

Water-soluble luminescent hybrid aminoclay grafted with lanthanide complexes synthesized by a Michael-like addition reaction and its gas sensing application in PVP nanofiber

Qing-Feng Li,^a Lin Jin,^a LiLi Li,^a Wenpei Ma,^a Zhenling Wang,^{*a} Jianhua Hao^{*b}

^a The Key Laboratory of Rare Earth Functional Materials and Applications, Zhoukou Normal University, Zhoukou 466001, P. R. China.

^b Department of Applied Physics, The Hong Kong Polytechnic University, Hong Kong, P. R. China.

*Corresponding author. *E-mail*: zlwang2007@hotmail.com or jh.hao@polyu.edu.hk

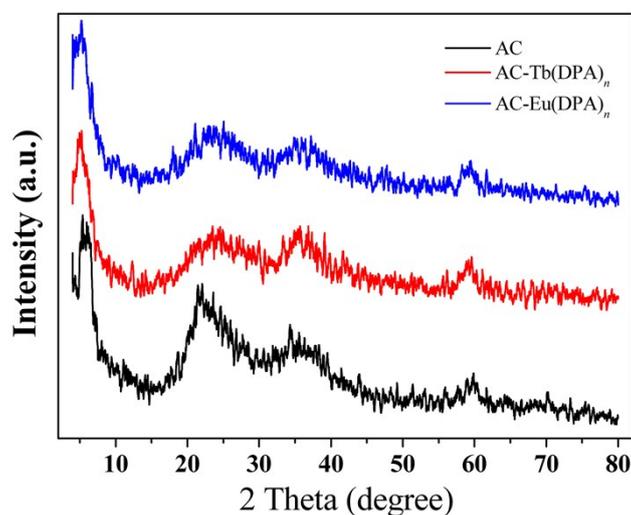


Fig. S1 XRD pattern of AC, AC-Tb(DPA)_n and AC-Eu(DPA)_n.

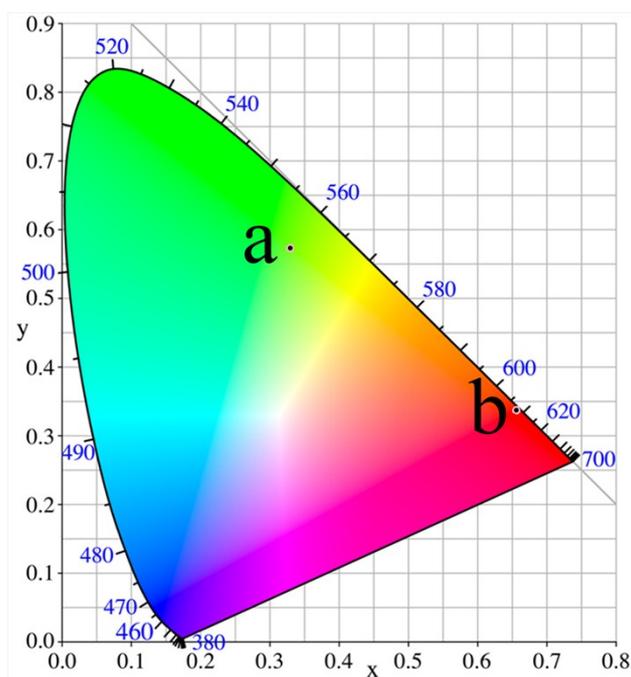


Fig. S2 Chromaticity diagram (CIE) of the AC-Tb(DPA)_n (a) and AC-Eu(DPA)_n (b) under 280 nm UV illumination.

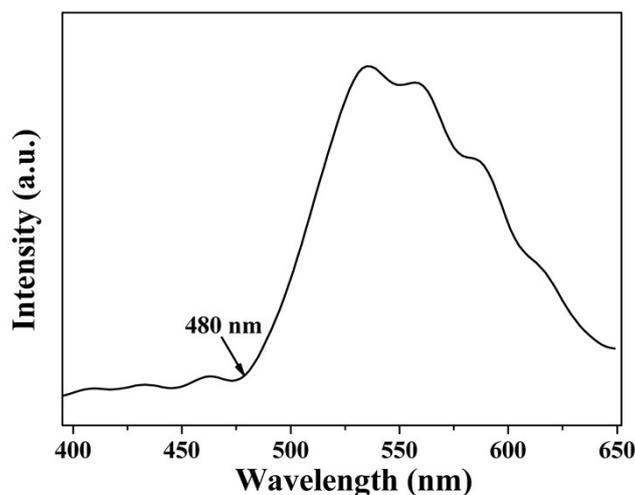


Fig. S3 Phosphorescence spectrum of Na₃[Gd(1)₃] at 77K.

