Synthesis of 1

A mixture of $Zn(NO_3)_2.6H_2O$ (0.029g, 0.1mmol) and $[Na_2(trans\text{-}AZT)(H_2O)_5]$ (0.0127 g, 0.05 mmol) in 10ml of water and 10ml of ethanol was stirred for 5 minute. Then 0.0468 g (0.3 mmol) of 2,2'-bpy was added to the mixture, the new mixture was heated and stirred for 1h and the yellow precipitates dissolved slowly. The resulting mixture was filtered and yellow crystals were obtained by slow evaporation of the filtrate after several days and washed with EtOH (yield, *ca* 62%). Elemental analysis: Anal. Calcd. (%) for **1** $C_{31}H_{36}N_{12}O_9Zn$, *M*r = 786.11: C, 47.32; H, 4.57; N, 21.37; Found (%):C, 47.31; H, 4.72; N, 21.27.

Synthesis of 2

A mixture of $ZnCl_2.4H_2O$ (0.020g, 0.1mmol) and $[Na_2(trans\text{-}AZT)(H_2O)_5]$ (0.0508 g, 0.2 mmol) in 10ml of water and 10ml of ethanol was stirred for 5 minute. Then 0.018g (0.3 mmol) of ethylenediamine in1ml of water was added to the mixture, the new mixture was heated and stirred for 1h and the yellow precipitates dissolved slowly. The resulting mixture was filtered and yellow crystals were obtained by slow evaporation of the filtrate after several days and washed with EtOH (yield, *ca* 69%). Elemental analysis: Anal. Calcd. (%) for **2** $C_{10}H_{30}N_{26}O_2Zn$, *M*r = 611.99: C, 19.63; H, 4.94; N, 59.51; Found (%):C, 19.59; H, 5.07; N, 59.63.

Synthesis of 3.

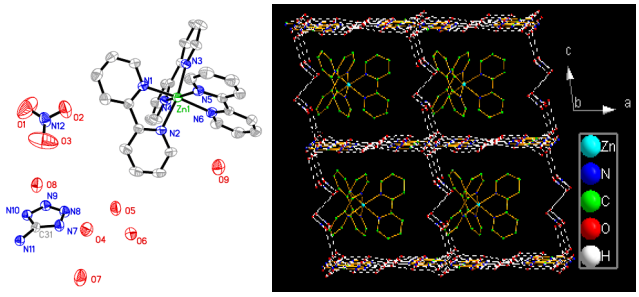
A mixture of $NiCl_2.6H_2O$ (0.0237 g, 0.1 mmol) and $[Na_2(trans\text{-}AZT)(H_2O)_5]$ (0.0254 g, 0.1 mmol) in 10ml of water and 10ml of ethanol was stirred for 5 minute. Then 0.0468 g (0.3 mmol) of 2,2'-bpy was added to the mixture, the new mixture was heated and stirred for 1h and the brown precipitates dissolved slowly. The resulting mixture was filtered and red crystals were obtained by slow evaporation of the filtrate after several days and washed with EtOH (yield, *ca* 67%). Elemental analysis: Calcd. (%) for **3** $C_{64}H_{68}N_{32}Ni_2O_{10}$, *M*r = 1562.92: C, 49.14; H, 4.35; N, 28.66; Found (%): C, 48.83; H, 4.26; N, 28.36.

Fluorescence imaging experiments: compounds **1**-**3** were dissolved in ethanol, respectively. The lamellae that suitable for microscopy experiments were prepared by coating the solution on a cover glass and drying in air. Imaging experiments were conducted with a confocal laser scanning microscope(510 META DUO SCAN) with oil-immersion objective lens 63x (NA=1.4, Plan-Apochromat). The incident beam (408nm) is split by beam splitter and focused by an objective into a small volume. The amplifier gain was set at 1.00 and the pixel time was 3.20 μs.

For the lambda scan, the emission was collected from 417 to 748nm. For the plane imaging scan, green emission was collected with a 505-570nm window and red emission was collected with a 650nm window.

