SUPPORTING INFORMATION FOR:

Molecular sensing and discrimination by a luminescent terbium-phosphine oxide coordination material

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Experimental Section

Materials and Measurements. 1,4-Dibromobenzene and PCl_3 (Aldrich), $Tb(NO_3)_3{\bullet}6H_2O$ (Alfa Aesar) HCl and H_2O_2 (Fisher Scientific) were used as received. Tetrahydrofuran, *N,N*-dimethylformamide, diethyl ether, chloroform and dichloromethane (Fisher Scientific) were purified prior to use by degassing followed by column distillation on an Innovative Technologies Inc. PureSolv system, and stored on molecular sieves under dry N_2 prior to use. PCM-15 was synthesised by heating mixtures in 20 capped scintillation vials using graphite thermal baths, with the vials submerged below the internal solvent level. Infrared spectra were collected on crystalline analyte using a Nicolet Avatar 330 FT-IR spectrometer fitted with attenuated total reflectance apparatus. Thermogravimetric analysis (TGA) was performed under He atmosphere at a scan rate of 2 °C min^{-1} in the range 25−800 °C using a TA instruments Q50 analyzer. NMR analyses ^1H and ^{31}P were recorded in-house using a 300 MHz Oxford Instruments Cryomagnetic Systems spectrometer. Elemental analyses were performed by Intertek QTI, Whitehouse, NJ.

Photoluminescence Measurements. All spectroscopic data was obtained in the solid-state unless otherwise noted. Luminescent measurements were recorded on a Photon Technology International QM 4 spectrophotometer equipped with a 6-inch diameter K Sphere-B integrating sphere. For quantum yield measurements, the integrating sphere was used. Quantum yield was calculated by dividing the area under the emission peaks of the complex by the difference between the area under the excitation peak of the sample from that of a blank solution ($A_{em(sample)}/(A_{ex(blank)} - A_{ex(sample)})$, where A = area under peak).[c]

PXRD Patterns. The phase purity of the PCM-15 samples was confirmed by analysis of powdered crystalline samples that were sealed inside borosilcate capillary tubes and spun *in situ* to prevent preferential orientation of the crystallites. Spectra were recorded on a Stoe Stadi-P diffractometer, operating in Debye–Scherrer geometry using CoKα radiation (1.790 Å). Reflection data was collected in the range 5.0–40.0° 2θ using multiple scans, which were subsequently averaged. The XRPD spectra were then compared directly to their corresponding simulated patterns that were generated in PLATON[d] using hkl reflection data obtained from the single crystal experiment.

Synthesis of trilithium salt of *tris*(*p*-carboxylato)triphenylphosphine ({$P(C_6H_4$-*p*-$CO_2Li)_3$}; tctpLi$_3$). This ligand was prepared using the reported method,[a] which is a modified version of the original procedure reported by Amengual *et al.*[b] that directly provides the trilithium salt. The salt was dried under vacuum to afford a pale yellow solid that was stored under N2 (yield 68% based on the tris(*p*-bromo)triphenylphosphine intermediate). ^{1}H NMR (D_2O; 300 MHz): δ = 7.38 (t, 6H); 7.70 ppm (dd, 6H); ^{31}P NMR (D_2O; 162 MHz): δ = -6.66 ppm.

Synthesis of *tris*(*p*-carboxylic)triphenylphosphine oxide ({$P(=O)(C_6H_4\text{-}_p\text{-}CO_2H)_3$}; tctpo$H_3$). TctpLi$_3$ (100 mg, 2.4 mmol) was dissolved into H_2O (10 mL) in a round-bottomed glass reactor tube fitted with magnetic stirred bar and heavy-duty Teflon-sealed screw cap. H_2O_2 (5 mL, 30%) was added and the mixture was vigorously stirred for 24 h. The resulting mixture was then cooled in an ice bath and acidified with ice cold HCl solution (1.0 M) to yield a white precipitate of potbcH_3 that was isolated by vacuum filtration, washed with ether and dried under vacuum (yield: 614 mg, 63%). ν_{max} (solid/cm^{-1}): 2929 w, 1699 m br, 1652 m, 1565 w, 1395 m, 1262 m br, 1161 m, 1103 s, 1017 m, 962 s, 933 s, 894 br s, 704 m; ^{1}H NMR (dmso; 300 MHz): δ = 7.92 (d, 6H), 8.15 (d, 6H) ppm; ^{31}P NMR (dmso; 300 MHz): δ = 26 ppm.