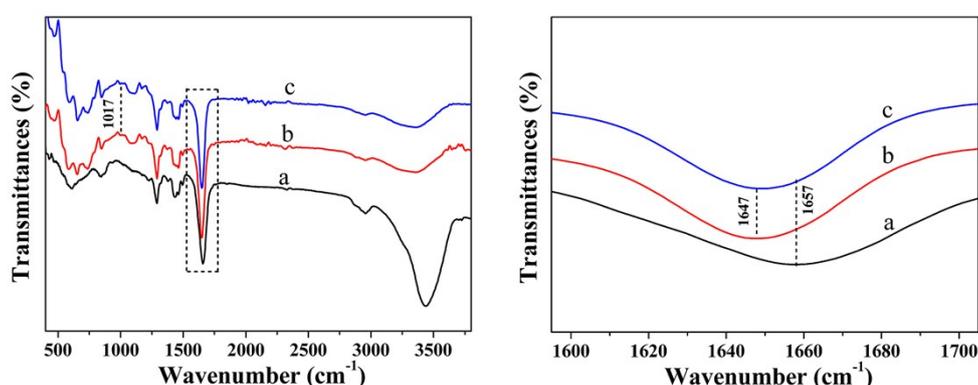


Fig. S4 FT-IR spectra of PVP (a), PVP-AC-Tb(DPA)_n (b) and PVP-AC-Eu(DPA)_n (c). The peak at 1657 cm⁻¹ was attributed to the stretching vibration of amide carbonyl group of PVP based on there reasons, 1: the amino group in PVP-Ln(DPA)_n is protonated (The pH was adjusted in the synthesis), and the vibration absorption peak of protonated amino group usually move toward lower wave-number compared with that of corresponding amino group; 2: AC-Ln(DPA)_n is distributed in PVP at a low relatively level (about 16 % wt); 3: amide carbonyl group always exhibits a strong absorption band at 1690-1630 cm⁻¹. Moreover, a weak infrared absorption peak of Si-O at 1017 cm⁻¹ was also found in Fig. S4b and c. The low content of AC-Ln(DPA)_n in PVP (about 16% wt) result in a weak absorption intensity of AC-Ln(DPA)_n.

Table S1 The PL data including excitation wavelength (λ_{ex}), emission wavelength (λ_{em}), lifetimes (τ), CIE coordinates and quantum efficiency (η) of AC-Ln(DPA)_n and PVP-AC-Ln(DPA)_n.

Sample	λ_{ex} (nm)	λ_{em} (nm)	τ (ms)	CIE	η (%)
AC-Tb(DPA) _n	280	491, 542, 582, 621	1.64	$x = 0.33, y = 0.57$	8.3
AC-Eu(DPA) _n	280	594, 615, 649, 695	1.50	$x = 0.66, y = 0.34$	10.5
PVP-AC-Tb(DPA) _n	280	491, 542, 582, 621	1.46	$x = 0.33, y = 0.57$	23.2

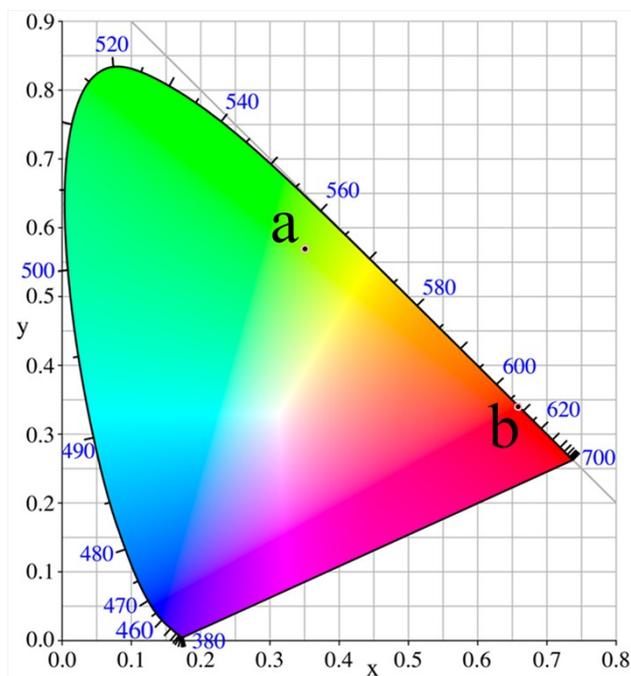


Fig. S5 The CIE chromaticity coordinates of PVP-AC-Tb(DPA)_n (a) and PVP-AC-Eu(DPA)_n (b).

