Electronic Supporting Information (ESI) for

Achieving blue-excitable yellow-emitting Ca-LMOF phosphor via water induced phase transformation

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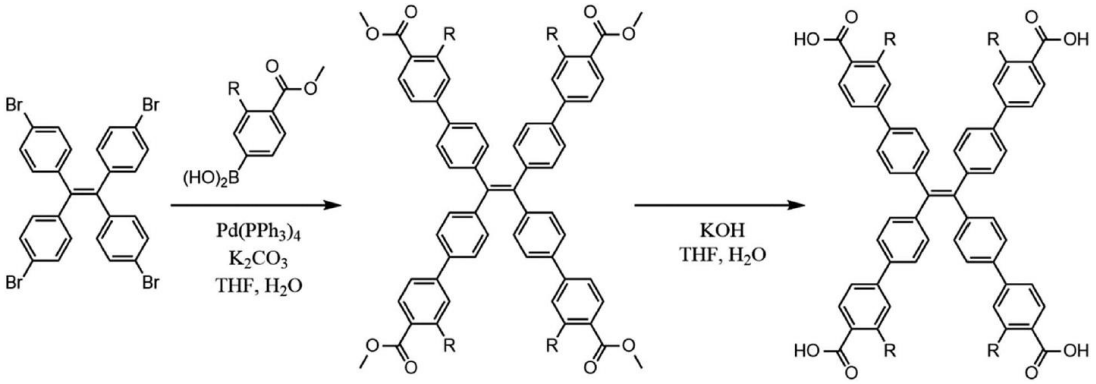
Table S1 Crystallographic data and structural refinement detail for **1** and **2′** [1].

Empirical formula	$C_{108}H_{62}Ca_4F_8O_{19}$	$C_{54}H_{38}CaO_{10}$
Formula weight	1975.89	886.92
Crystal system	Triclinic	Monoclinic
Space group	*P*-1	*C*2/*c*
T/K	100(2) K	150(2) K
λ/ Å	0.7288 Å	1.54178
a/ Å	10.0419(5)	46.0700(16)
b/ Å	15.6393(7)	7.8309(3)
c/ Å	42.1081(19)	12.0264(4)
α/°	92.477(2)	90
β/°	91.364(2)	103.8640(10)
γ/°	91.427(2)	90
V/ Å^3	6602.7(5)	4212.4(3)
Z	2	4
D_c/ Mg·m^{-3}	0.994	1.399
μ/mm^{-1}	0.239	1.825
F(000)	2028	1848
Measured refls.	82534	20252
Independent refls.	21120	4186
R_{int}	0.0635	0.0355
No. of parameters	1288	311
GOF	1.076	1.067
[a]R_1, [b]wR_2 [$I > 2\sigma(I)$]	0.0600, 0.1757	0.0356, 0.0891
[a]R_1, [b]wR_2 (all data)	0.0794, 0.1853	0.0383, 0.0914

[a]$R_1 = \sum \| F_o \| - | F_c | / \sum | F_o |$. [b]$wR_2 = [\sum w(F_o^2 \quad F_c^2)^2 / \sum w(F_o^2)^2]^{1/2}$



Scheme 1 Sythesis of H_4tcbpe (R = H) and H_4tcbpe-F (R = F).

Syntheses of the organic ligands: The chromophoric ligands H_4tcbpe and H_4tcbpe-F were synthesized using a previously reported method in our literature (**Scheme 1**).[2]

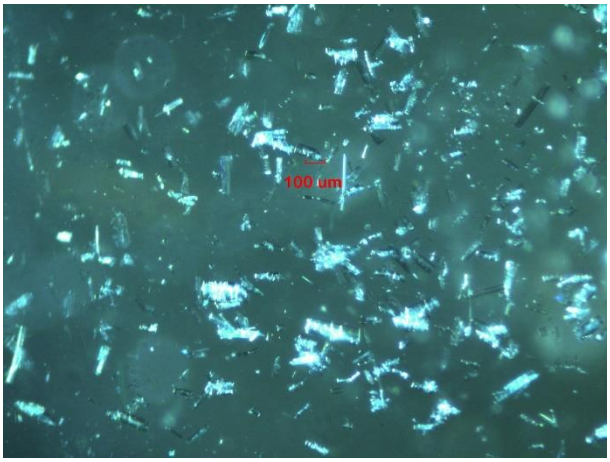


Fig. S1 The crystal image of **1**.

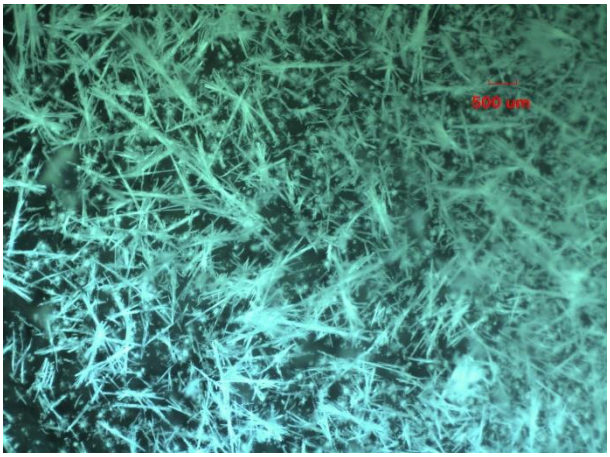


Fig. S2 The crystal image of **2**.

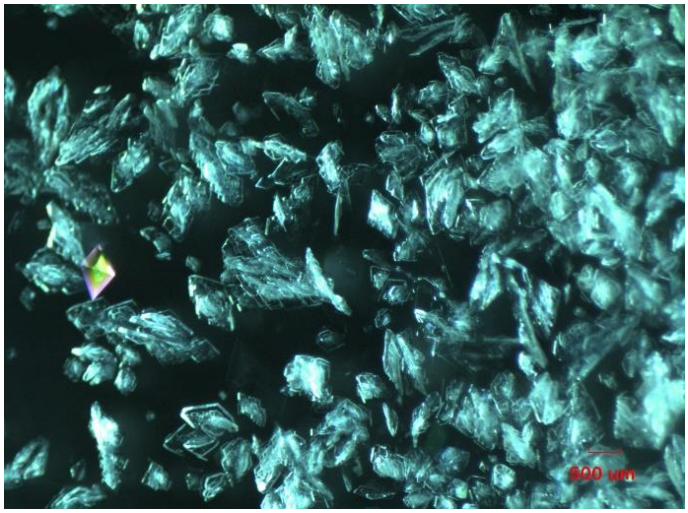


Fig. S3 The crystal image of **1′**.

