Supporting Information

Instrumentation Information

1. Single crystal X-ray diffractometer system:

Single-crystal X-ray diffraction intensity data were collected on a BrukerX8 APEX diffractometer equipped with a CCD area detector and Mo Kα radiation ($\lambda = 0.71073$ Å)

2. Powder X-ray diffractometer:

Room-temperature powder diffraction patterns were measured on a Bruker D2 PHASER desktop diffractometer at 300-W (30 kV, 10 mA) power.

3. TG analyzer:

TGA curves were measured on a Perkin-Elmer Pyris 1 thermal analyzer with samples held in platinum pans in a continuous N_2 flow atmosphere and heated at a constant rate of 10 ^{o}C min^{-1}.

4. Elemental analysis:

Elemental analysis was carried out on a Foss Heraeus CHN-O-Rapid analyzer with 5 mg of each sample.

5. Photoluminescence spectrometer system:

Solid-state PL spectra were measured on powder samples on a Fluorolog-3 spectrofluorometer equipped with a Xe lamp (450-W) as the excitation light source.

6. Electron paramagnetic resonance (EPR) spectra measurements:

X-band EPR spectra were measured on a Bruker, Elexsys E-580 spectrometer.

7. UV-Vis spectra measurements:

UV-Vis spectra were measured on powder samples on a Hitachi U-3010 spectrophotometer.

8. Solid-state^{31}P NMR spectra measurements:

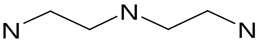
500 MHz solid-state ^{31}P NMR spectra were measured on powder samples on a Bruker DSX-400WB NMR spectrometer.

Synthesis Method

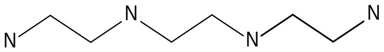
ZG-*n*N was synthesized by heating a mixture of Ga_2O_3 (0.375mmol; 0.0703 g), $Zn(NO_3)_2 \cdot 6H_2O$ (1 mmol; 1M 1mL), H_3PO_4 (6 mmol; 0.405 mL), linear polyamine (3~4mmol), H_2O (5 mL), and ethylene glycol (EG) (6 mL) in a 23-mL Teflon-lined acid digestion bomb at 160or 180 °C for 3 days.

		$Zn(NO_3)_2 \cdot 6H_2O$ (mmol)	**Ga_2O_3 (mmol)**	**amine* (mmol/mL)**	**H_3PO_4 (mmol)**	**EG (mL)**	**H_2O (mL)**
160 °C 3 Days	**ZG-3N-L**	1	0.375	deta 4/0.435	6	6	5
	ZG-4N-L			teta 3.5/0.512			
	ZG-5N-L			tepa 3/0.574			
	ZG-6N-L			peha 3/0.765			
180 °C 3 Days	**ZG-3N-H**	1	0.375	deta 4/0.435	6	6	5
	ZG-4N-H			teta 3.5/0.512			
	ZG-5N-H			tepa 3/0.574			
	ZG-6N-H			peha 3/0.765			

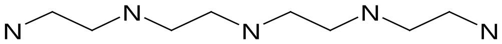
*deta = diethylenetriamine,



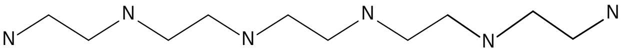
teta = triethylenetetramine,



tepa = tetraethylenepentamine,



peha = pentaethylenehexamine,



Single-Crystal X-ray Structure Analysis

Crystals of **ZG-*n*N** were selected for indexing and intensity data collections at 296 K. The measurements were performed on Bruker APEX DUO diffractometer systems equipped with a CCD area detector and Mo Kα radiation (λ= 0.71073 Å). For all crystals, frame widths of 0.5^{o} were judged as appropriate, and full hemispheres of data were collected using the Bruker APEX2[a] software suite to carry out overlapping φ and ω scans at different detector (2θ) settings.Empirical absorption corrections based on symmetry-equivalent reflections were applied using the SADABS program,[b] and all calculations were performed using the PC version of the SHELXL program package.[c] On the basis of systematic absences and statistics of intensity distribution, the space group was determined to be $I4_132$ for all crystals of **ZG-*n*N**. Direct methods were used to locate Zn, P, and O atoms in all structures. Since the atomic numbers of Zn and Ga are too close, their occupancies could not be refined freely but constrained to values close to the ICP-AES data. The templates were severely disordered, besides N and adjacent C, none of the organic moieties were ableto be located on difference maps. Unassigned electron densities were removed by using SQUEEZE in PLATON software package.[c] More details are given in CIFs CCDC 1560817-1560824.

[a] Bruker (2010) APEX2. Bruker AXS Inc., Madison, Wisconsin, USA

[b] G. M. Sheldrick (2002). SADABS. University of Göttingen, Germany

[c] G. M. Sheldrick, *ActaCryst.*, 2008, **A64**, 112; (d) A. L. Spek, *ActaCryst.*, 2009, **D65**, 148.

Table S1 Crystallographic data for ZG-*n*N

	ZG-3N-L	**ZG-3N-H**
formula*	$(H_3deta)_{x/3}[Zn_xGa_{1-x}PO_4]$(x = 0.62)	$(H_3deta)_{x/3}[Zn_xGa_{1-x}PO_4]$ (x = 0.63)
fw	183.94	184.25
space group	$I4_132$	$I4_132$
a, Å	18.0307(4)	18.0121(3)
volume, $Å^3$	5861.9(4)	5843.8(3)
Z	48	48
ρcalcd, g cm^{-3}	2.501	2.513
μ, mm^{-1}	5.490	5.502
$<E^2-1>$	0.902	0.897
Reflections collected	20676	18932
Largest diff. peak and hole $eÅ^{-3}$	0.254 and -0.192	0.229 and -0.301
λ, Å	0.71073	0.71073
R1[a] [I > 2sigma(I)]	0.0138	0.0152
*w*R2[b] [I > 2sigma(I)]	0.0424	0.0480
flack parameter x	0.012(14)	0.009(16)
SAV %	33.8 %	33.8 %

	ZG-4N-L	**ZG-4N-H**
formula*	$(H_4teta)_{x/4}[Zn_xGa_{1-x}PO_4]$ (x = 0.60)	$(H_4teta)_{x/4}[Zn_xGa_{1-x}PO_4]$ (x = 0.60)
fw	184.62	184.62
space group	$I4_132$	$I4_132$
a, Å	17.9925(6)	17.9625(5)
volume, $Å^3$	5824.7(6)	5795.6(5)
Z	48	48
ρcalcd, g cm^{-3}	2.526	2.539
μ, mm^{-1}	5.538	5.566
$<E^2-1>$	0.889	0.891
Reflections collected	19721	20358
Largest diff. peak and hole $eÅ^{-3}$	0.251 and -0.169	0.241 and -0.232
λ, Å	0.71073	0.71073
R1[a] [I > 2sigma(I)]	0.0125	0.0152
*w*R2[b] [I > 2sigma(I)]	0.0360	0.0450
flack parameter x	0.014(12)	0.014(15)
SAV %	34.0 %	33.9 %