Synthesis of PCM-15 ([Tb(tctpo)(OH_2)].2dmf•H_2O). TctpoH_3 (20 mg, 48 μmol) and terbium nitrate (80 mg, 184 μmol) were mixed in dmf (3.0 mL), thf (4.0 mL), H_2O (1.0 mL) and HCl (36.5%, 1 drop). The resultant slurry was stirred until complete dissolution occurred. The solution was then heated in a scintillation vial at 85 ºC for 4 days (yield 23 mg, 64%). After treatment of as-synthesized PCM-15 in vacuum at 150 °C to remove solvent, found: C, 42.5; H, 2.28; N, 0.17%. $C_{21}H_{12}O_7PTb$ requires: C, 44.5; H, 2.14; N, 0%. ν_{max} (solid/cm^{-1}): 3585 m, 3692 w, 2764 m, 2899 s, 2462 m, 2313 m, 1719 br m, 1465 w, 1387 s, 1256 m, 1166 s, 1059 s, 867 w, 756 m, 713 s.

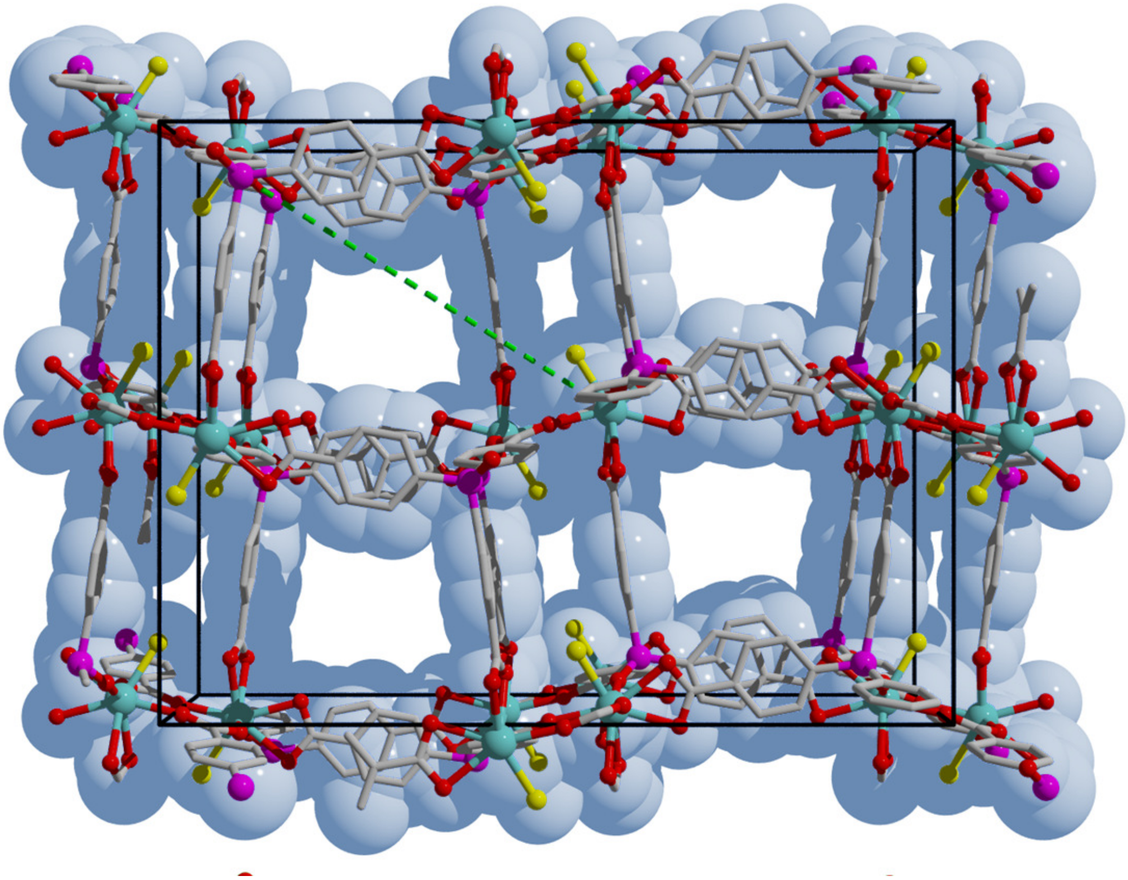

Figure S1: Overlay of structural and space-filling views of PCM-15 along the *b*-axis; green dashed line shows largest corner-to-corner accessible distance (14.2 Å); Tb = cyan; P = magenta; OH_2 = yellow.

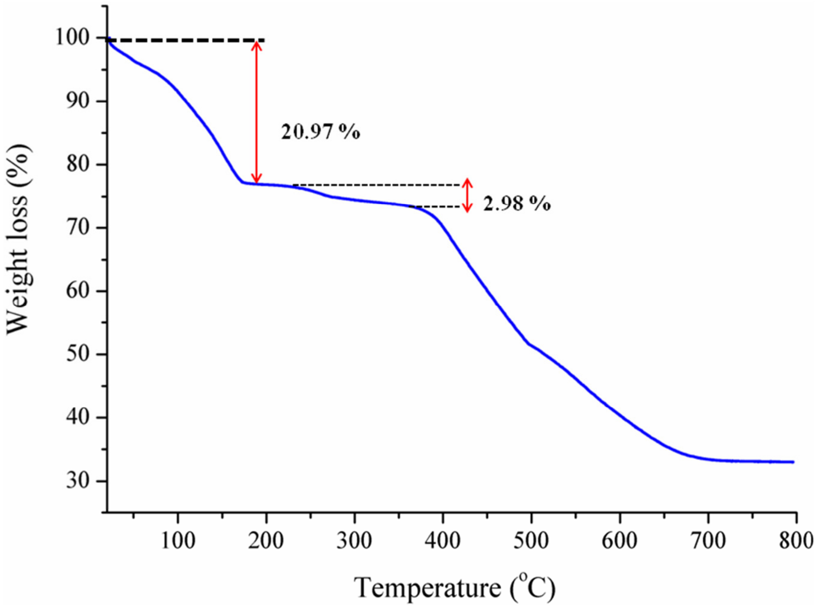

Figure S2: TGA analysis of as synthesised PCM-15 under He carrier flow.

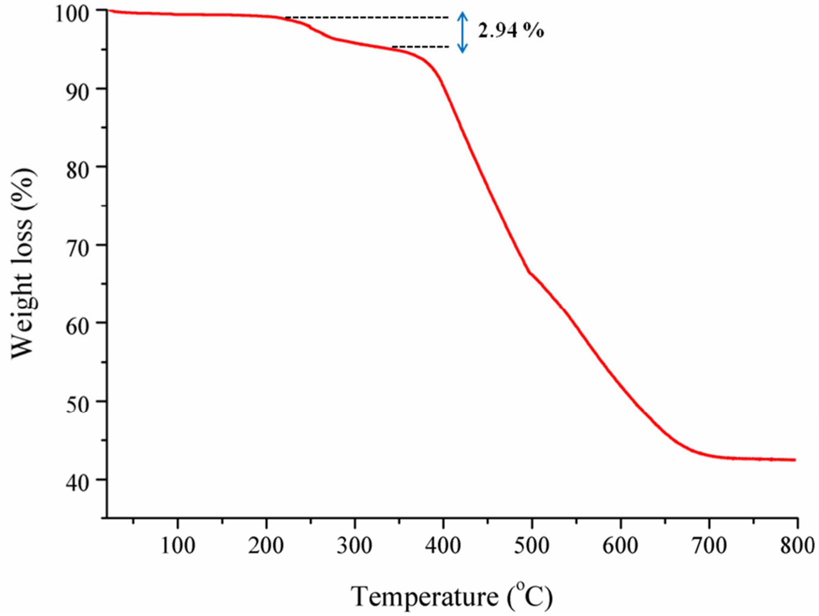

Figure S3: TGA analysis of preactivated (190 °C and 1 x10^{-10} bar for 6 h) PCM-15 under He carrier flow

