Supplementary Information (SI) for Dalton Transactions.

Thiacalix[4]arene-Capped Ln(III) Aggregated with "Hand in Hand" Structures and their Luminescent Properties

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Contents

Materials and Measurements

The raw materials include Terbium acetate ($Ln(Ac)_3$) (Ln = Tb, Eu), CH_3OH, *N,N'*-Dimethylformamide (DMF), $CHCl_3$ and HCl (12 mol/L) with a purity of ≥99 % were purchased from Aladdin Biochemical Technology Corporation (Shanghai, China). Meanwhile, 3,5-bis(3'-carboxy-phenyl)-1,2,4-triazole (H_2BCT) with a purity of 97 % was purchased from Henghua Technology Corporation (Jinan, China). The raw reagents were stored in a dry Ar-filled glove box with controlled oxygen and moisture levels below 0.1 ppm and used without further purification. All the above raw reagents were used as received without forther purification. In addition, it is worth mentioning that 4-tert-butylthiacalix[4]arene (H_4TC4A) was prepared by using the literature method.[1]

Powder X-ray diffraction (PXRD) pattern was recorded with a Bruker D8 Advance Phaser diffractometer equipped with a diffracted beam monochromator set for Cu-Kα radiation (λ = 1.5418 Å). The diffraction pattern was taken from 5 to 80 ° (2θ) with a scan step width of 0.02 ° and a fixed counting time of 1 s/step. Figure 1 shows the XRD results of the pure phase Tb^{III}_4/Eu^{III}_4-TC4A powders (red one), in which the theoretical XRD pattern (black one, simulated from the CIF files of Tb^{III}_4/Eu^{III}_4-TC4A is used as the reference.

The morphologies, microstructures and element quantitative analysis of the prepared samples were investigated by field emission scanning electron microscope & energy dispersive spectrometer (JEOL JSM-IT800). All XPS measurements were collected using a Thermo Scientific K-Alpha X-ray photoelectron spectrometer with Al Ka X-ray source, and AVANTAGE software was used to fit the peaks.

Fourier transform infrared (FT-IR) spectra of the samples were recorded on a Thermo Scientific Nicolet iS5 infrared spectrometer. The samples and dry KBr were mixed with a mass ratio of 1:100 and ground into fine powder, and then pressed into transparent sheets on the tablet machine. The prepared sheet was put in the sample chamber of the IR spectrophotometer, and the FT-IR spectra were measured. Figure S3 confirmed the bonding mode inside the aggregates **1** and **2**, respectively. Wherein, the peaks around 1500 cm^{-1} could be due to the telescopic vibration of the C=C bonds, the peaks around 1600 cm^{-1} could be due to the telescopic vibration of the C=O bonds, the peaks around 1700 cm^{-1} could be due to the telescopic vibration of the C=N bonds, the peaks around 3000 cm^{-1} could be due to the telescopic vibration of the C-H bonds, the peaks around 3500 cm^{-1} could be due to the telescopic vibration of the N-H bonds, respectively.

Thermal gravimetric analysis (TGA) and differential scanning calorimetry (DSC) of these two compounds were carried out on a NETZSCH STA 449F3 instrument at a temperature range of 40 - 800 ^{o}C with a heating rate of 10 ^{o}C • min^{-1} in an atmosphere of flowing Ar.

The elemental analyses of the two compounds were carried out on a Elementar UNICUBE instrument.

The CIE 1931 (Commission International d'Eclairage) diagram is a universal method for obtaining the whole possible colours by combining three primary colours which has been extensively used to visualize the intensity change of the emission bands and quantify the tenability of emission colours. The emission spectrum of **1** is converted to the x and y coordinates in the CIE chromaticity diagram (Figure S6). The chromaticity coordinate (x, y) is found to be (0.37, 0.56) for the compound. The result further verifies the overall emission colour of **1** is bright green.