	ZG-5N-L	**ZG-5N-H**
formula*	$(\mathrm{H_5tepa}\ )_{x/5}[\mathrm{Zn}_x\mathrm{Ga}_{1-x}\mathrm{PO}_4]$ (x = 0.57)	$(\mathrm{H_5tepa}\ )_{x/5}[\mathrm{Zn}_x\mathrm{Ga}_{1-x}\mathrm{PO}_4]$(x = 0.60)
fw	184.37	185.40
space group	$I4_132$	$I4_132$
a, Å	18.023(1)	18.0053(7)
volume, Å^3	5854.2(1)	5837.2(7)
Z	48	48
ρcalcd, g cm^{-3}	2.510	2.532
μ, mm^{-1}	5.528	5.527
$<E^2\text{-}1>$	0.895	0.887
Reflections collected	17342	19587
Largest diff. peak and hole eÅ^{-3}	0.259 and -0.187	0.227 and -0.192
λ, Å	0.71073	0.71073
R1^a [I > 2sigma(I)]	0.0147	0.0131
*w*R2^b [I > 2sigma(I)]	0.0397	0.0357
flack parameter x	0.028(14)	0.017(12)
SAV %	33.8 %	33.8 %

	ZG-6N-L	**ZG-6N-H**
formula*	$(\mathrm{H_6peha})_{x/6}[\mathrm{Zn}_x\mathrm{Ga}_{1-x}\mathrm{PO}_4]$ (x = 0.54)	$(\mathrm{H_6peha})_{x/6}[\mathrm{Zn}_x\mathrm{Ga}_{1-x}\mathrm{PO}_4]$ (x = 0.56)
fw	183.80	184.51
space group	$I4_132$	$I4_132$
a, Å	17.949(3)	17.9470(2)
volume, Å^3	5783(3)	5780.6(2)
Z	48	48
ρcalcd, g cm^{-3}	2.533	2.544
μ, mm^{-1}	5.614	5.604
$<E^2\text{-}1>$	0.886	0.885
Reflections collected	22042	18531
Largest diff. peak and hole eÅ^{-3}	0.233 and -0.168	0.322 and -0.312
λ, Å	0.71073	0.71073
R1^a [I > 2sigma(I)]	0.0115	0.0155
*w*R2^b [I > 2sigma(I)]	0.0333	0.0439
flack parameter x	0.011(11)	0.027(15)
SAV %	33.6 %	33.6 %

*Due to severe disorder problem, electron densities related to organic moieties were removed by using SQUEEZE in PLATON software package. Only the inorganic part $[\mathrm{Zn}_x\mathrm{Ga}_{1-x}\mathrm{PO}_4]$ was refined, and the proposed formula was written with unassigned polyamine for charge balance. The data were all collected at 296 K.

Table S2 ICP-AES results for ZG-*n*N

	Formula	**Zn/Ga**
ZG-3N-L	$(H_3deta)_{x/3}[Zn_xGa_{1-x}PO_4]$ $x = 0.62$	1.6
ZG-3N-H	$(H_3deta)_{x/3}[Zn_xGa_{1-x}PO_4]$ $x = 0.63$	1.7
ZG-4N-L	$(H_4teta)_{x/4}[Zn_xGa_{1-x}PO_4]$ $x = 0.60$	1.5
ZG-4N-H	$(H_4teta)_{x/4}[Zn_xGa_{1-x}PO_4]$ $x = 0.60$	1.5
ZG-5N-L	$(H_5tepa\ )_{x/5}[Zn_xGa_{1-x}PO_4]$ $x = 0.57$	1.3
ZG-5N-H	$(H_5tepa\ )_{x/5}[Zn_xGa_{1-x}PO_4]x = 0.60$	1.5
ZG-6N-L	$(H_6peha)_{x/6}[Zn_xGa_{1-x}PO_4]$ $x = 0.54$	1.2
ZG-6N-H	$(H_6peha)_{x/6}[Zn_xGa_{1-x}PO_4]$ $x = 0.56$	1.3

Table S3 EA results for ZG-*n*N

	C (%)		N (%)		H (%)	
	Cal.	Exp.	Cal.	Exp.	Cal.	Exp.
ZG-3N-L	5.38	5.83	4.72	5.04	1.79	2.36
ZG-3N-H	5.47	5.75	4.79	4.92	1.82	2.24
ZG-4N-L	5.85	5.76	4.55	4.54	1.79	2.21
ZG-4N-H	5.85	5.71	4.55	4.54	1.79	2.15
ZG-5N-L	5.93	6.25	4.33	4.60	1.73	2.07
ZG-5N-H	6.23	6.35	4.53	4.71	1.82	2.29
ZG-6N-L	5.87	5.95	4.16	4.22	1.66	2.16
ZG-6N-H	6.07	6.71	4.25	4.68	1.72	2.24

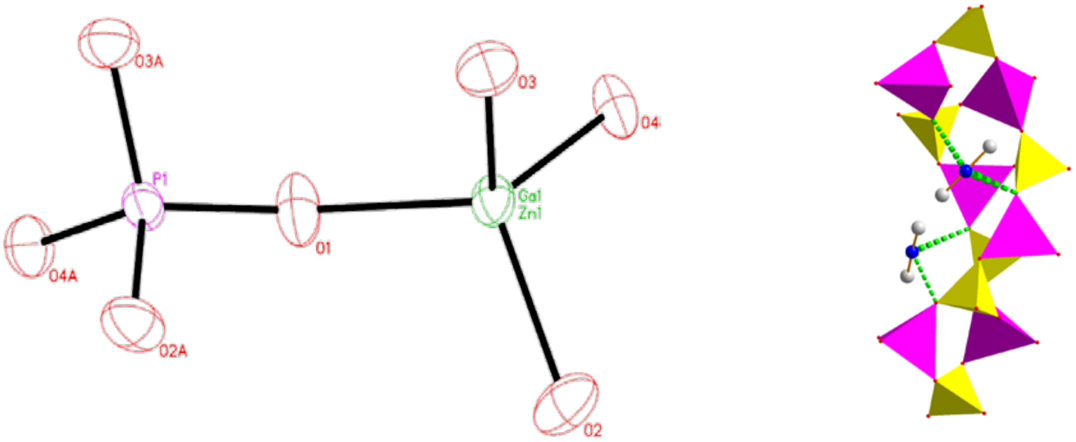


Fig. S1 Structure plots for ZG-*n*N: (left) an ORTEP showing the asymmetric unit, and (right) section of the inorganic helical chain (in polyhedral representation, where Zn/Ga polyhedra in purple and P in yellow) of ZG-3N-160 with organic template moieties (in ball-and-stick drawing, where N atom in blue and C atom in grey). Due to disorderliness of the occluded templates, only ammonium head with an adjacent carbon atoms were given in the plot. The distance ~2.75 Å observed between N atom of the organic and O atom of the inorganic indicates hydrogen bonds (green dotted lines) are likely to occur.

