Supplementary Material for:

Luminescent Carbon Dots in a New Magnesium Aluminophosphate Zeolite

Yanyan Wang,[a] Yi Li,[a] Yan Yan,[a] Jun Xu,[b] Buyuan Guan,[a] Qiang Wang,[b] Jiyang Li*,[a] and Jihong Yu[a]

[a] State Key Laboratory of Inorganic Synthesis and Preparative Chemistry, College of Chemistry, Jilin University, Changchun 130012, P. R. China. Fax: (+86) 431-85168614; E-mail: lijiyang@jlu.edu.cn

[b] State Key Laboratory of Magnetic Resonance and Atomic and Molecular Physics, Wuhan Institute of Physics and Mathematics, the Chinese Academy of Sciences, Wuhan 430071, P. R. China.

1. Syntheses of JU92 and JU92-tem

The reagents and solvents employed in the synthesis were commercially available and used as received without further purification. JU92 was prepared under hydrothermal conditions in the reaction system of MgO-Al_2O_3-P_2O_5-*n*-methylpiperazine(NMP)-H_2O. Typically, pseudoboehmite (Al_2O_3, 62%) and magnesium acetate ($Mg(CH_3COO)_2 \cdot 4H_2O$) were dispersed in a solution of orthophosphoric acid (85 wt%) in water under vigorous stirring at room temperature. Then, NMP ($C_5H_{12}N_2$, Aldrich) was added to this mixture. After stirring for one hour, a homogeneous gel with an overall molar composition of $1.0Al_2O_3$: 0.67MgO: $3.89P_2O_5$: 3.17NMP: $350H_2O$ was formed, which was heated under autogenously pressure at 180 ºC in a 15 mL Teflon-lined stainless steel autoclave for 3 days. The white crystals were washed in distilled water and dried at room temperature overnight. The product was recovered with a yield of 86 wt% based on Al.

The as-synthesized product was calcined upon different temperatures. JU92 was placed into a normal furnace and heated from RT to different temperature, such as 300, 470, 550, 600, 650 at a temperature ramp rate of 1 ºC min^{-1} in air and a 4 h isothermal hold at the respective temperature. The carbonization of SDAs was occurring in this process, and the degree of carbonization depended on the heating temperature. The calcined samples were denoted as JU92-tem (tem = 300, 470, 550, 600 and 650). JU92-550-10, JU92-550-12 and JU92-550-24 were prepared by calcined JU92 at a temperature ramp rate of 1 ºC min^{-1} in air from RT to different temperature, and isothermal hold for 10 h or 12 h or 24 h.

2. Experimental characterization

Powder X-ray diffraction (PXRD) and high temperature powder X-ray diffraction (HT-PXRD) data were collected on a Rigaku D/max-2550 diffractometer with Cu Kα radiation (λ = 1.5418 Å). For HT-PXRD, the as-synthesized sample was smeared on a platinum filament and data were collected from room temperature to 700 °C with a heating rate of 10 °C min^{-1}. Inductively coupled plasma (ICP) analysis was performed on a Perkin-Elmer Optima 3300DV spectrometer. Elemental analysis was conducted on a Perkin-Elmer 2400 elemental analyzer. Thermogravimetric analysis (TGA) was carried out on a TA Q500 analyzer in air with a heating rate of 10 °C min^{-1} from RT to 800 °C. Notably, a pretreatment of heating JU92-300 and JU92-470 at 300 °C for 1 h was

performed to remove the adsorbed water before TGA analysis. The TEM and HRTEM images were taken on a JEOL JEM-3010 transmission electron microscope operating at an accelerating voltage of 300 kV. The X-ray photoelectron spectra (XPS) were recorded on a VG ESCALAB MK II electron spectrometer.

^{13}C solid-state NMR were performed at room temperature on an InfinityPlus-400 spectrometer operating at B_0 = 9.7T. ^{25}Mg NMR experiments were performed using a Varian 600 spectrometer operating at a magnetic field strength of 14.1 T. The resonance frequencies in this field strength were 36.72 MHz. ^{25}Mg static DFS-QCPMG[1] spectra were acquired with a chemagnetics 7.5 mm MAS probe. Double frequency sweep (DFS) was used as preparatory sequences to enhance the sensitivity of ^{25}Mg spectra. A selective $\pi/2$ pulse width of 9 μs and recycle delay of 0.5 s were applied. The interpulse and inter-acquisition delays were set to 90 μs. The number of MG loops was 14. The acquisition time for each echo was 1.1 ms. ^{25}Mg chemical shifts were referenced to a 1.0 M $MgCl_2$ aqueous solution. The DFS-QCPMG spectra were simulated analytically using the DMFIT software package.[2]