Crystallographic Analysis

The data were collected using a Bruker D8 Venture Phaser CCD diffractometer equipped with monochromatic Cu-Kα radiation (λ = 1.54178 Å) operating at 40 kV and 40 mA under 180 K. The crystal structure was solved by direct method using SHELX-97 crystallographic software package. Moreover, absorption corrections were performed through the SCALE program for the area detector and integrated with the SAINT program.[2] The program XPREP was applied for the absorption correction (multi-scan) and the structure was checked using PLATON in case of additional symmetry elements.[3] Finally, the crystal structures of **1** and **2** were confirmed. Table S1 summarizes the crystal data and structure refinements of the compounds. CCDC 2405580 and 2405582 contain the supplementary crystallographic data for this paper.

Squeeze Results

SQUEEZE Result for $C_{210.51}H_{245.02}Cl_2N_{11.26}O_{36}S_{16}Tb_8$

```
# SQUEEZE RESULTS (Version = 111124)
# Note: Data are Listed for all Voids in the P1 Unit Cell
# i.e. Centre of Gravity, Solvent Accessible Volume,
# Recovered number of Electrons in the Void and
# Details about the Squeezed Material
loop_
   _platon_squeeze_void_nr
   _platon_squeeze_void_average_x
   _platon_squeeze_void_average_y
   _platon_squeeze_void_average_z
   _platon_squeeze_void_volume
   _platon_squeeze_void_count_electrons
   _platon_squeeze_void_content
    1   0.000   0.500   0.500        712        120 ' '
    2 -0.022   0.264   0.794        14           0 ' '
    3   0.022   0.736   0.206         14          0 ' '
    4   0.051   0.006   0.908         17          0 ' '
    5   0.145   0.873   0.376         63         16 ' '
    6   0.231   0.756   0.851         63         16 ' '
    7   0.500   0.000   1.000        711        120 ' '
    8   0.268   0.256   0.649         63         16 ' '
    9   0.355   0.373   0.124         63         16 ' '
   10   0.453   0.505   0.593         16          0 ' '
   11   0.478   0.236   0.294         14          0 ' '
   12   0.522   0.764   0.706         14          0 ' '
   13   0.546   0.495   0.407         16          0 ' '
   14   0.645   0.627   0.876         63         16 ' '
   15   0.731   0.744   0.351         63         16 ' '
   16   0.768   0.244   0.149         63         16 ' '
   17   0.855   0.127   0.624         63         16 ' '
   18   0.953   0.995   0.093         16          0 ' '
```

SQUEEZE gives 368 electrons/unit cell for the voids of **1**. Combining the results of TG analysis and the elemental analysis, the suitable formula for this compound might be $[Tb_8(\mu_4\text{-}OH)_2Cl_2(TC4A)_4(BCT)_2(DMF)_{5.26}(CH_3OH)_{2.74}(H_2O)_2]\bullet 2CH_3OH\bullet 2DMF$.

SQUEEZE Result for $C_{210.59}H_{245.89}Cl_2N_{11.30}O_{36}S_{16}Eu_8$

```
# SQUEEZE RESULTS (Version = 111124)
# Note: Data are Listed for all Voids in the P1 Unit Cell
# i.e. Centre of Gravity, Solvent Accessible Volume,
# Recovered number of Electrons in the Void and
# Details about the Squeezed Material
loop_
  _platon_squeeze_void_nr
  _platon_squeeze_void_average_x
  _platon_squeeze_void_average_y
  _platon_squeeze_void_average_z
  _platon_squeeze_void_volume
  _platon_squeeze_void_count_electrons
  _platon_squeeze_void_content
   1  0.000  0.500  0.500       776       127 ' '
   2 -0.021  0.264  0.793        14         0 ' '
   3  0.021  0.736  0.207        14         0 ' '
   4  0.500  0.000  1.000       776       127 ' '
   5  0.146  0.872  0.377        61        16 ' '
   6  0.231  0.755  0.852        63        15 ' '
   7  0.268  0.255  0.648        63        15 ' '
   8  0.354  0.372  0.123        62        16 ' '
   9  0.479  0.236  0.293        14         0 ' '
  10  0.520  0.764  0.707        14         0 ' '
  11  0.646  0.628  0.877        61        16 ' '
  12  0.731  0.745  0.352        63        15 ' '
  13  0.768  0.245  0.148        63        15 ' '
  14  0.854  0.128  0.623        62        16 ' '
```

SQUEEZE gives 378 electrons/unit cell for the voids of **2**. Combining the results of TG analysis and the elemental analysis, the suitable formula for this compound might be $[Eu_8(\mu_4\text{-}OH)_2Cl_2(TC4A)_4(BCT)_2(DMF)_{5.30}(CH_3OH)_{2.70}(H_2O)_2]\bullet 3CH_3OH\bullet 2DMF$.