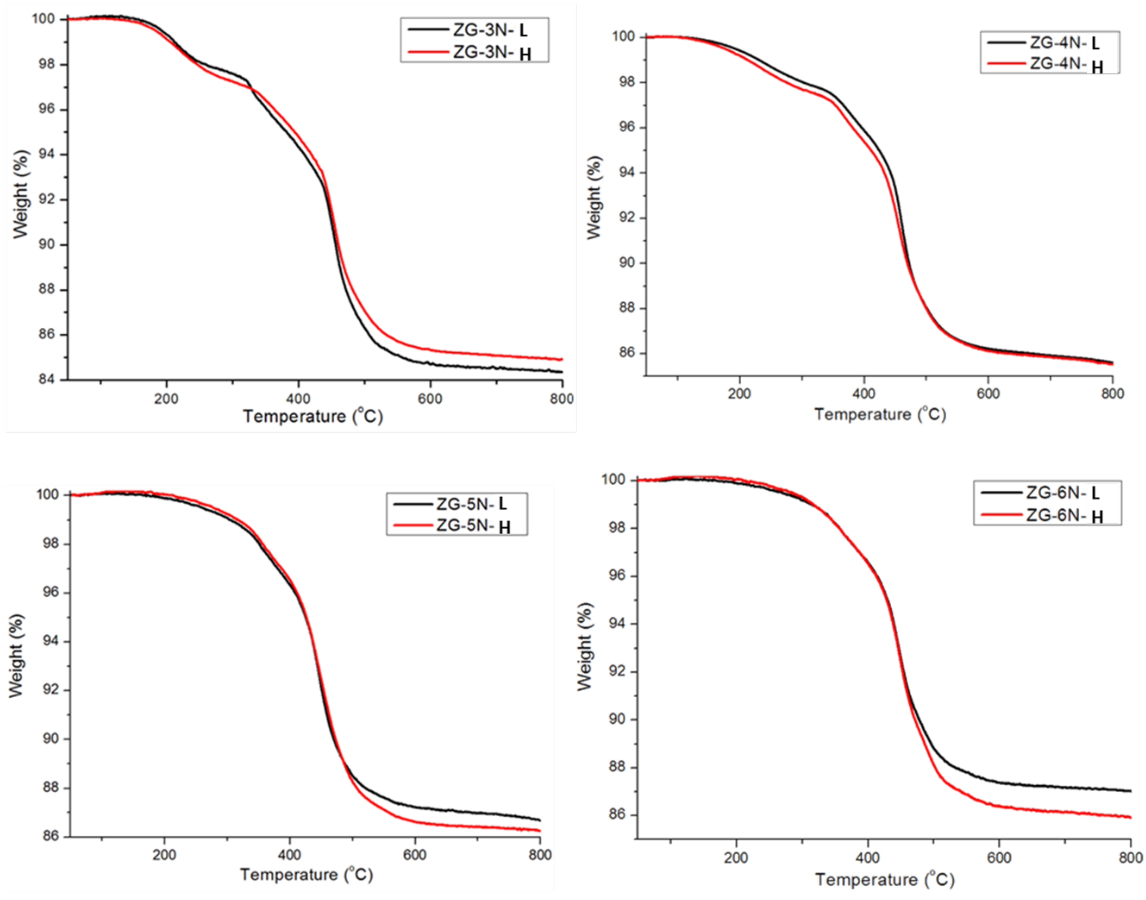
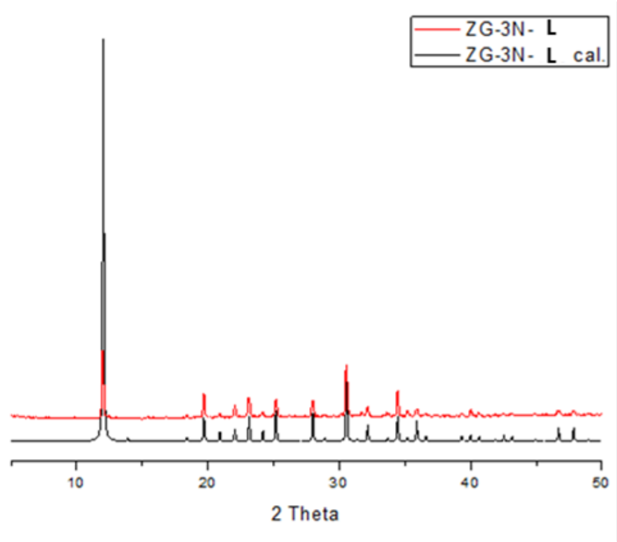
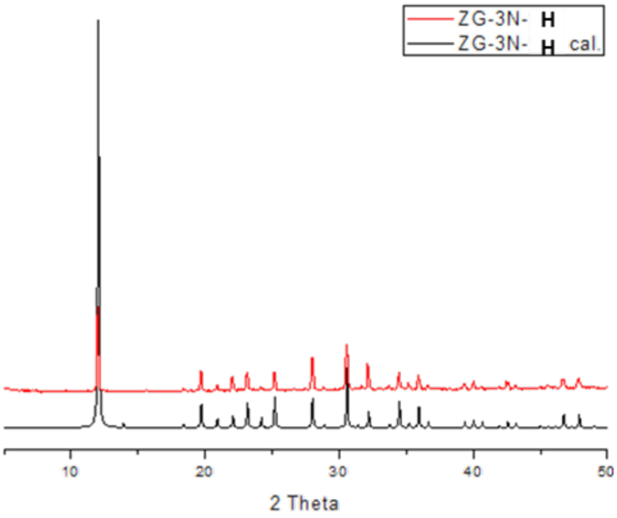
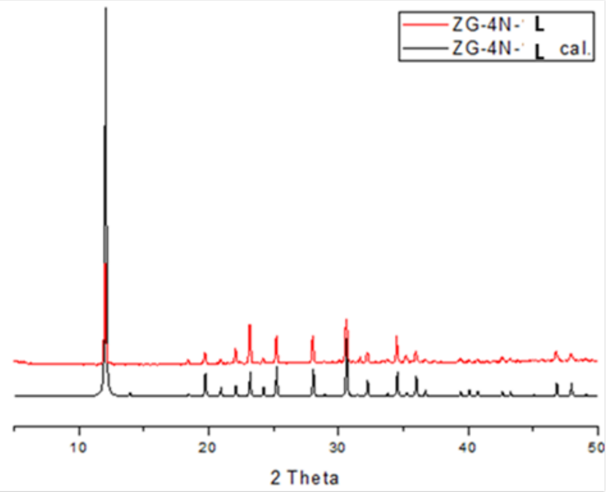
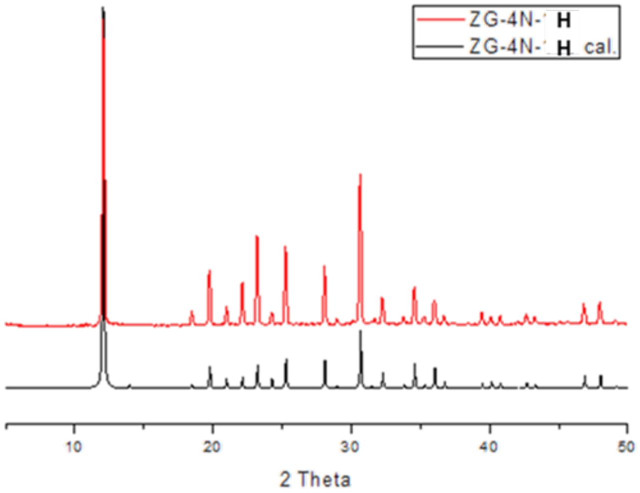