Fluorescence spectra were recorded on Fluromax-4 spectrophotometer (HORIBA), with excitation and emission slit widths of 1.0 nm or 3.0 nm. The absolute fluorescence quantum yields were measured on an Edinburgh FLS920 steady-state fluorimeter (excited at 365 nm). The external photoluminescent quantum yields ($ø$) were measured at room temperature through the Wrighton-Ginley-Morse technique and calculated using the following equation: $ø = E/(R_{std}\text{-Rsmpl})$, where E is the integrated area under the emission spectrum of the composite phosphor, and R_{std} and R_{smpl} are the integrated areas under the diffuse reflectance spectra of the reflecting standard and the composite phosphor, respectively, at a fixed excitation wavelength. The procedure for the quantum yield estimation is as follows: (1) measurement of the diffuse reflectance spectrum of the reflecting background; (2) simultaneous measurement of the diffuse reflectance and emission spectra of the ground composite phosphors; (3) integration of the obtained spectra and calculation of the quantum yield using the above equation.

3. Single-crystal X-ray diffraction

Suitable single crystals of JU92 and JU92-300 with dimensions of 0.17 × 0.15 × 0.12 mm^3 and 0.32 × 0.22 × 0.18 mm^3, respectively, were selected for single-crystal X-ray diffraction analyses.

The intensity data were collected on a Bruker SMART APEX Ⅱ CCD diffractometer by oscillation scans using graphite-monochromated Mo Kα radiation (λ = 0.71073 Å) at temperature of 23±2 °C. Cell refinement and data reduction were accomplished with the SAINT processing program.[3] The structures were solved in the space group $P2_1/n$ and $P2_1/c$, respectively, by direct methods and refined by full matrix least-squares technique with the SHELXTL crystallographic software package.[4] The heaviest atoms of Al, Mg, P and O could be unambiguously located, and the C and N atoms were subsequently located in the difference Fourier maps. It should be noted that the C(3) atom of NMP in JU92 was disordered over two positions C(3) and C(3)' with the same occupancy, and O(18) atom has a half occupancy. For JU92-300, the NMP molecule was disordered over two positions with C(4) and N(2) atoms occupying the same position. All non-hydrogen atoms were refined anisotropically. Experimental details for the structure determination are presented in Table S2. The atomic coordinates are presented in Table S3. CCDC 922472 (JU92) and CCDC 922473 (JU92-300) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Supplementary References

[1] R. W. Schurko, I. Hung and C. M. Widdifield, *Chem. Phys. Lett.* 2003, **379**, 1.

[2] D. Massiot, F. Fayon, M. Capron, I. King, S. Le Calvé, B. Alonso, J.-O. Durand, B. Bujoli, Z. Gan and G. Hoatson, *Magn. Reson. Chem.* 2002, **40**, 70.

[3] SAINT, Bruker AXS Inc., 5465 East Cheryl Parkway, Madison, WI, 53711–5373, USA, 2000.

[4] SHELXTL, Bruker AXS Inc., 5465 East Cheryl Parkway, Madison, WI, 53711–5373, USA, 2000.

Table S1. Compositional and TG analyses for JU92 and its calcined samples.

		Mg (wt %)	Al (wt %)	P (wt %)	C (wt %)	H (wt %)	N (wt %)	TG (wt %)
JU92	Exp.	4.28	14.3	22.0	5.24	1.73	2.41	10.89
	Cal.	4.25	14.34	21.95	5.31	1.77	2.48	13.81
JU92-300	Exp.	4.45	14.9	22.9	5.53	1.37	2.52	5.96
	Cal.	4.48	15.11	23.13	5.60	1.31	2.61	9.51
JU92-470	Exp.	–	–	–	4.66	1.02	0.32	2.02
JU92-550	Exp.	–	–	–	3.68	1.36	0.20	–
JU92-600	Exp.	–	–	–	3.78	1.27	0.21	–
JU92-650	Exp.	–	–	–	3.42	1.27	0.21	–

Table S2. Crystal data and structure refinement for JU92 and JU92-300.[a]