Table S1 Crystal data and structural refinement parameters of **1** and **2**.

Crystal data and structural refinements of these two aggregates .

Common name	**1**	**2**
Sum formula	$C_{218.51}H_{267.02}Cl_2N_{13.26}O_{46}S_{16}Tb_8$ (including solvent molecules)	$C_{219.59}H_{271.89}Cl_2N_{13.30}O_{41}S_{16}Eu_8$ (including solvent molecules)
Moiety formula	$C_{210.51}H_{245.02}Cl_2N_{11.26}O_{36}S_{16}Tb_8$ (without solvent molecules)	$C_{210.59}H_{245.89}Cl_2N_{11.30}O_{36}S_{16}Eu_8$ (without solvent molecules)
Formula weight	5574.43 g/mol	5553.12 g/mol
Temperature	180 K	180 K
Crystal system	Monoclinic	Monoclinic
Space group	$P2_1/n$ (No. 4)	$P2_1/n$ (No. 4)
Unit cell dimensions	a = 17.8840 (4) Å; b = 23.2926 (5) Å; c = 30.3921 (6) Å;	a = 17.9372 (4) Å; b = 23.3395 (6) Å; c = 30.4245 (7) Å;
Volume	12561.3 (5) $Å^3$	12639.1 (5) $Å^3$
Z	2	2
Calculated density	1.474 g/cm^3	1.459 g/cm^3
Absorption coefficient	12.799 mm^{-1}	15.930 mm^{-1}
Goodness-of-fit on F^2	1.054	1.227
Total data	26740	20781
Unique data	23635	17378
Final R indices $[F_0^2 > 2\sigma(F_0^2)]^{[a]}$	R_1 = 0.0389; wR_2 = 0.0963	R_1 = 0.0650; wR_2 = 0.1323
R indices	R_1 = 0.0457; wR_2 = 0.1037	R_1 = 0.0793; wR_2 = 0.1420

[a] $R_1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$ and $wR_2 = [\Sigma w(F_o^2 - F_c^2)^2/ \Sigma wF_o^4]^{1/2}$ for $F_o^2 > 2\sigma(F_o^2)$

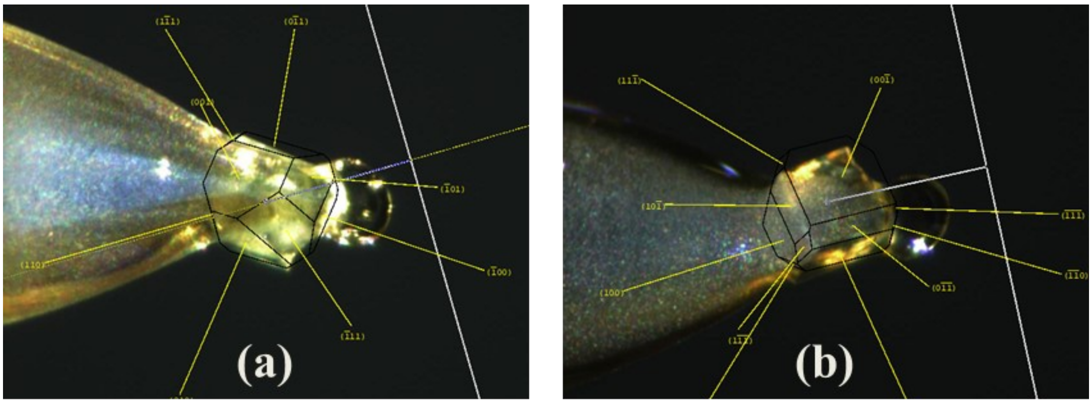


Figure S1 RID measurements of (a) **1** and (b) **2**.