The thermol gravimetric(TG) analysis of **1** and **3** was carried out on a TG-209 instrument in flowing N_2 with a heating rate of 10□/min.

X-ray crystallography and data collection: The crystals were filtered from the solution and immediately coated with a hydrocarbon oil on the microscope slide. Suitable crystals were mounted on glass fibers with silicone grease and placed in a Bruker Smart APEX(II) area detector using graphite monochromated MoKα radiation (λ= 0.71073 Å) at 296(2) K. Its structures was solved by direct methods and successive Fourier difference syntheses (SHELXS-97) and refined by full–matrix least-squares procedure on F^2 with anisotropic thermal parameters for all non-hydrogen atoms (SHELXL-97). Hydrogen atoms were added theoretically and were riding on their parent atoms.



(a) (b)

Fig. 6 (a) The atomic labeling scheme of **1,** (b) the 3D supramolecular structure viewed along the crystallographic b axis of **1.**

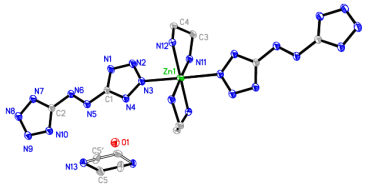


Fig. 7 The atomic labeling scheme of **2.**

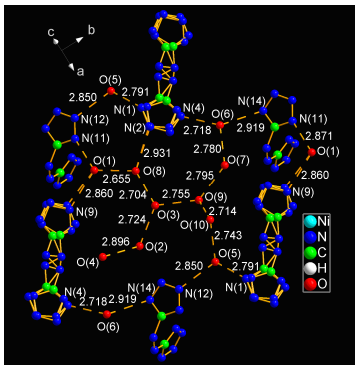


Fig. 8 The hydrogen bonding interactions in **3**.

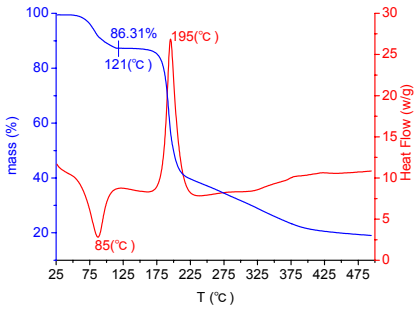


Fig. 9 The TG analysis digarm of **1**.

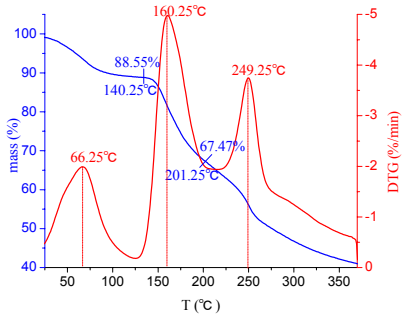


Fig. 10 The TG analysis digarm of **3**.

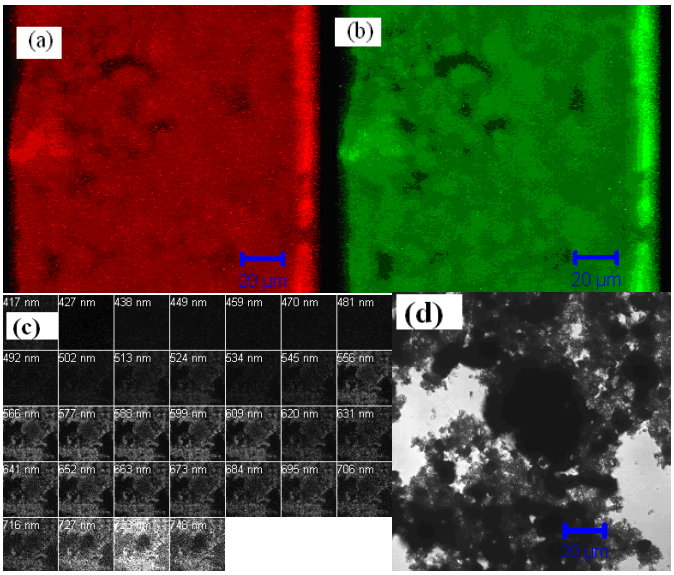
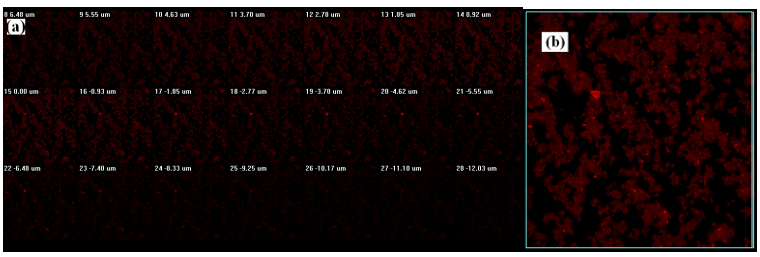