compounds	JU92	JU92-300
empirical formula	$MgAl_3P_4O_{17.5}C_{2.5}H_{10}N$	$MgAl_3P_4O_{16}C_{2.5}H_7N$
formula weight	563.24	536.22
temperature	296(2) K	293(2) K
wavelength(Å)	0.71073	0.71073
crystal system, space group	Monoclinic, $P2_1/n$	Monoclinic, $P2_1/c$
unit cell dimensions		
a (Å)	8.2208(6)	8.4084(5)
b (Å)	14.7180(11)	14.4558(9)
c (Å)	14.2654(11)	16.3592(8)
α (deg)	90	90
β (deg)	91.5330(10)	120.037(2)
γ (deg)	90	90
volume($Å^3$)	1725.4(2)	1721.42(17)
Z, calculated density(mg/m^3)	4, 2.168	4, 2.069
absorption coefficient(mm^{-1})	0.722	0.712
F(000)	1132	1072
crystal size(mm^3)	0.17 × 0.15 × 0.12	0.32 × 0.22 × 0.18
θ range(°) for data collection	1.99–28.35	2.01–28.31
limiting indices	$-10 \le h \le 10$, $-19 \le k \le 16$, $-18 \le l \le 19$	$-11 \le h \le 11$, $-19 \le k \le 13$, $-20 \le l \le 21$
reflections collected/unique	12541/4292, [R(int) = 0.0474]	12471/4274, [R(int) = 0.0363]
completeness to θ (%)	28.35, 99.6	28.31, 99.9
absorption correction	semi-empirical from equivalents	semi-empirical from equivalents
max and min transmission	0.7457 and 0.6503	0.8825 and 0.8042
refinement method	full-matrix least-squares on F^2	full-matrix least-squares on F^2
data/restraints/parameters	4292/0/271	4274/36/262
goodness-of-fit on F^2	1.097	1.078
final R indices [$I > 2\sigma(I)$]	$R_1 = 0.0483$, $wR_2 = 0.1324$	$R_1 = 0.0434$, $wR_2 = 0.1101$
R indices (all data)	$R_1 = 0.0666$, $wR_2 = 0.1457$	$R_1 = 0.0578$, $wR_2 = 0.1166$
largest diff. peak and hole ($eÅ^{-3}$)	0.819 and -0.553	0.768 and -0.504

[a] $R_1 = \sum(\Delta F/\sum(F_o))$, $wR_2 = (\sum[w(F_o^2 - F_c^2)])/\sum[w(F_o^2)^2]^{1/2}$ and $w = 1/\sigma^2(F_o^2)$.

Table S3. Selected bond lengths [Å] and angles [deg] for JU92 and JU92-300.

JU92		JU92-300	
P(1)-O(3)	1.482(3)	P(1)-O(7)	1.508(3)
P(1)-O(4)	1.511(3)	P(1)-O(13)	1.511(3)
P(1)-O(2)	1.520(3)	P(1)-O(16)	1.515(3)
P(1)-O(1)	1.538(3)	P(1)-O(6)	1.531(3)
P(2)-O(5)	1.495(3)	P(2)-O(1)	1.493(3)
P(2)-O(8)	1.509(3)	P(2)-O(2)	1.528(2)
P(2)-O(6)	1.526(3)	P(2)-O(5)	1.534(2)
P(2)-O(7)	1.529(3)	P(2)-O(3)	1.536(2)
P(3)-O(11)	1.492(3)	P(3)-O(15)	1.492(3)
P(3)-O(12)	1.528(3)	P(3)-O(12)	1.520(3)
P(3)-O(13)	1.527(3)	P(3)-O(14)	1.527(3)
P(3)-O(9)	1.528(3)	P(3)-O(8)	1.540(2)
P(4)-O(16)	1.494(3)	P(4)-O(9)	1.492(3)
P(4)-O(10)#1	1.533(3)	P(4)-O(10)	1.520(2)
P(4)-O(14)	1.538(2)	P(4)-O(4)	1.529(3)
P(4)-O(15)	1.538(3)	P(4)-O(11)	1.538(3)
Al(1)-O(8)#2	1.707(3)	Al(1)-O(3)	1.710(3)
Al(1)-O(9)	1.719(3)	Al(1)-O(16)	1.718(3)
Al(1)-O(10)	1.722(3)	Al(1)-O(11)	1.726(3)
Al(1)-O(2)#3	1.723(3)	Al(1)-O(8)	1.746(2)
Al(2)-O(13)#4	1.720(3)	Al(2)-O(10)#2	1.715(2)
Al(2)-O(1)	1.726(3)	Al(2)-O(12)	1.725(3)
Al(2)-O(6)#5	1.733(3)	Al(2)-O(2)#3	1.726(3)
Al(2)-O(14)	1.738(3)	Al(2)-O(6)	1.745(3)
Al(3)-O(4)#6	1.715(3)	Al(3)-O(13)	1.717(3)
Al(3)-O(12)	1.718(3)	Al(3)-O(4)#4	1.721(3)
Al(3)-O(15)	1.730(3)	Al(3)-O(5)#2	1.725(2)
Al(3)-O(7)#5	1.731(3)	Al(3)-O(14)#5	1.731(3)
Mg(1)-O(11)#1	1.977(3)	Mg(1)-O(9)	1.907(3)
Mg(1)-O(3)#6	1.995(3)	Mg(1)-O(1)#1	1.918(3)
Mg(1)-O(5)	2.038(3)	Mg(1)-O(15)#6	1.965(3)
Mg(1)-O(16)	2.052(3)	Mg(1)-O(7)	1.967(3)
Mg(1)-O(17)	2.110(3)	N(1)-C(1)#12	1.408(9)
Mg(1)-O(18)	2.367(6)	N(1)-C(4)	1.437(11)
N(1)-C(1)	1.492(7)	N(1)-C(1)	1.652(11)
N(1)-C(2)#11	1.496(7)	N(2)-C(3)	1.387(13)
N(1)-C(3)	1.567(14)	N(2)-C(2)	1.496(12)
C(1)-C(2)	1.490(9)	C(1)-C(3)#12	1.508(16)
		C(1)-C(2)	1.509(13)
O(3)-P(1)-O(4)	110.7(2)		
O(3)-P(1)-O(2)	111.3(2)	O(7)-P(1)-O(13)	111.60(16)
O(4)-P(1)-O(2)	107.9(2)	O(7)-P(1)-O(16)	110.70(16)