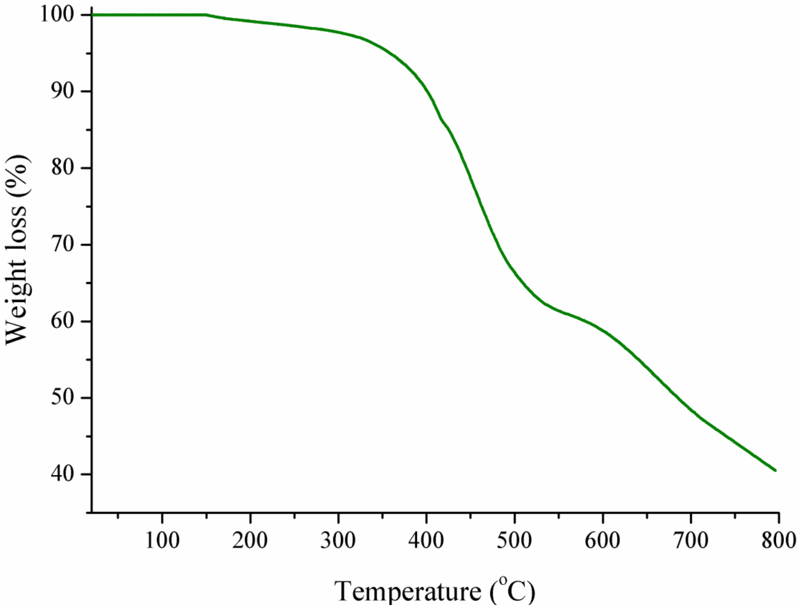

Figure S4: TGA analysis of preactivated (300 ^{o}C and 1 x10^{-10} bar for 6 h) PCM-15 under He carrier flow.

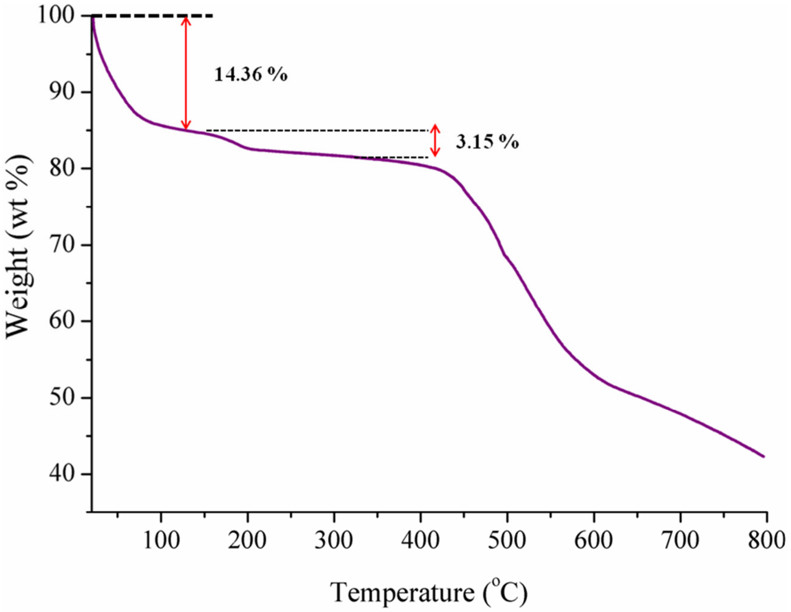

Figure S5: TGA analysis of preactivated PCM-15 exposed to EtOH vapour under He carrier flow.