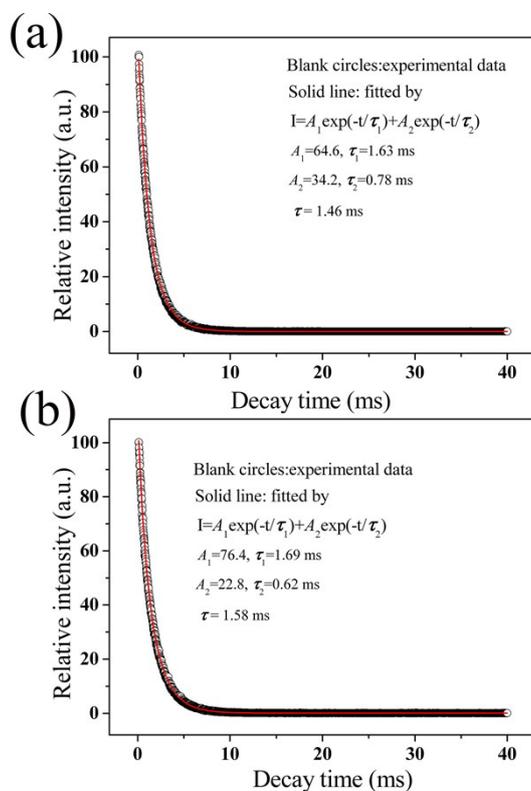


Fig. S6 Luminescence decay curves of PVP-AC-Tb(DPA)_n (a) and PVP-AC-Eu(DPA)_n (b).

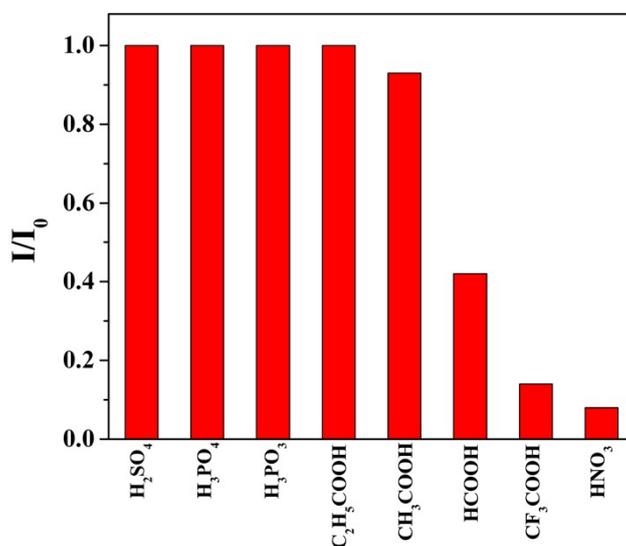


Fig. S7 Luminescence intensity changes after exposure of PVP-AC-Tb(DPA)_n to different acid vapors. There is no direct contact between the sample and liquid acid (1 mL in 250 mL sealed container) in this experiment, and the effects of spontaneous formation of acid vapor on the luminescence intensity were only investigated.

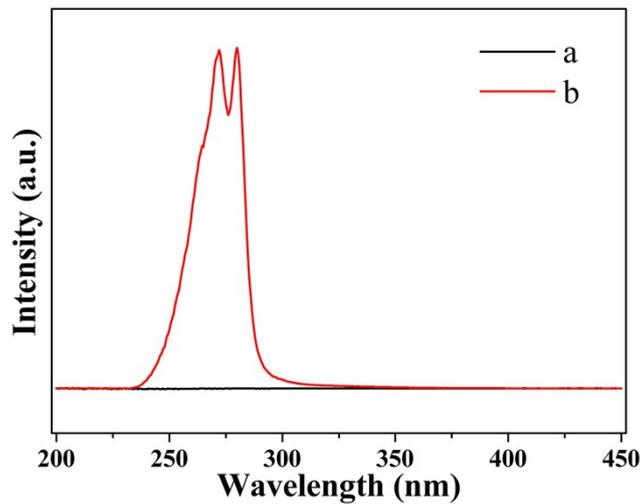


Fig. S8 PL excitation spectra of PVP-AC-Eu(DPA)_n after exposure to HCl vapor (a) and then Et₃N vapors (b).