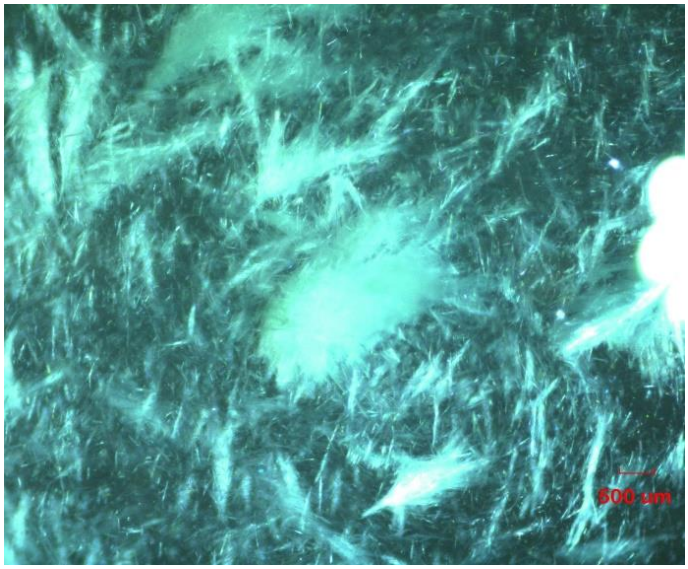


Fig. S4 The crystal image of **2′**.

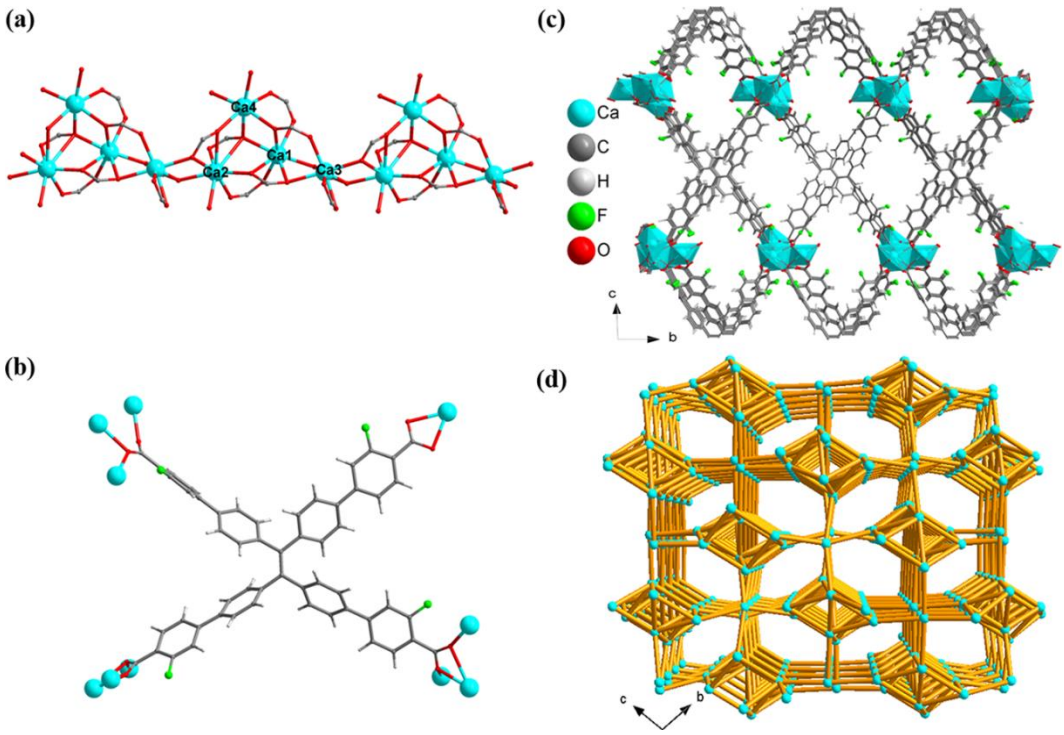


Fig. S5 (a) The coordination environment for Ca^{2+}. (b) The coordination mode of tcbpe-F in **1**. (c) and (d) are the 3D structure and the topology of **1** viewed along the *a* axis.

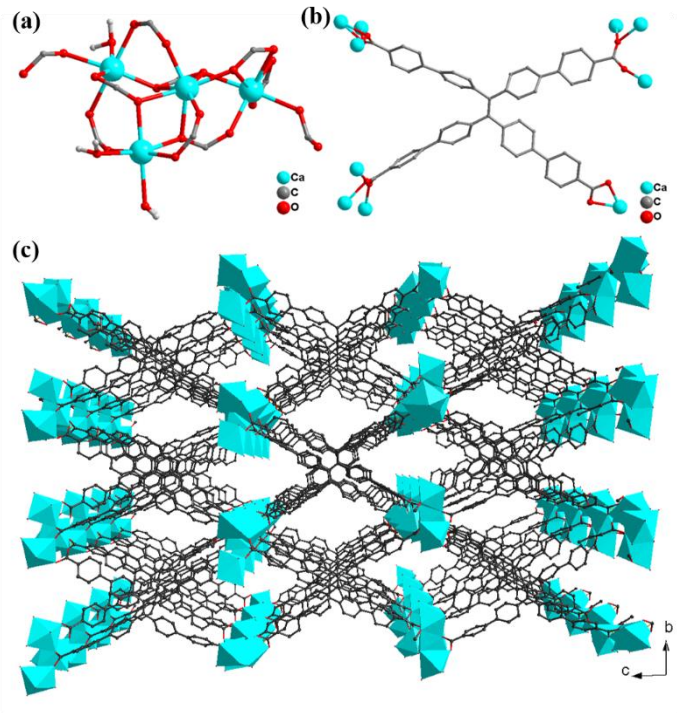


Fig. S6 (a) The coordination environment for Ca^{2+}. (b) The coordination mode of tcbpe in **2**. (c) The 3D structure of **2**.