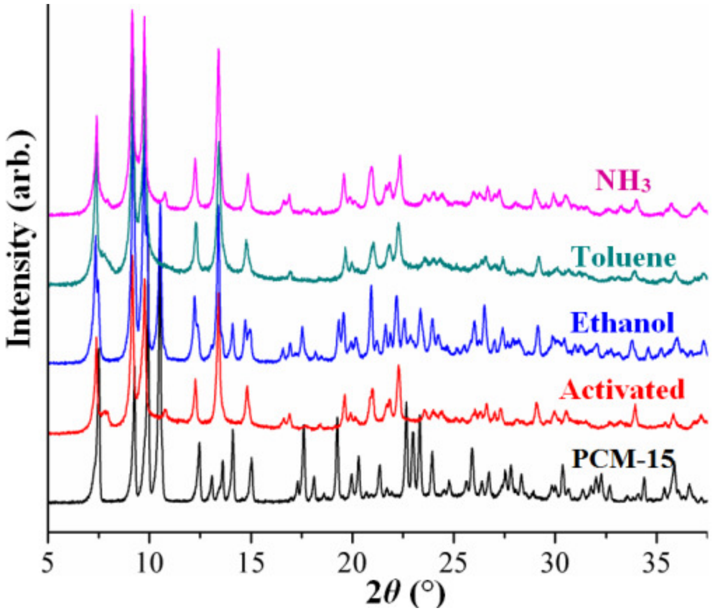

Figure S6. PXRD patterns of as-synthesized PCM-15 (black), the activated form (red), and after exposure to three molecular guest adsorbates.

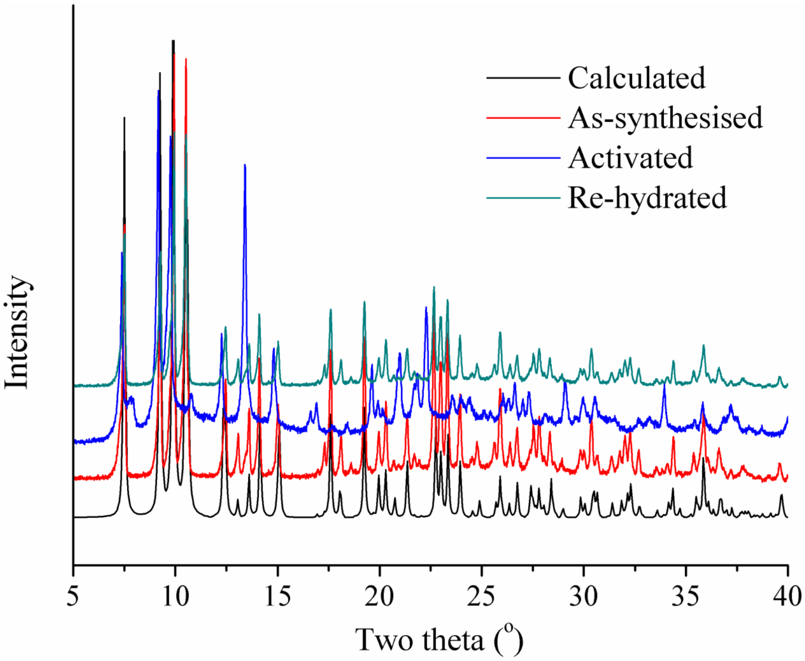

Figure S7. PXRD data showing retention of crystallininty upon desolvation and subsequent rehydration of the activated PCM-15 solid.

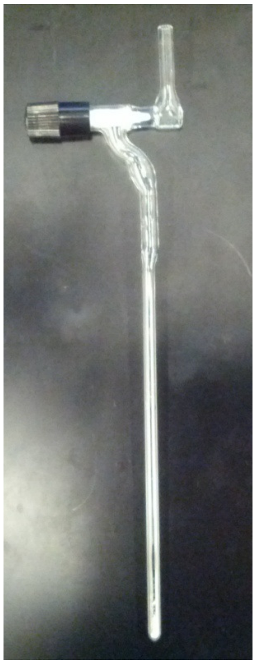

Figure S8A: Picture of a custom-made quartz cell fitted with a gas-tight Teflon valve.