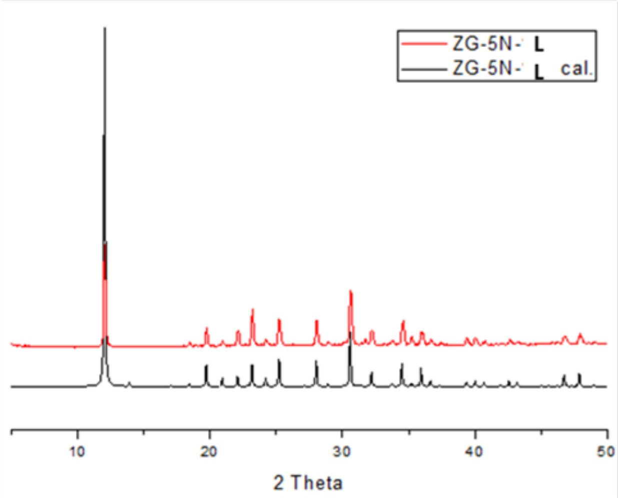
Fig. S2 TGA curve for ZG-*n*N

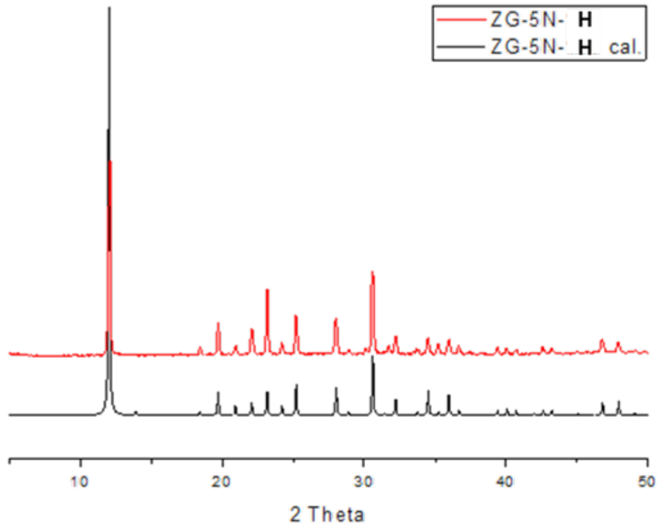

ZG-3N- L
ZG-3N- L cal.
10
20
30
40
50
2 Theta


ZG-3N- H
ZG-3N- H cal.
10
20
30
40
50
2 Theta


ZG-4N- L
ZG-4N- L cal.
10
20
30
40
50
2 Theta


ZG-4N- H
ZG-4N- H cal.
10
20
30
40
50
2 Theta


ZG-5N- L
ZG-5N- L cal.
10
20
30
40
50
2 Theta


ZG-5N- H
ZG-5N- H cal.
10
20
30
40
50
2 Theta

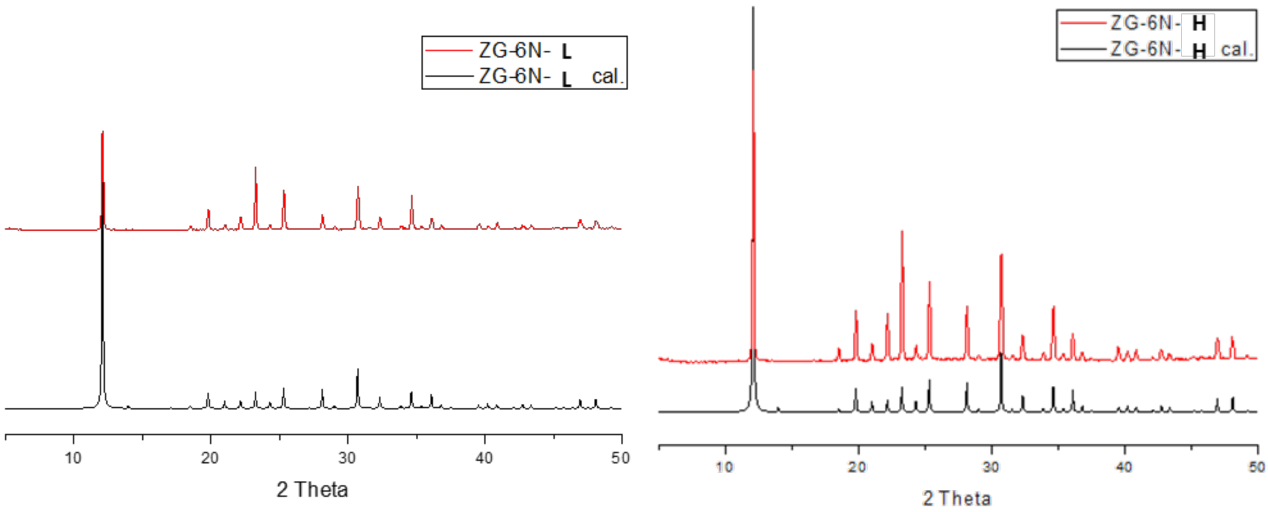
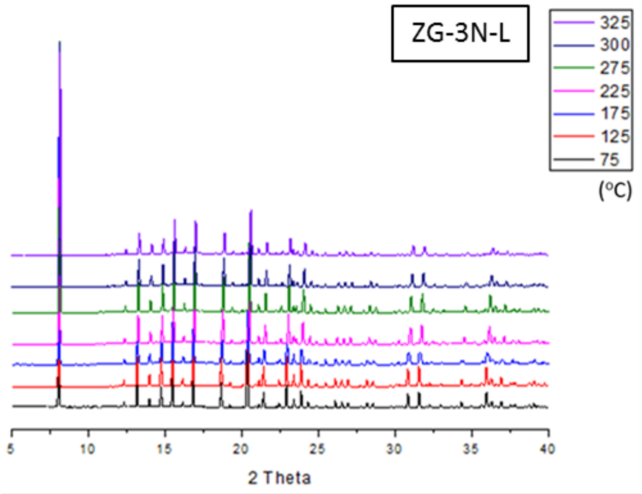
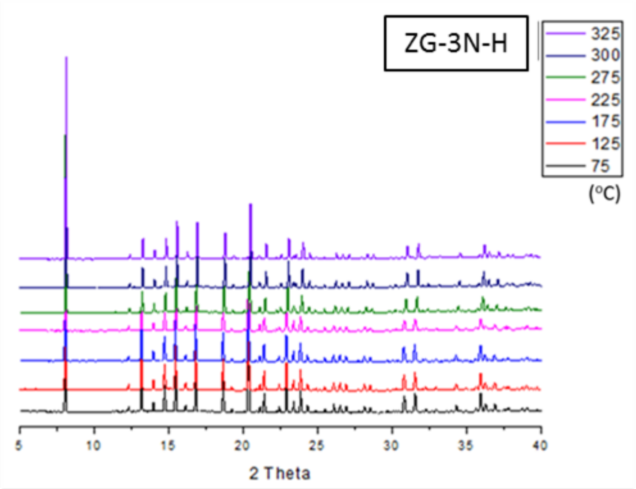
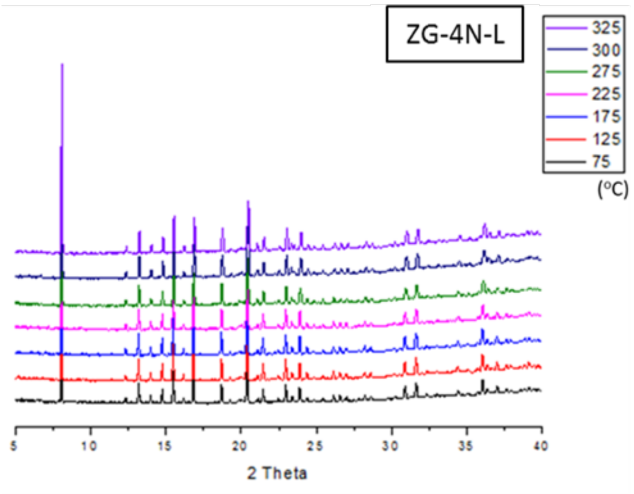
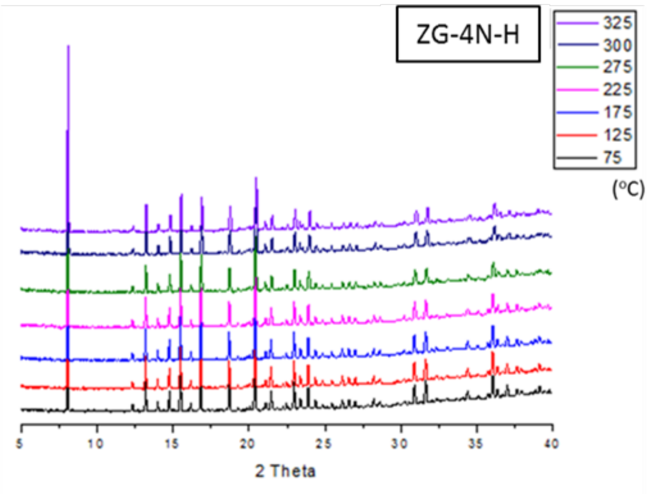