Fig. 11 Multi-photoluminescence images of **1** by confocal microscopy, (a) red image at all depths, (b) green image at all depths, (c) transparent images at different emission wavelength, (d) transparent image.



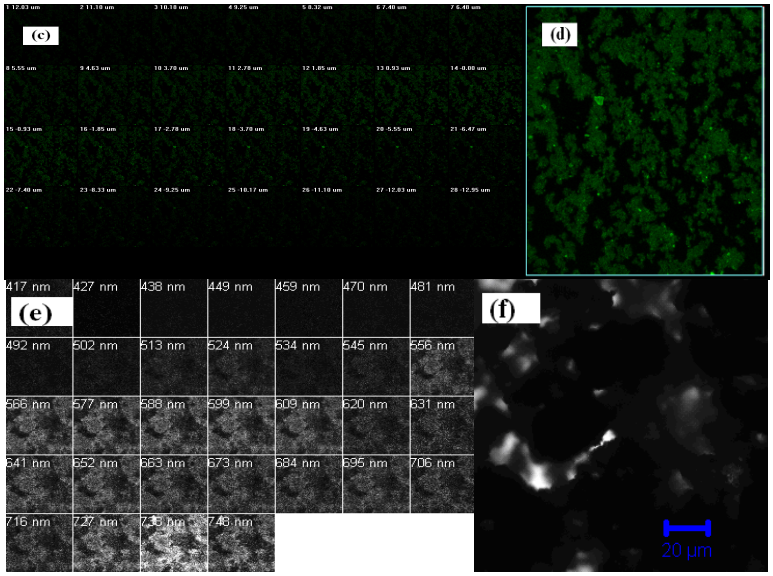


Fig. 12 Multi-photoluminescence images of **2** by confocal microscopy, (a) red image at different depths, (b) red image at all depths, (c) green image at different depths, (d) green image at all depths, (e) transparent images at different emission wavelength, (f) transparent image.

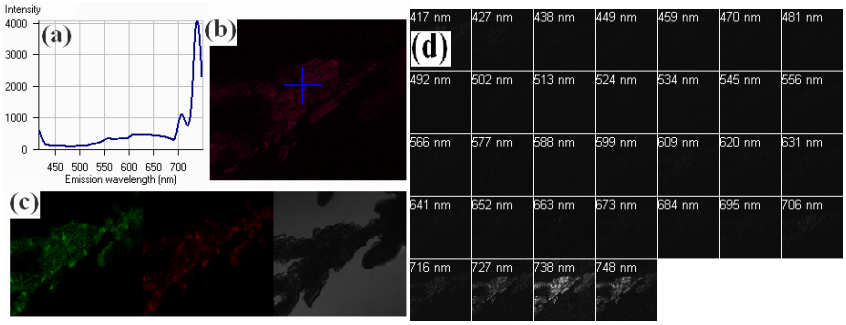


Fig. 13 Multi-photoluminescence images and emission spectrum of **3** by confocal microscopy with lasing induced by 408nm pulsed excitation, (a) emission spectrum at labeling location, (b) photoluminescence image at labeling location, (c) green and red image, (d) transparent images at different emission wavelength.