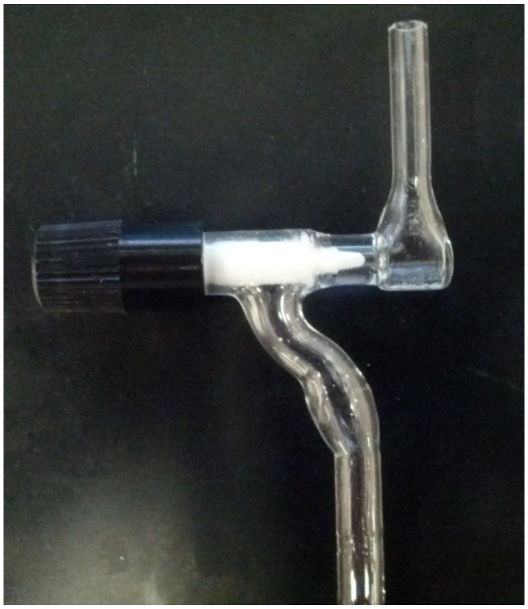

Figure S8B: The gas-tight Teflon valve.

Table S1. Absolute values for relative luminescence intensities and corresponding calculated lifetimes as observed for guest-loaded PCM-15.

	Integrated Relative Intensity	*± error*	*Calculated Luminescence Lifetime (ms^{-1})**
As-synthesized	**0.60**	**0.01**	**0.580**
Desolvated	***1.00***	--	***0.967***
CH_4	1.00	0.10	0.967
H_2	0.98	0.09	0.987
Toluene	0.97	0.04	0.997
Cyclohexane	0.90	0.20	1.075
n-hexane-*D14*	0.91	0.05	1.063
CO	0.90	0.10	1.075
D_2O	0.88	0.02	1.099
CO_2	0.88	0.03	1.099
Benzene	0.85	0.04	1.138
Methanol	0.68	0.08	1.422
Ethanol	0.70	0.20	1.382
O_2	0.66	0.06	1.465
H_2O	0.56	0.08	1.727
DMSO	0.55	0.02	1.758
n-hexane	0.53	0.09	1.825
NH_3	0.40	0.10	2.418

* Lifetimes were calculated using, $\tau = \Phi \cdot \tau_0$, where Φ is the measured luminescence quantum yield and τ_0 is the natural emissive lifetime of the Tb(III) ion (4.7 ms).[e]

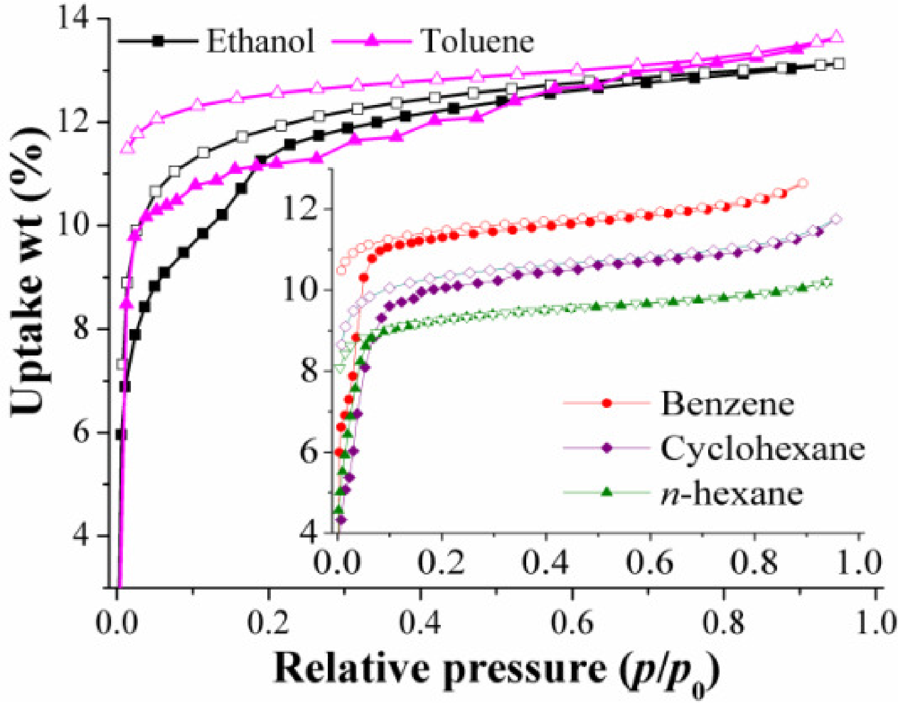

Figure S8. Adsorption-desorption isotherms for organic vapours in PCM-15.