Fig. S3 PXRD patterns for ZG-*n*N. These data were collected with λ= 1.5418 Å









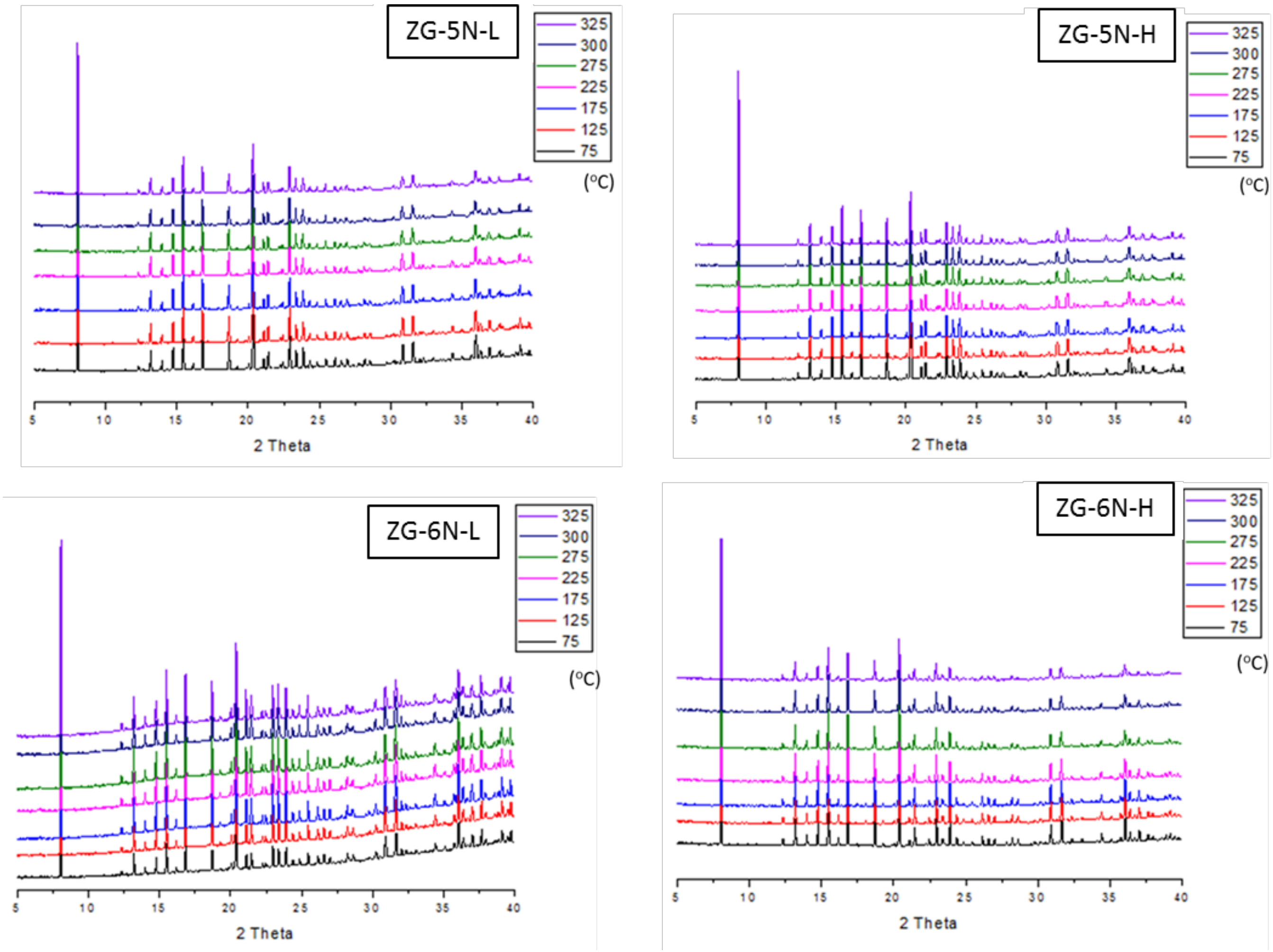


Fig. S4 PXRD patterns at variable temperature for ZG-*n*N. These data were collected with λ= 1.03 Å at NSRRC BL01C2.