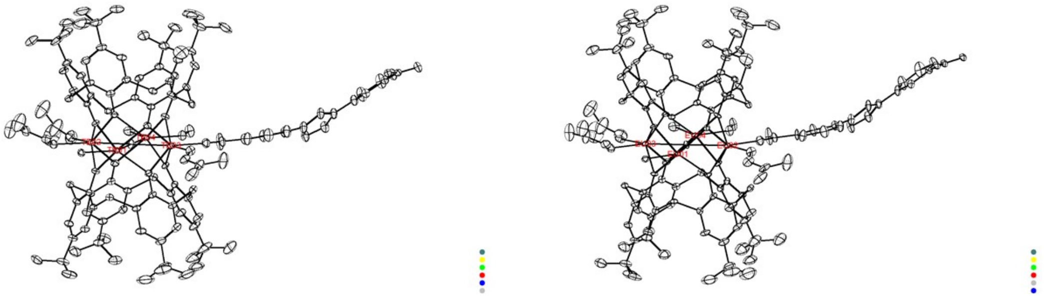


Figure S2 ORTEP style plots of compounds **1** and **2** in the solid state. Ellipsoids are drawn at the 50% probability level. Hydrogen atoms are omitted for clarity.

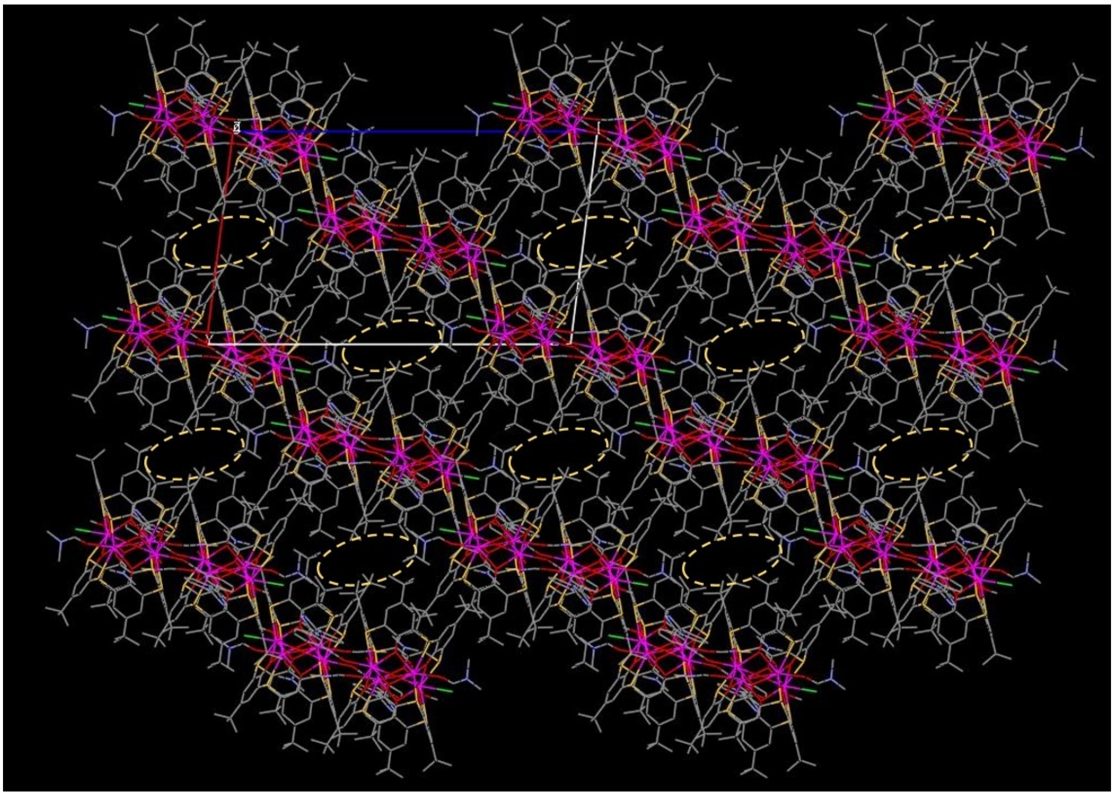
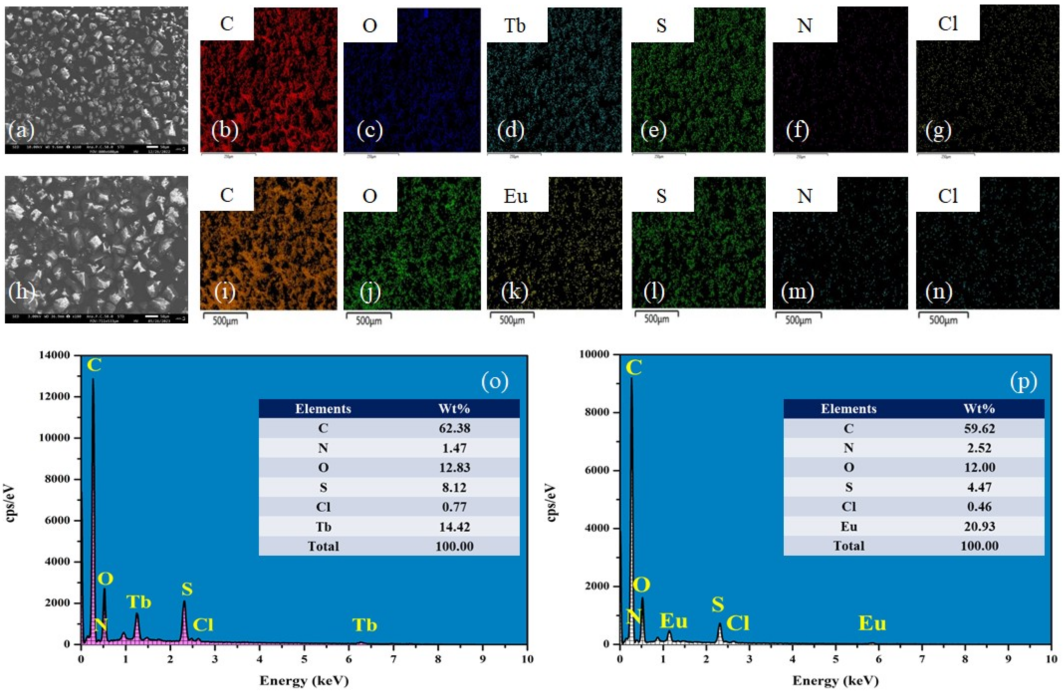