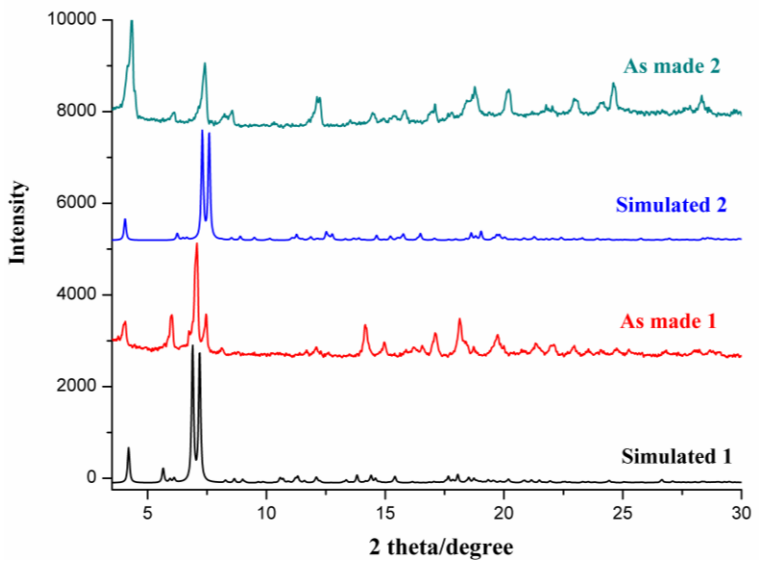


Fig. S7 PXRD patterns of the as-made **1** and **2**. Simulated PXRD patterns of **1** and **2** are included for comparison.

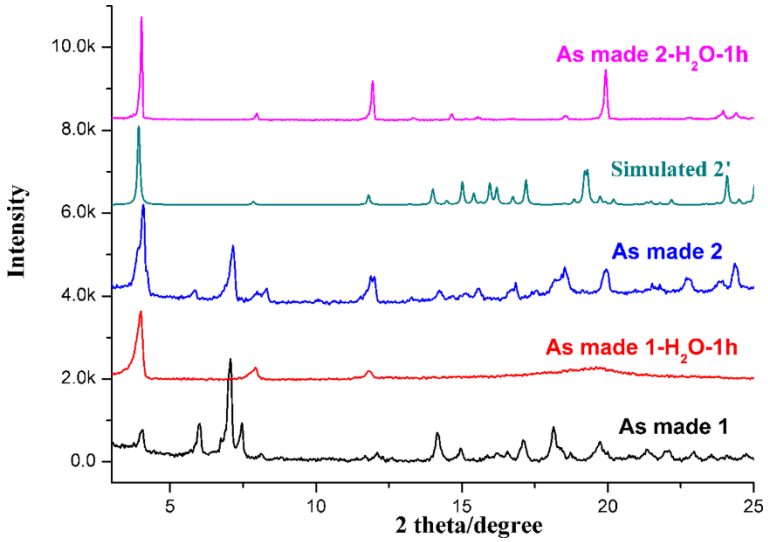


Fig. S8 PXRD patterns of the as-made **1** and **2**, and the corresponding samples after water treatment, along with the simulated PXRD pattern of **2′** for comparison.

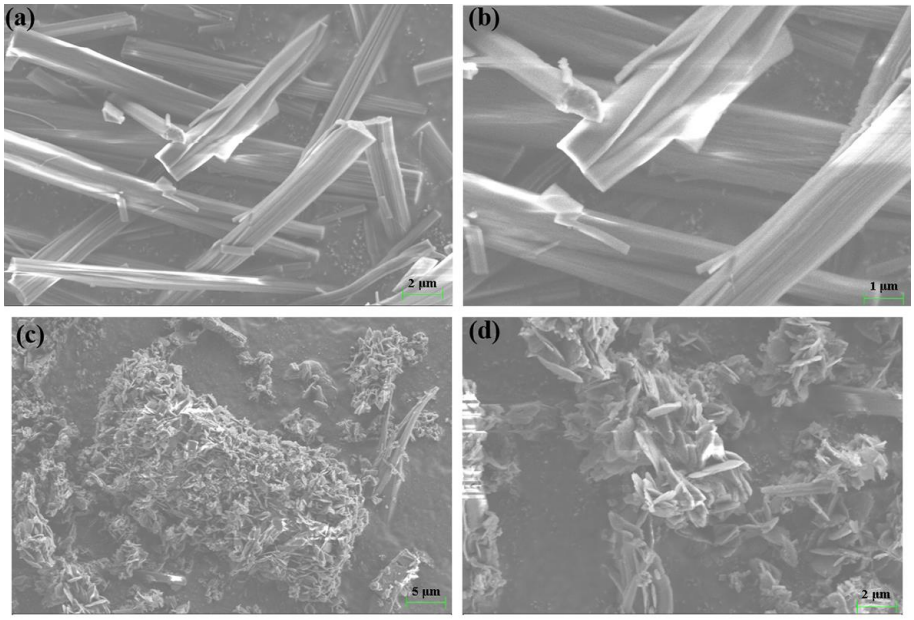


Fig. S9. The SEM photographs of **1** (a, b) and **1′** (c, d).

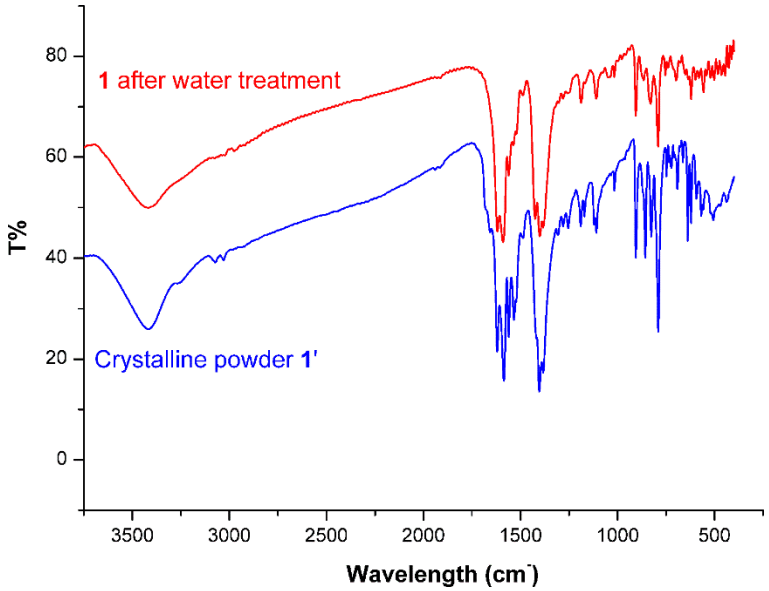


Fig. S10. The IR spectra of the water treated sample **1** and the crystalline powder sample of **1′**.