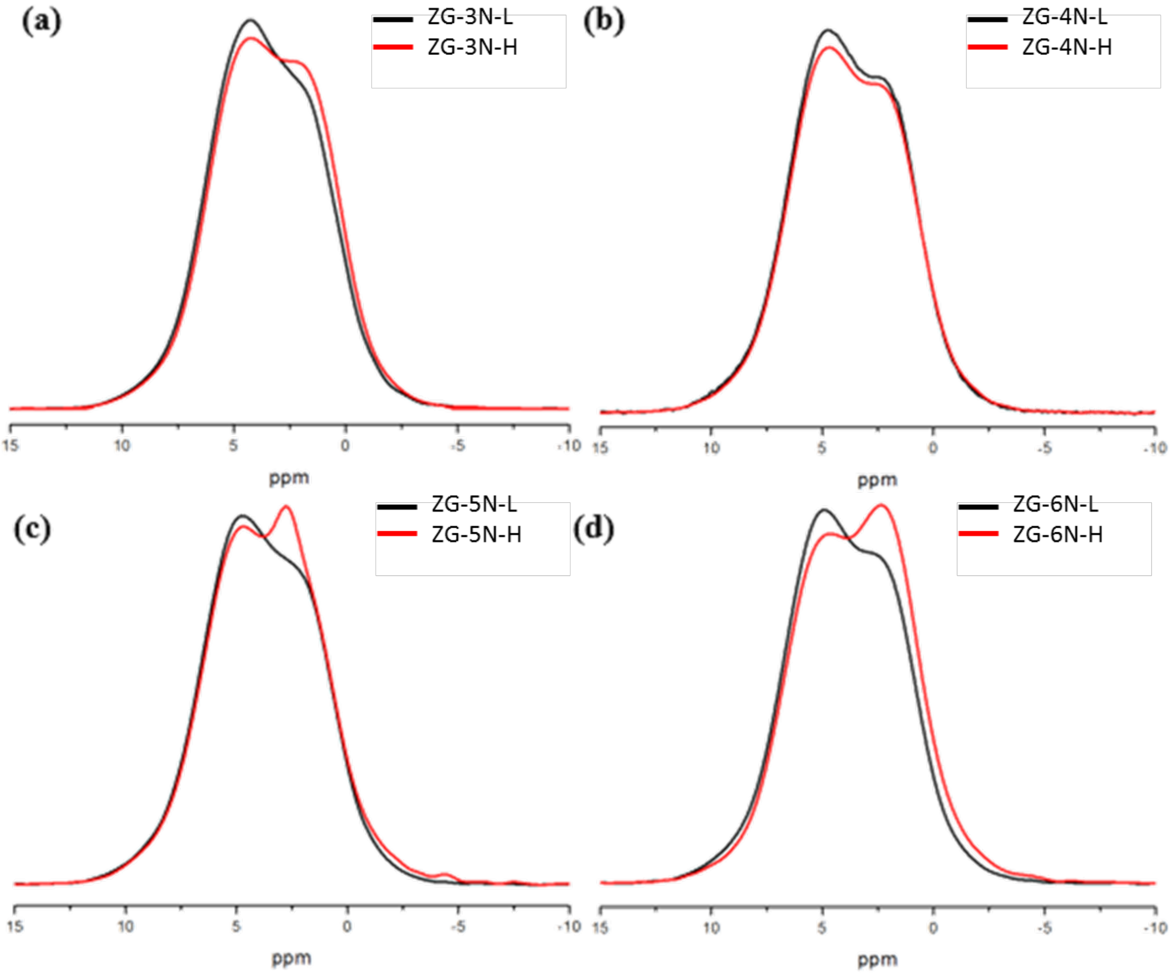


Fig. S5 Solid-state ^{31}P NMR spectra for ZG-*n*N

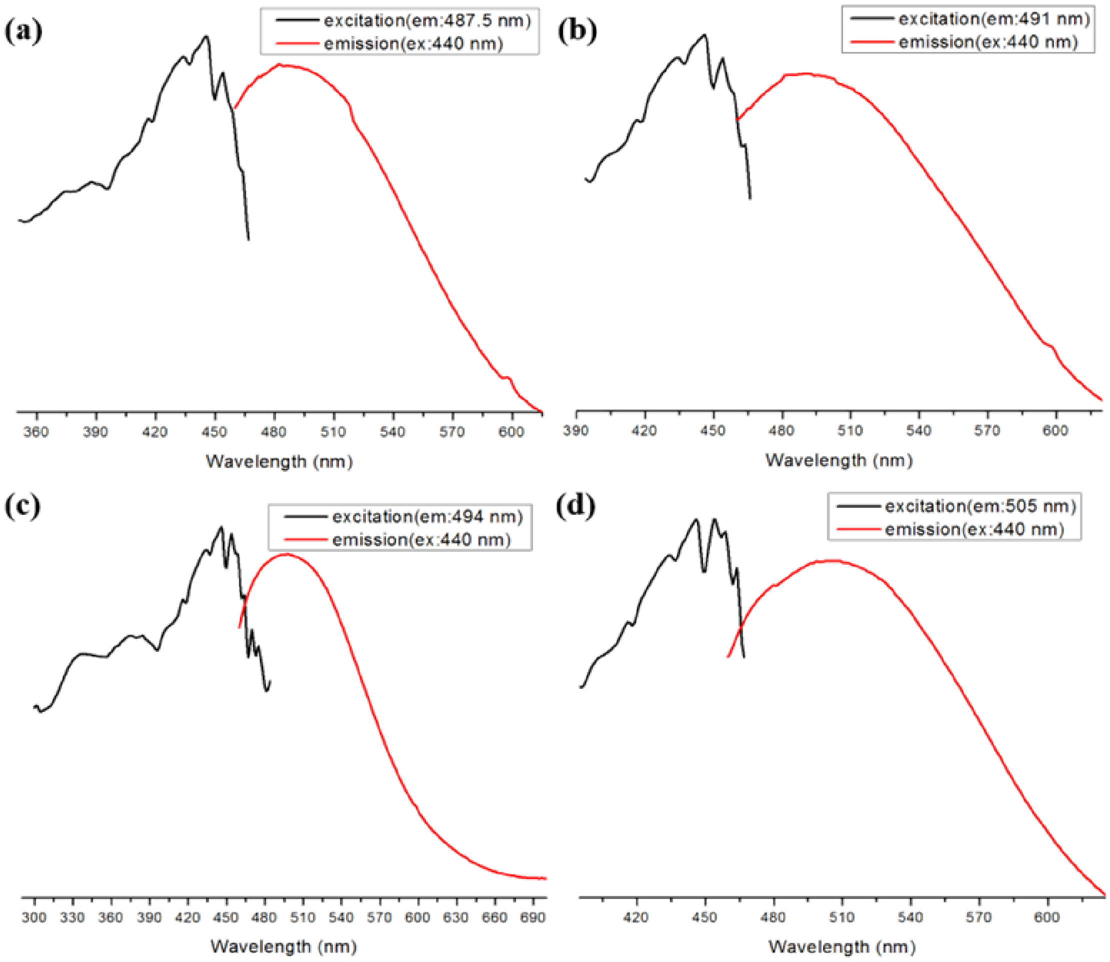


Fig. S6 PL spectra under the excitation of 440 nm for (a) ZG-3N-H (b) ZG-4N-H (c) ZG-5N-H (d) ZG-6N-H. The quantum yield for ZG-H group was largely increased from 10% to 26% when the excitation wavelength was changed from 360 nm to 440 nm.