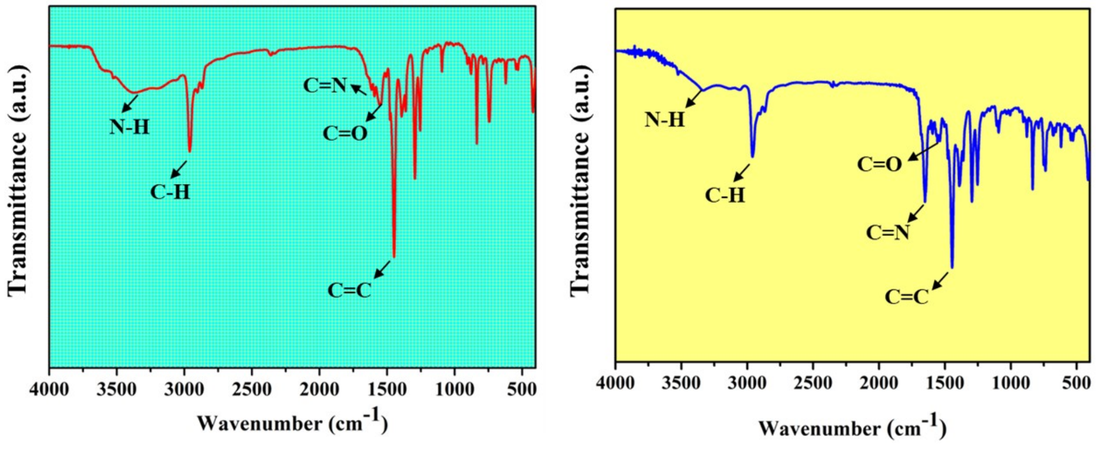
Figure S3 Stacking diagram of the extended structure of **1** showing some 1D channels along the *b* axis.



Elements	Wt%
C	62.38
N	1.47
O	12.83
S	8.12
Cl	0.77
Tb	14.42
Total	100.00

Elements	Wt%
C	59.62
N	2.52
O	12.00
S	4.47
Cl	0.46
Eu	20.93
Total	100.00

Figure S4 SEM images of (a) **1** and (h) **2** and EDS analysis of different elements in **1** (b-g, o) and **2** (i-n, p).