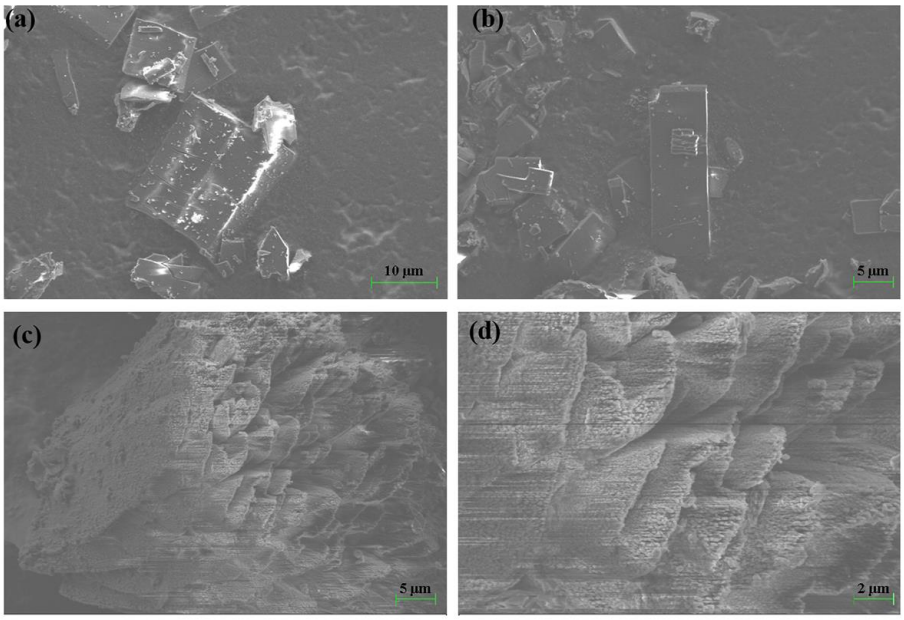


Fig. S11 The SEM photographs of **2** (a, b) and **2′** (c, d).

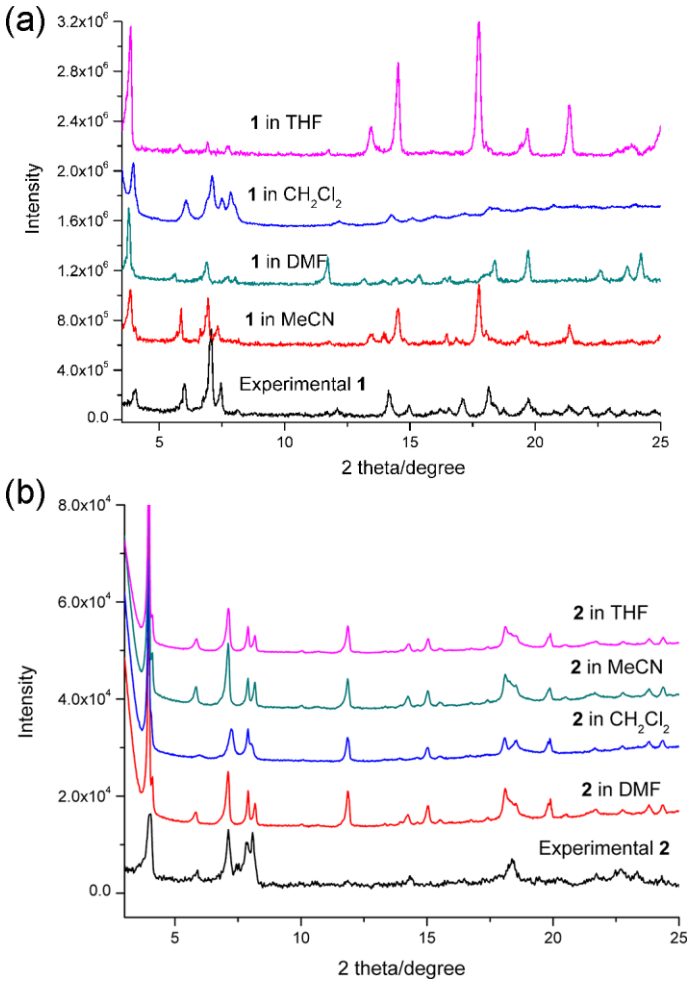


Fig. S12 The PXRD patterns of the as-made and solvent treated samples of **1** (a) and **2** (b).

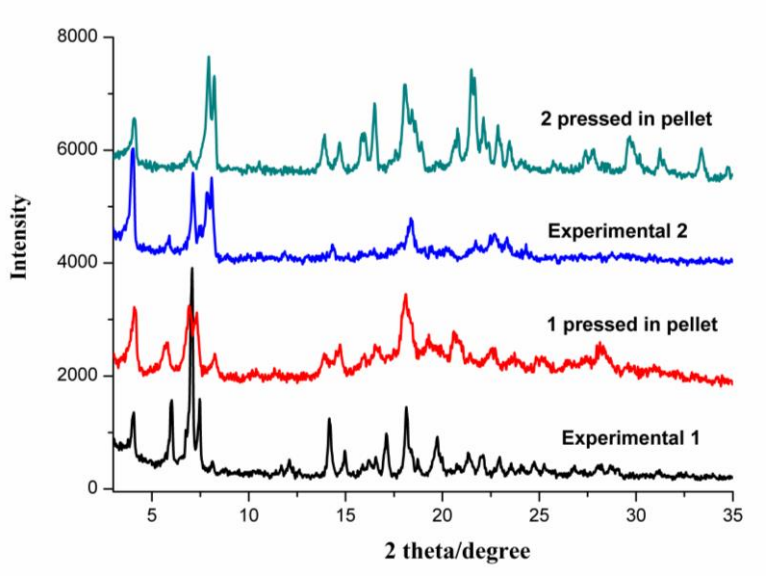


Fig. S13 The PXRD patterns of the as-made **1** and **2**, and the pressed pellets.