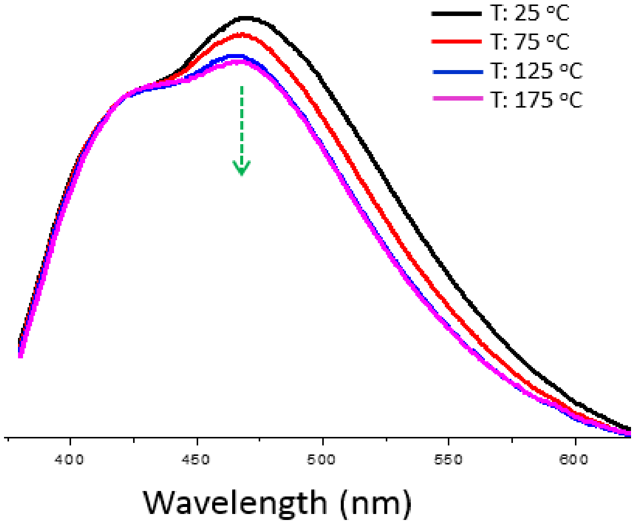


Fig. S7 Normalized PL spectra at variable temperature for ZG-3N-H excited by 360 nm

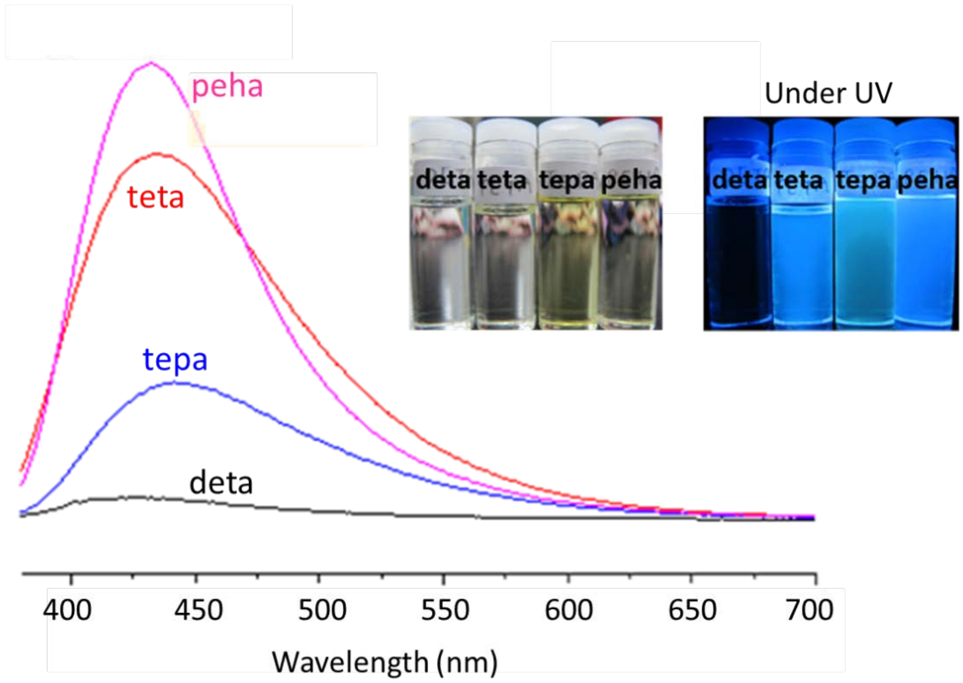


Fig. S8 PL spectra for deta, teta, tepa, and peha under the UV excitation of 360 nm. The samples were prepared by dissolving equal amount of polyamine in water at room temperature.