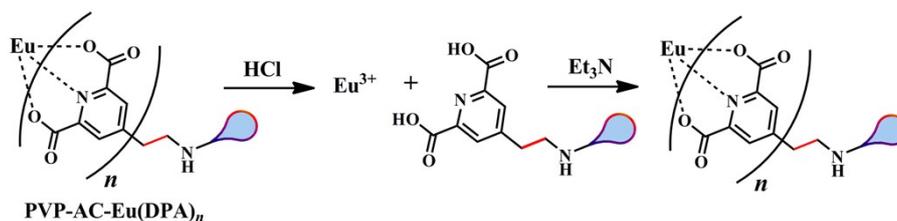


Fig. S9 Luminescence switching mechanism of PVP-AC-Eu(DPA)_n.

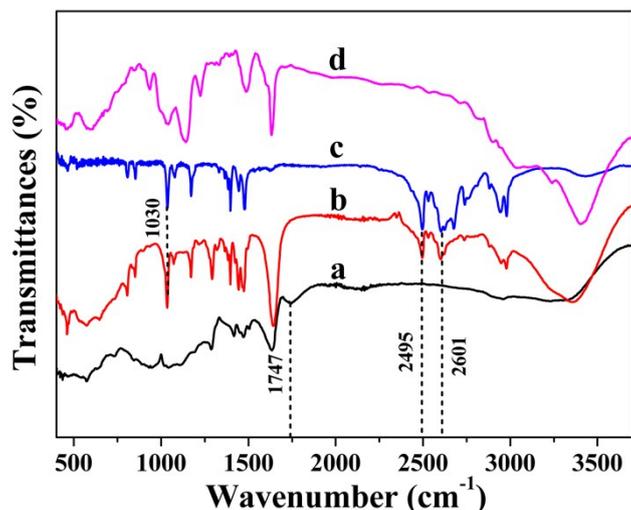


Fig. S10 FT-IR spectra of PVP-AC-Eu(DPA)_n after exposure to HCl vapor (a) and then Et₃N vapors (b), Et₃N hydrochloride (c) and HCl vapor treated AC (d). The FT-IR spectrum of pure Et₃N hydrochloride also show two significant absorption peaks at 2495 and 2601 cm⁻¹, which can be attributed to N-H stretching vibration of tertiary amine hydrochloride (Et₃N·HCl). However, no obvious absorption peaks were observed in the FT-IR spectrum of HCl vapor treated AC at 2495 and 2601 cm⁻¹, and a weak absorption peak, which can be ascribed to N-H stretching vibration of primary amine hydrochloride appeared at 2537 cm⁻¹. These results show that two new bands at 2495, 2601 cm⁻¹ in Fig. S10b can be ascribed to the N-H stretching vibration of Et₃N hydrochloride. However, after PVP-AC-Eu(DPA)_n exposure to HCl vapor and followed by Et₃N vapor, a new absorption peak appeared near 1017 cm⁻¹ (at 1030 cm⁻¹) in Fig. S10b, which can be attributed to the absorption of Et₃N hydrochloride as compared with the FT-IR spectra of pure Et₃N hydrochloride (Fig. S10c), and this position coincides with the that of Si-O peak.

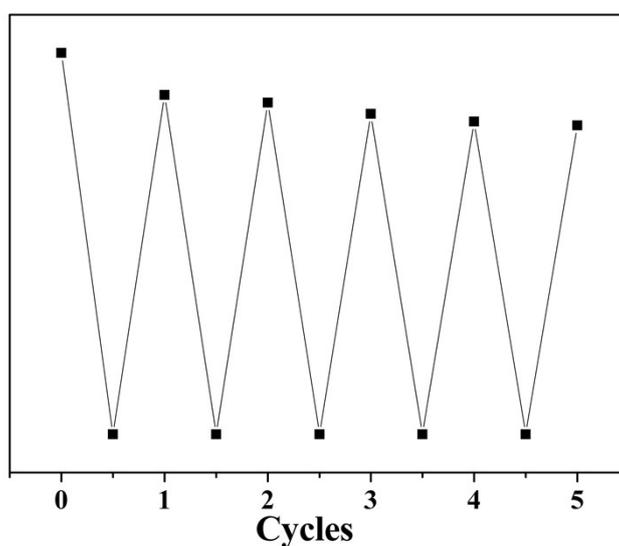


Fig. 11 Response of emission intensity of PVP-AC-Eu(DPA)_n at 615 nm during HCl-Et₃N cycles.