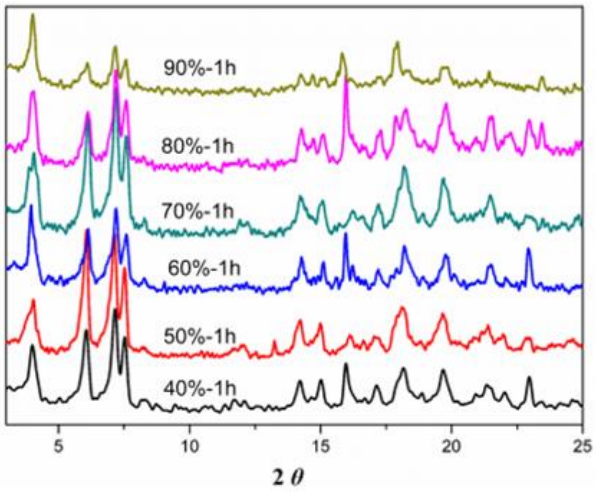


Fig. S14 The PXRD patterns of **1** after being kept in different moisture conditions for 1 h.

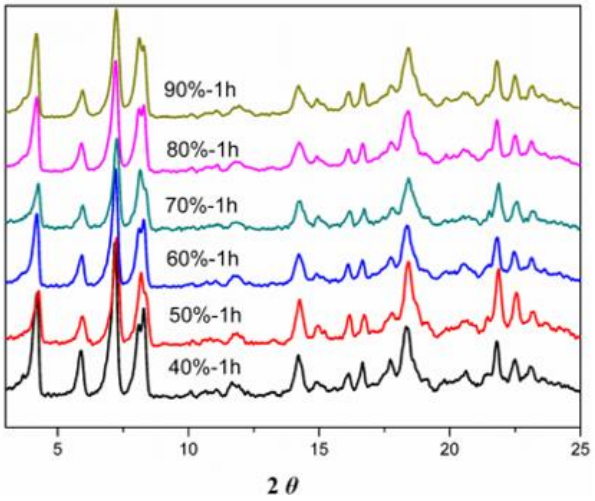


Fig. S15 The PXRD patterns of **2** after being kept in different moisture conditions for 1 h.

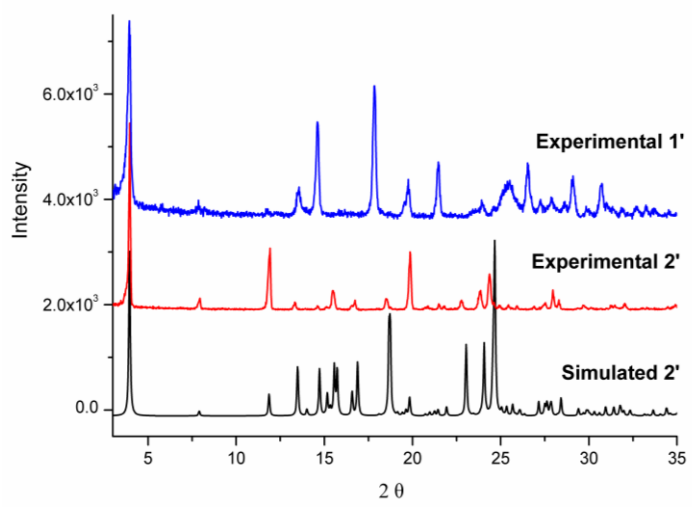


Fig. S16 The PXRD patterns of **1′** and **2′**. Simulated PXRD pattern of **2′** is included for comparison.[1]

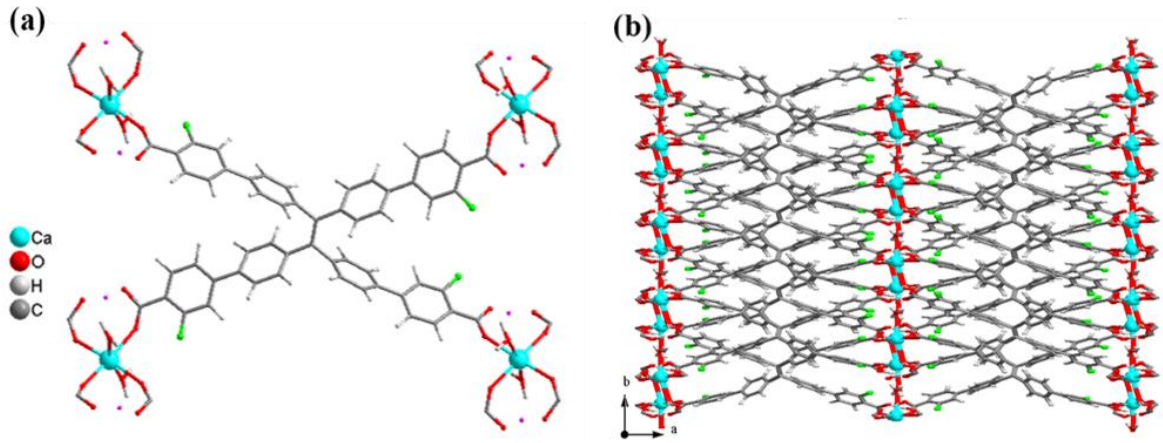


Fig. S17 (a) The coordination environment for Ca^{2+} and tcbpe-F in **1'**. The free proton atom has

been highlighted as rose. (b) The 3D structure of **1'** with 4-fold interpenetration.