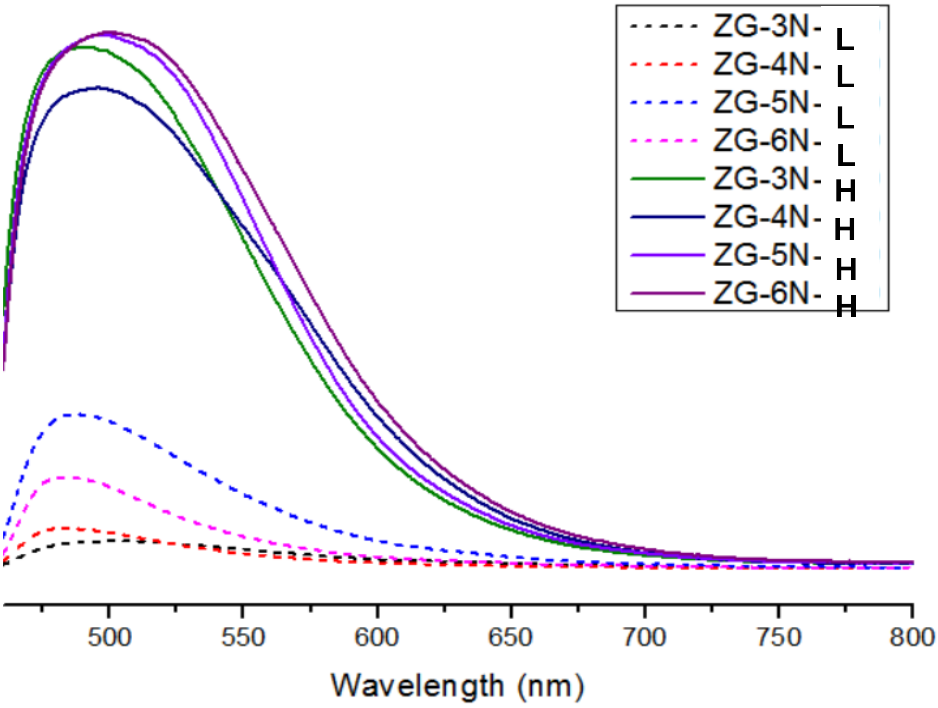


Fig. S9 PL emission spectra for ZG-L and ZG-H samples under theexcitation wavelength of 440 nm. ZG-L and ZG-H show similar emission bands with centers at ca. 500 nm. The intensity of emissions for ZG-H are stronger than that for ZG-L.

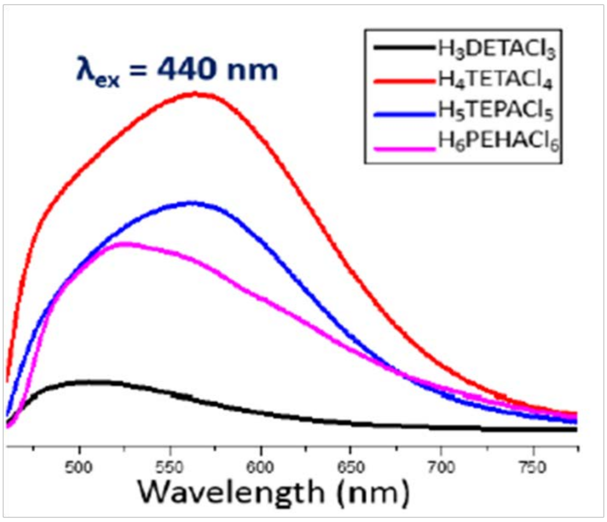


Fig. S10 PL emission spectra for polyamine salts. The samples were prepared by dissolving equal amount of polyamine in water at room temperature.Note that the intensities were much weaker as compared with that of the ZG-*n*N samples.

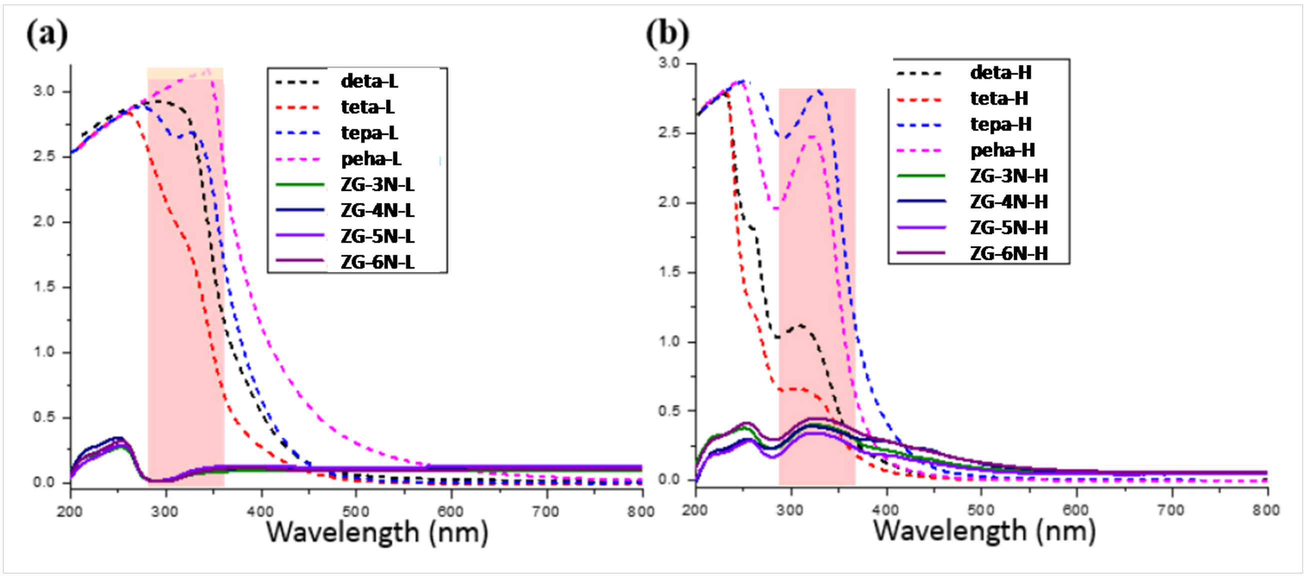


Fig. S11 UV-vis spectra for polyamines in water (dotted line). "L" and "H" indicated the samples that were heated respectively at 160 or 180 ^{o}C for 3 days.

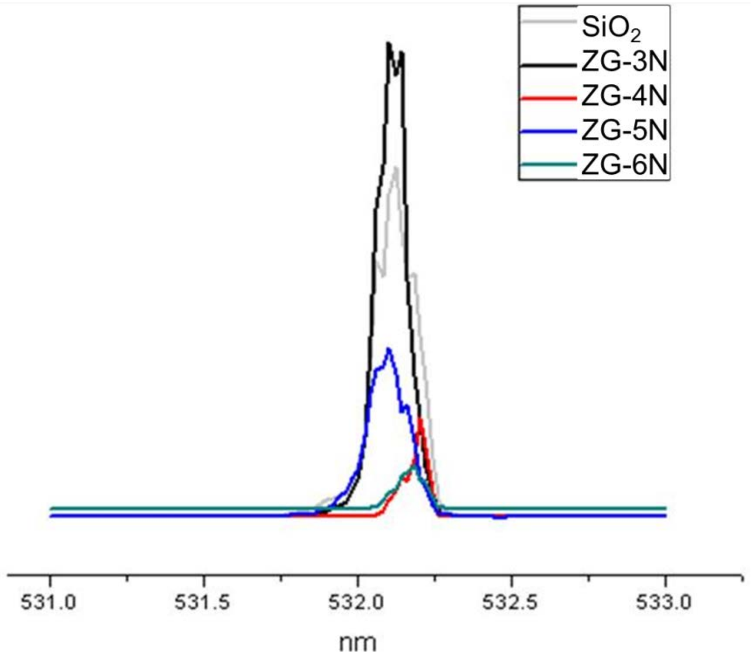


Fig. S12 SHG signals for ZG-*n*N