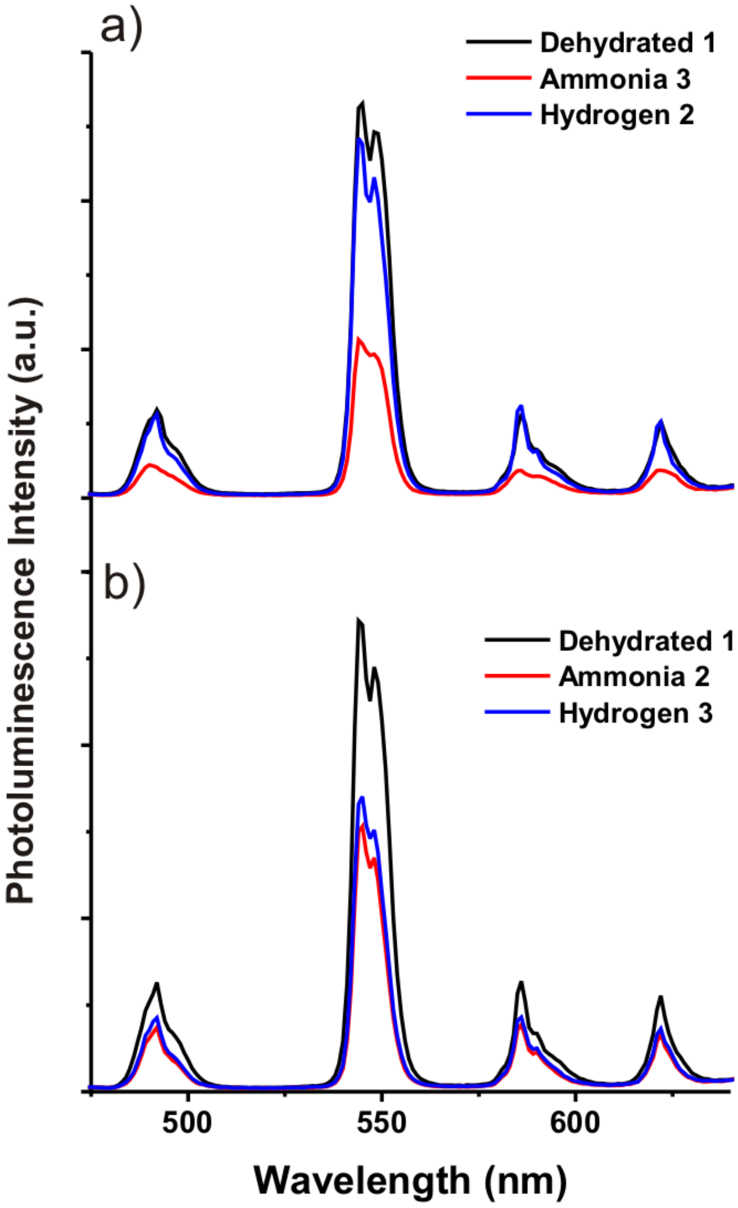

Figure S9. Competition experiments between NH_3 and H_2 in PCM-15: (a) activation→H_2→NH_3; (b) activation→NH_3→H_2.

References

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b. Amengual, R.; Genin, F.; Michelet, V.; Savignac, M.; Genêt, J.-P. *Adv. Synth. Catal*. **2002**, *344*, 393.

c. Aebischer, A.; Gumy, F.; Bünzli, J.-C. G. *Phys. Chem. Chem. Phys*., **2009**, *11*, 1346.

d. Spek, A. L. *Platon, a Multipurpose Crystallographic Tool*; Utrecht University: Utrecht, The Netherlands, **2009**.

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