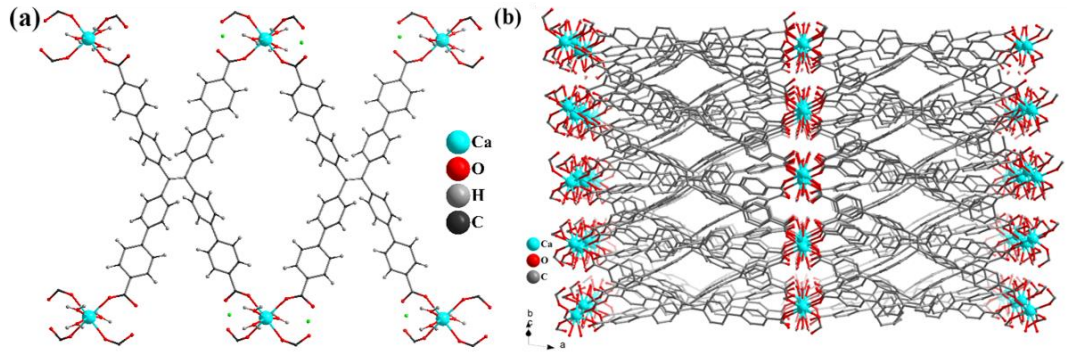


Fig. S18 (a) The coordination environment for tcbpe and Ca^{2+} in **2'**. The free proton atom has been highlighted as green. (b) The 3D structure with 4-fold interpenetration.[1]

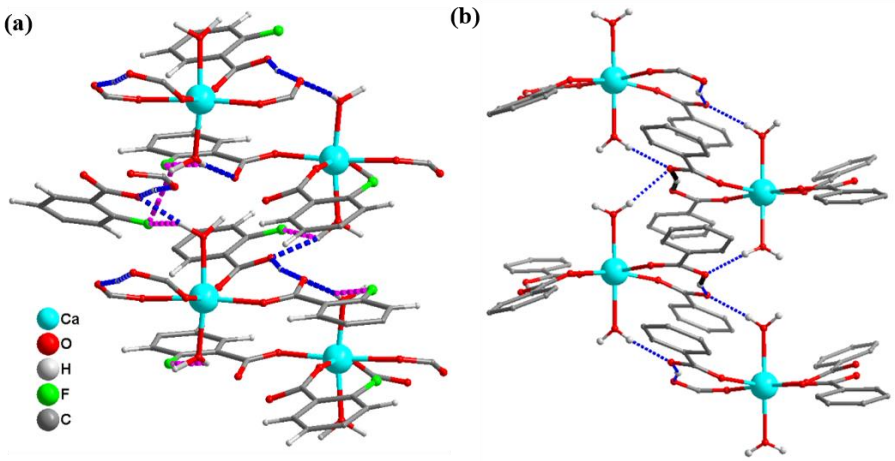


Fig. S19 (a) The H-bonding network in **1'**. The extra H-bonding between F and water is highlighted with pink-colored dotted line. (b) The H-bonding network in **2'**.

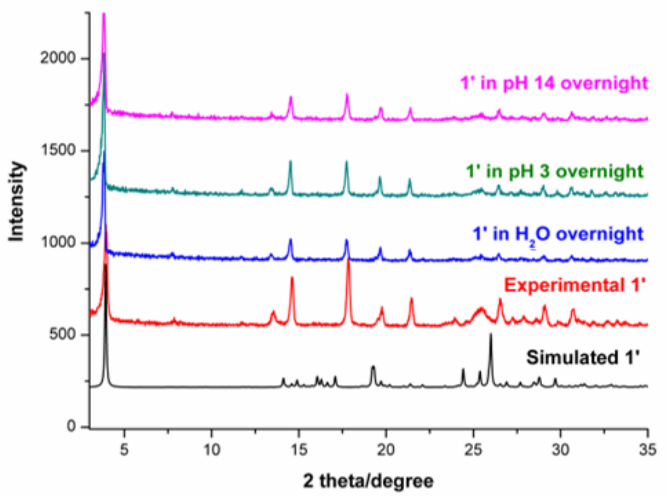


Fig. S20 The PXRD patterns of **1′** and **1′** after being treated in different conditions.

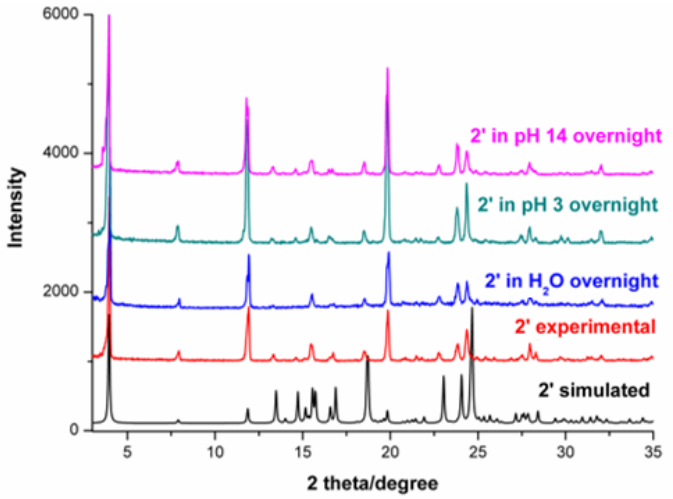


Fig. S21 The PXRD patterns of **2′** and **2′** after being treated in different conditions.

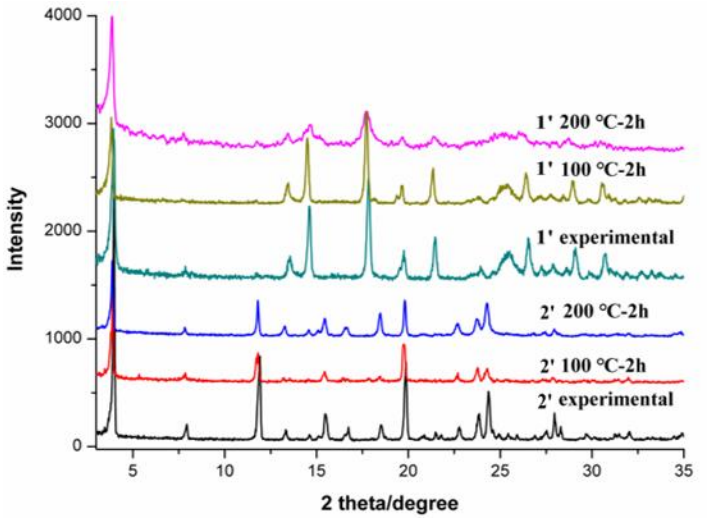


Fig. S22 The PXRD patterns of **1′** and **2′** after being treated at different temperatures in vacuum.