(a) **(b)**

Figure S5 FT-IR spectra of Solid-state (a) **1** and (b) **2**.

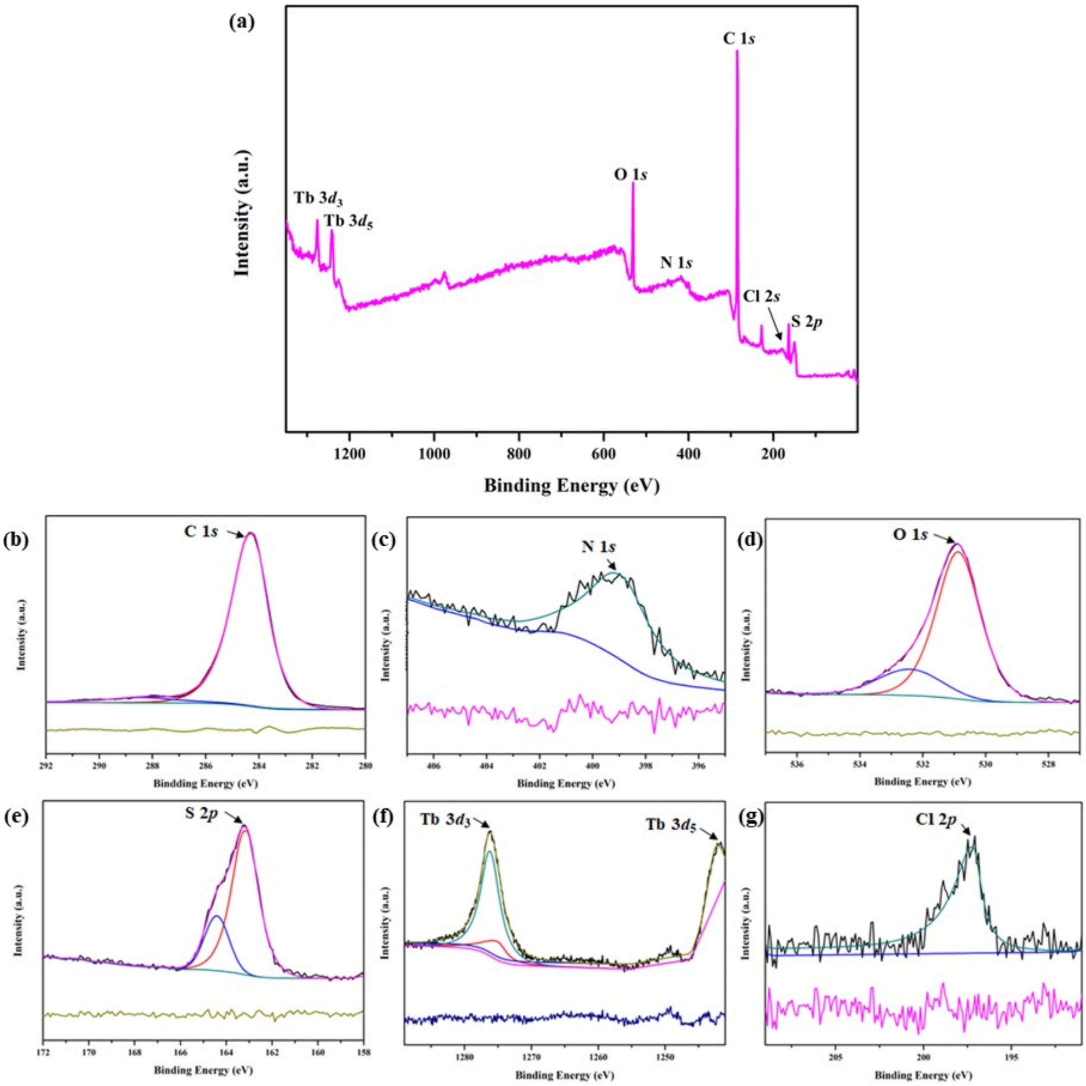


Figure S6 XPS patterns of **1**.

