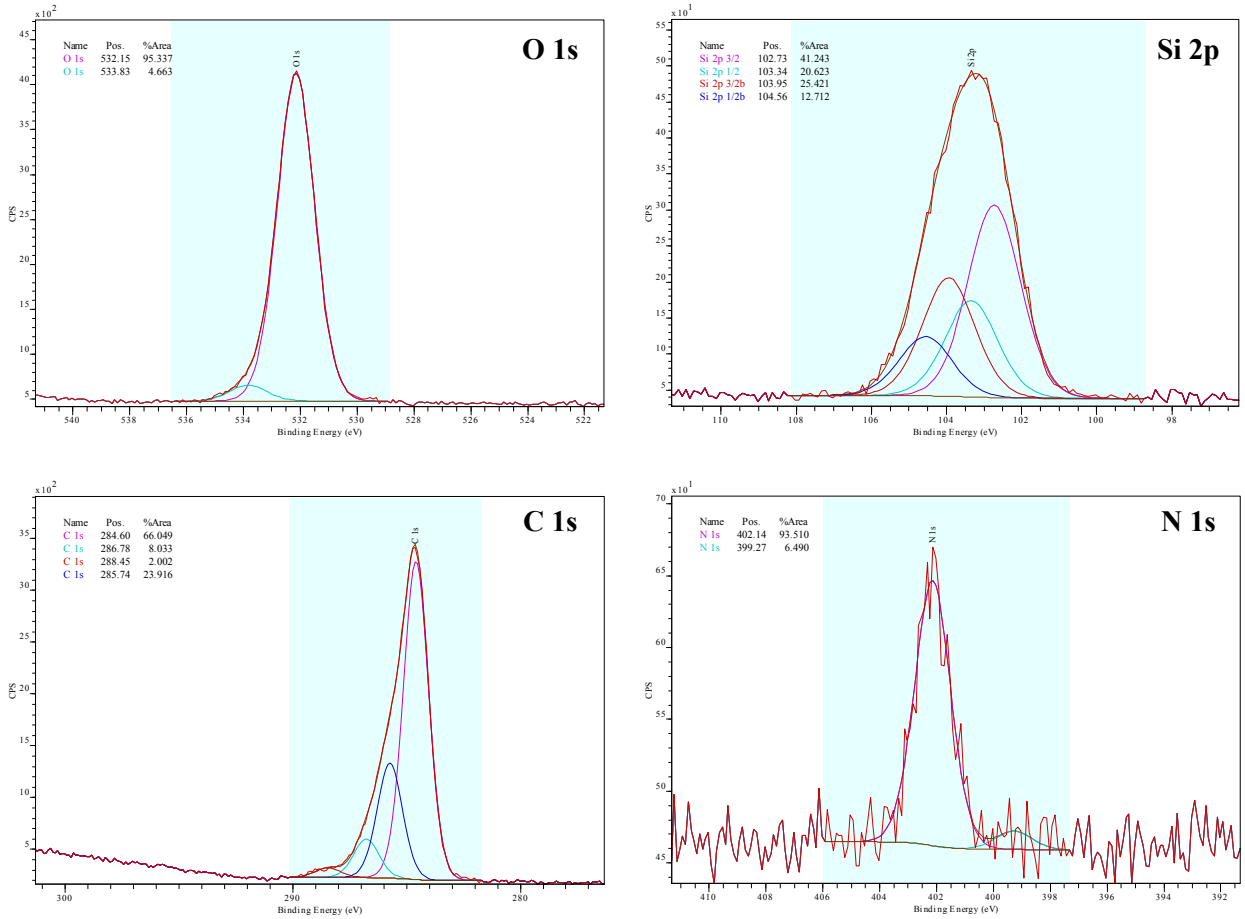

Figure S5. Deconvoluted XPS high-resolution spectra of C18-SiO_2 in the O 1s, Si 2p, C1s and N 1s core-level regions. The overall simulated spectra are represented by brown lines.

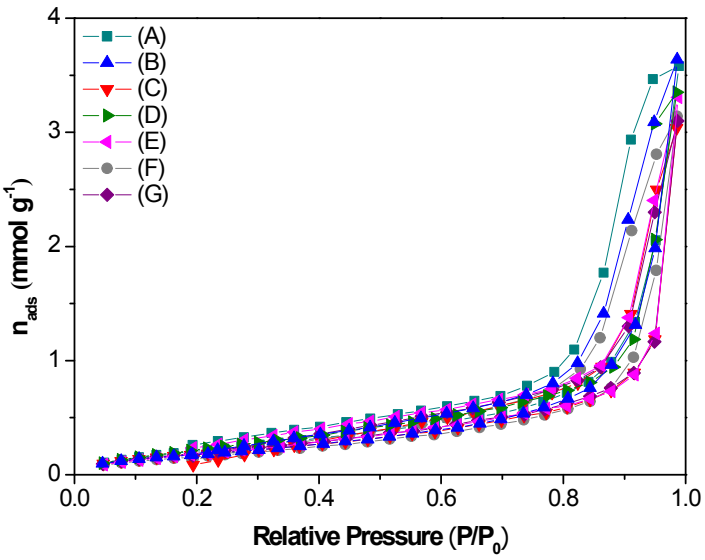

Figure S6. N_2 adsorption-desorption isotherms at –196 ºC of (A) C18-SiO_2, (B) C18-SiO_2@PMo_{11}, (C) C18-SiO_2@$Sm(PMo_{11})_2$, (D) C18-SiO_2@$Eu(PMo_{11})_2$, (E) C18-SiO_2@$Gd(PMo_{11})_2$, (F) C18-SiO_2@$Tb(PMo_{11})_2$ and (G) C18-SiO_2@$Dy(PMo_{11})_2$.