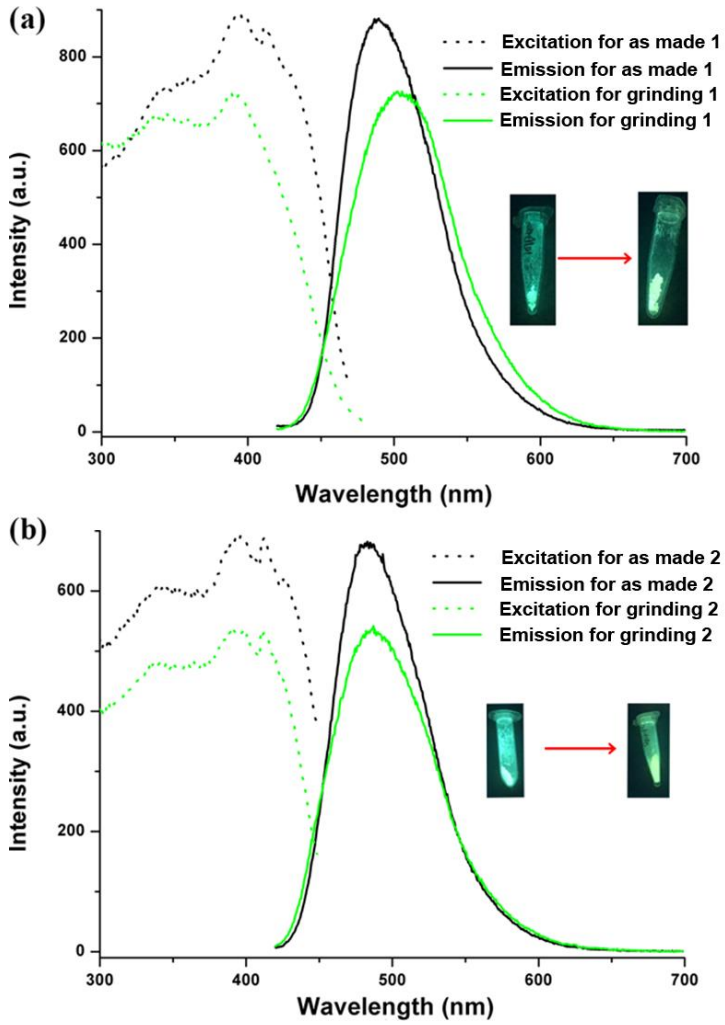


Fig. S23 The FL spectra of **1** (a) and **2** (b) before and after grinding. The insets are photographs taken before and after grinding at room temperature and under excitation using a 365 nm UV

lamp.

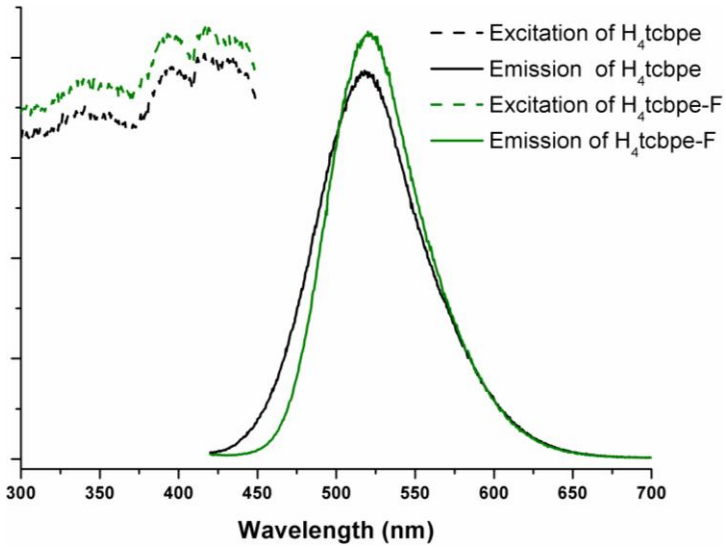


Fig. S24 The excitation and emission spectra of H_4tcbpe and H_4tcbpe-F ligands.

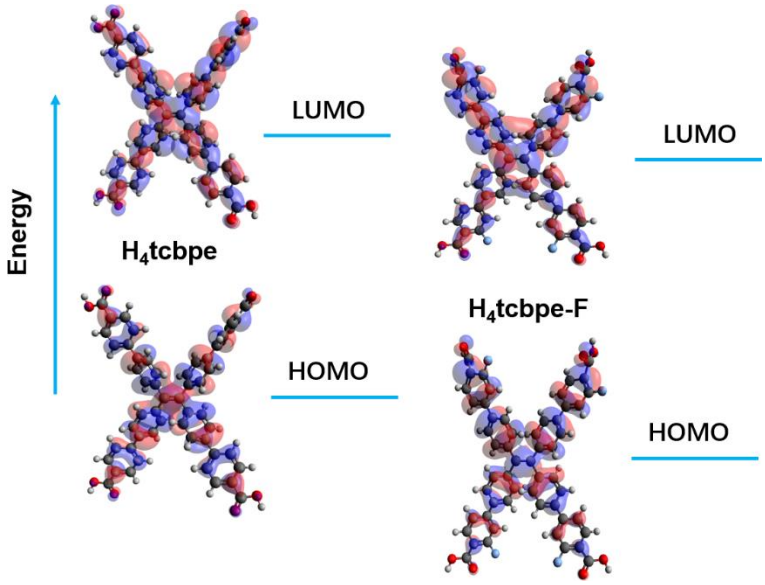


Fig. S25 The energies and compositions of HOMO and LUMO of the H_4tcbpe and H_4tcbpe-F.