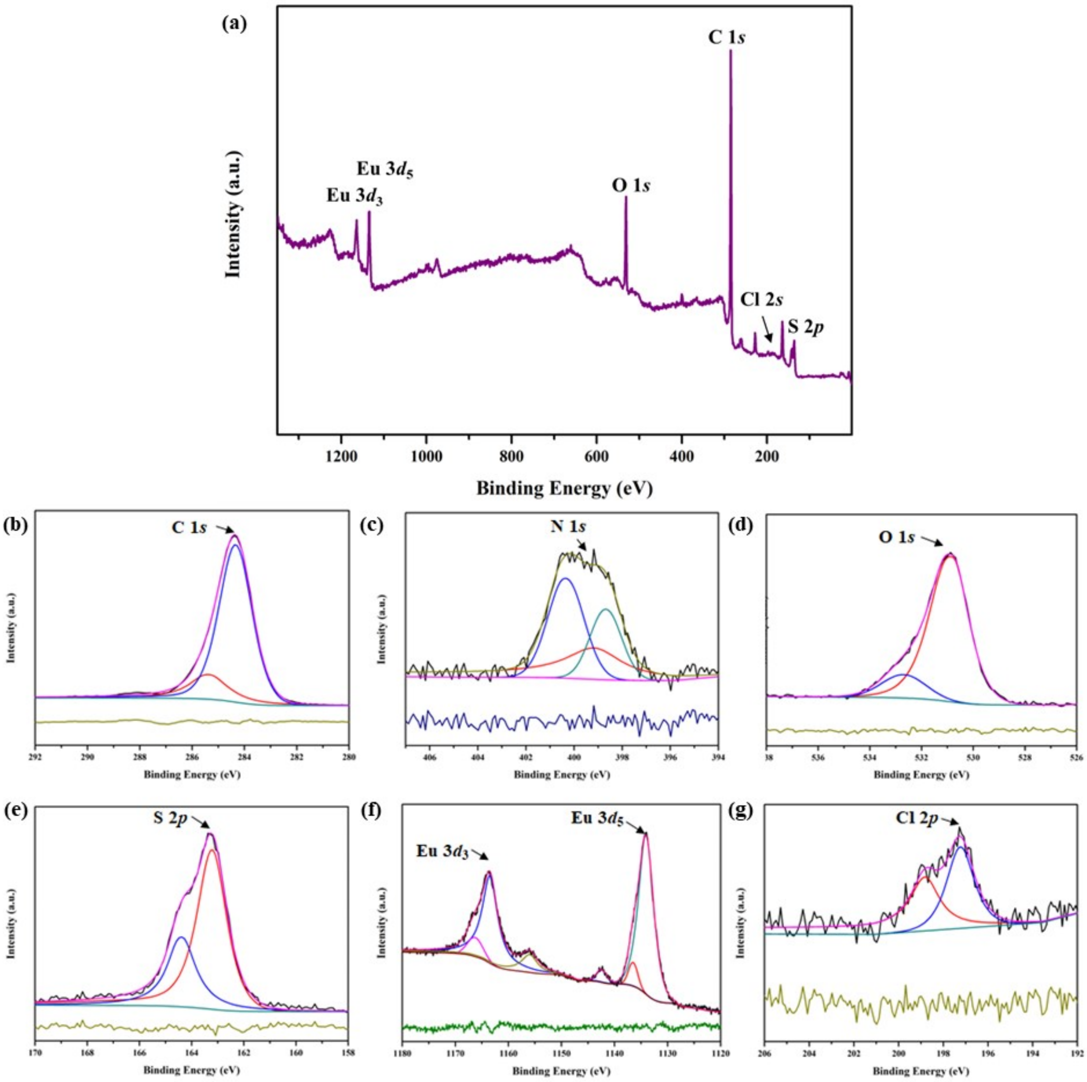


Figure S7 XPS patterns of **2**.

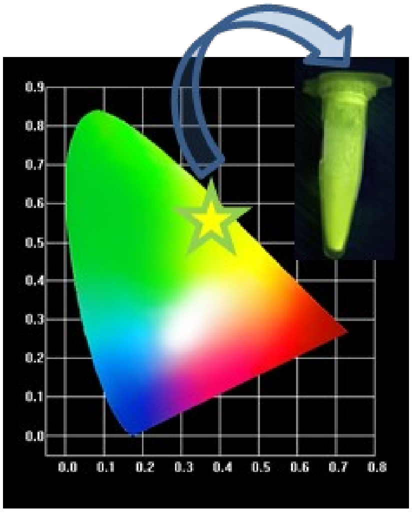


Figure S8 CIE 1931 diagram of the powders of **1**.

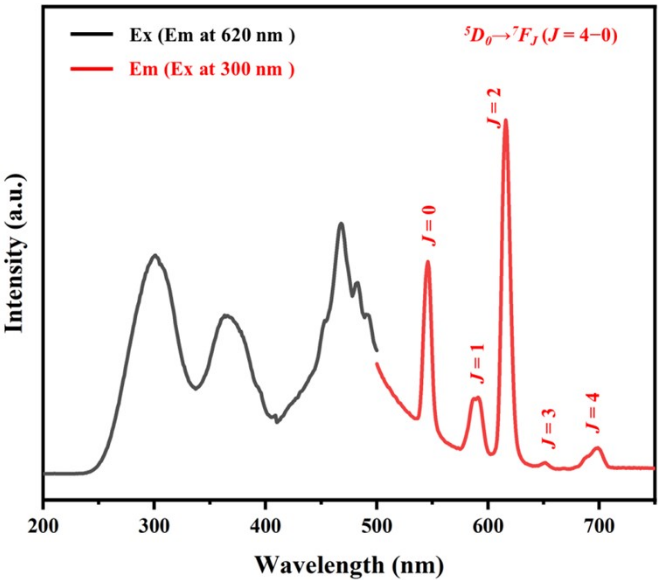


Figure S9 Solid-state excitation and emission spectra of **2**.

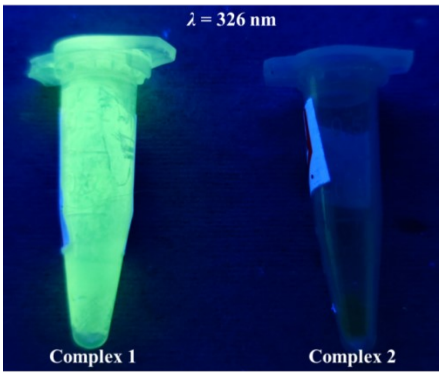


Figure S10 The photos of the samples of **1** and **2** under UV lamp irradiation (λ = 326 nm).

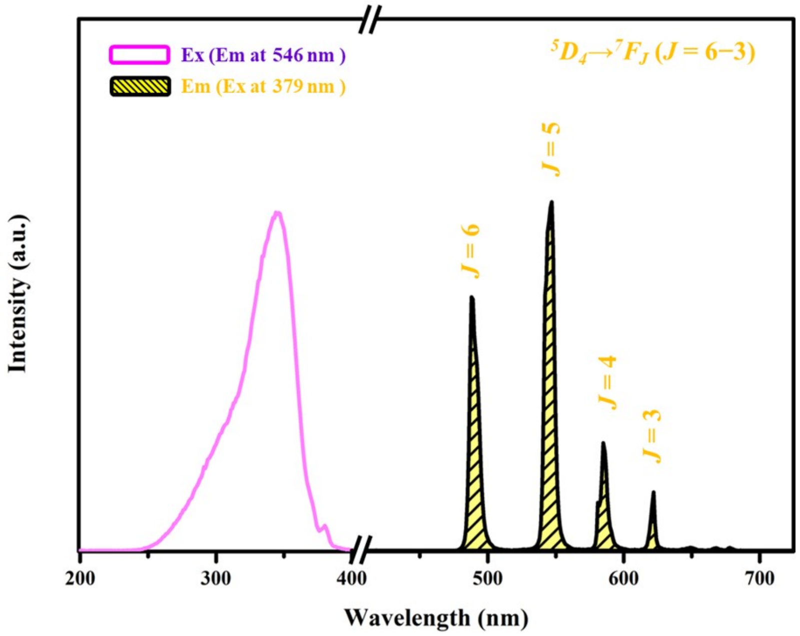


Figure S11 Solid-state excitation and emission spectra of **1** after soaked in methanol for several days.

References

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