Table S2 Calculated LUMO and HOMO energy levels for H_4tcbpe and H_4tcbpe-F.[3]

Ligand	LUMO (eV)	HOMO (eV)
H_4tcbpe	-2.46	-5.87
H_4tcbpe-F	-2.68	-6.10

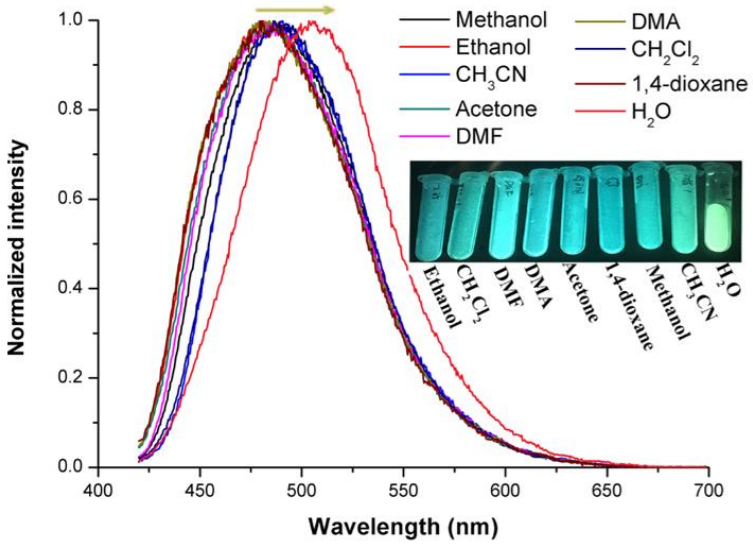


Fig. S26 The FL spectra of **2** after being dispersed at different solvents. Insets are photographs of the solvent-dependent FL under excitation with a 365 nm UV lamp.

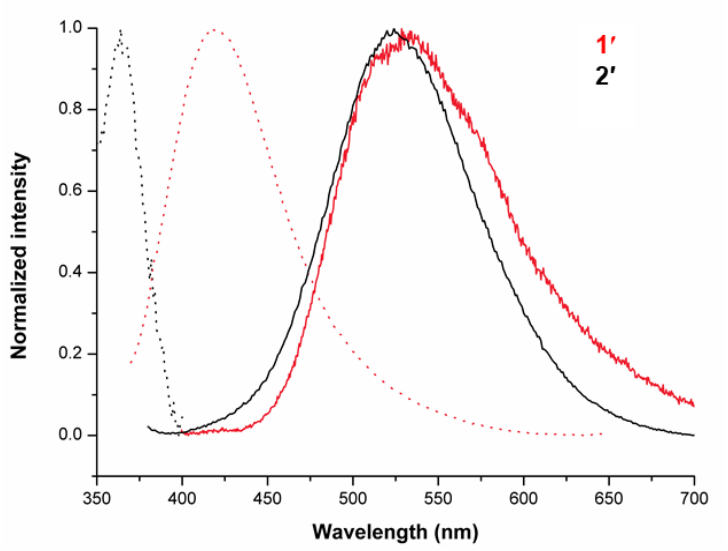


Fig. S27 The excitation and emission spectra of **1′** and **2′** in solid state.

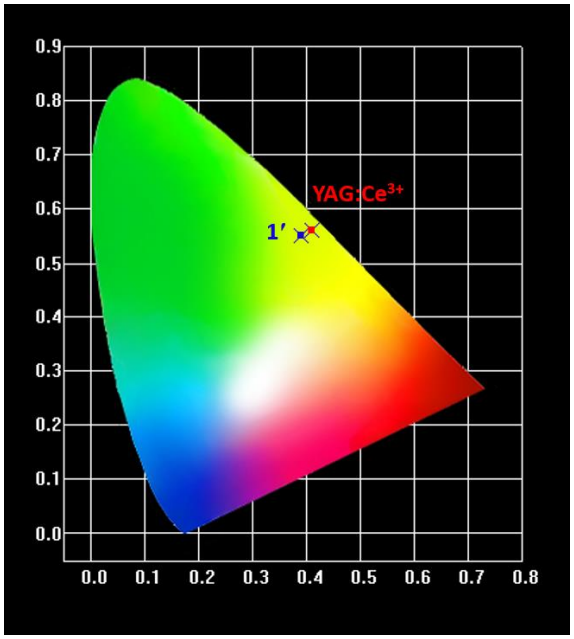


Fig. S28 The CIE coordinates of the activated **1′** compared with that of the commercial YAG:Ce^{3+}.

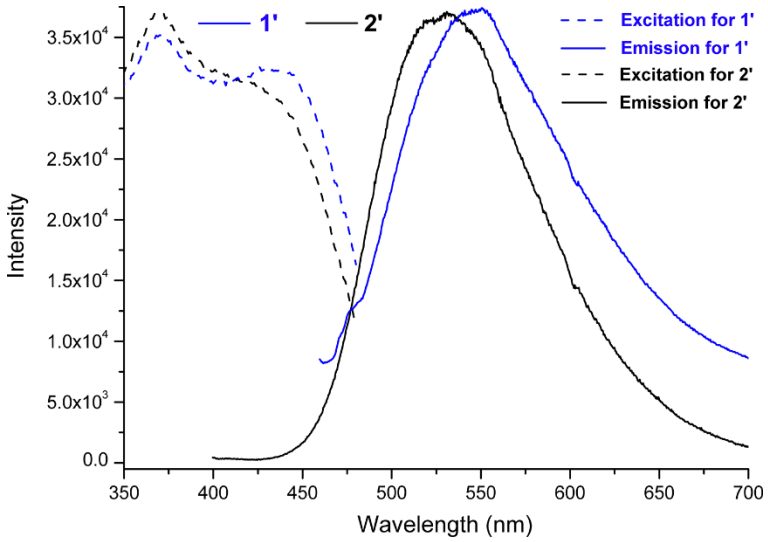


Fig. 29 The excitation and emission spectra of the activated **1'** and **2'**.

References

1. Z.-F. Wu, E. Velasco, C. Shan, K. Tan, Z.-Z. Zhang, Q.-Q. Hu, K. Xing, X.-Y. Huang, J. Li, *J. Mater. Chem. C*, 2020, **8**, 6820.

2. W. P. Lustig, Z. Shen, S. J. Teat, N. Javed, E. Velasco, D. M. O'Carroll, J. Li, *Chem. Sci.*, 2020, **11**, 1814.

3. W. P. Lustig, S. J. Teat, J. Li, *J. Mater. Chem. C*, 2019, **7**, 14739.