O(3)-P(1)-O(1)	112.32(17)	O(13)-P(1)-O(16)	108.24(17)
O(4)-P(1)-O(1)	106.90(18)	O(7)-P(1)-O(6)	109.53(16)
O(2)-P(1)-O(1)	107.51(16)	O(13)-P(1)-O(6)	106.32(16)
O(5)-P(2)-O(8)	110.2(2)	O(16)-P(1)-O(6)	110.35(15)
O(5)-P(2)-O(6)	111.68(16)	O(1)-P(2)-O(2)	111.11(16)
O(8)-P(2)-O(6)	108.10(17)	O(1)-P(2)-O(5)	111.51(15)
O(5)-P(2)-O(7)	110.83(17)	O(2)-P(2)-O(5)	107.78(14)
O(8)-P(2)-O(7)	106.0(2)	O(1)-P(2)-O(3)	112.27(16)
O(6)-P(2)-O(7)	109.77(17)	O(2)-P(2)-O(3)	107.46(15)
O(11)-P(3)-O(12)	109.63(16)	O(5)-P(2)-O(3)	106.45(14)
O(11)-P(3)-O(13)	112.44(17)	O(15)-P(3)-O(12)	111.69(16)
O(12)-P(3)-O(13)	107.86(17)	O(15)-P(3)-O(14)	111.86(17)
O(11)-P(3)-O(9)	112.43(16)	O(12)-P(3)-O(14)	108.02(16)
O(12)-P(3)-O(9)	107.30(16)	O(15)-P(3)-O(8)	111.44(15)
O(13)-P(3)-O(9)	106.94(16)	O(12)-P(3)-O(8)	108.51(15)
O(16)-P(4)-O(10)#1	112.13(17)	O(14)-P(3)-O(8)	105.02(14)
O(16)-P(4)-O(14)	111.27(15)	O(9)-P(4)-O(10)	111.81(15)
O(10)#1-P(4)-O(14)	104.90(15)	O(9)-P(4)-O(4)	112.35(16)
O(16)-P(4)-O(15)	112.12(15)	O(10)-P(4)-O(4)	107.24(14)
O(10)#1-P(4)-O(15)	108.16(16)	O(9)-P(4)-O(11)	110.40(16)
O(14)-P(4)-O(15)	107.90(15)	O(10)-P(4)-O(11)	107.79(16)
O(8)#2-Al(1)-O(9)	107.75(15)	O(4)-P(4)-O(11)	107.00(15)
O(8)#2-Al(1)-O(10)	107.59(17)	O(3)-Al(1)-O(16)	109.38(14)
O(9)-Al(1)-O(10)	111.58(14)	O(3)-Al(1)-O(11)	112.09(14)
O(8)#2-Al(1)-O(2)#3	110.7(2)	O(16)-Al(1)-O(11)	113.67(15)
O(9)-Al(1)-O(2)#3	109.47(14)	O(3)-Al(1)-O(8)	106.94(13)
O(10)-Al(1)-O(2)#3	109.76(16)	O(16)-Al(1)-O(8)	108.65(13)
O(13)#4-Al(2)-O(1)	111.44(15)	O(11)-Al(1)-O(8)	105.79(13)
O(13)#4-Al(2)-O(6)#5	113.52(15)	O(10)#2-Al(2)-O(12)	106.64(14)
O(1)-Al(2)-O(6)#5	108.68(14)	O(10)#2-Al(2)-O(2)#3	110.83(13)
O(13)#4-Al(2)-O(14)	105.70(14)	O(12)-Al(2)-O(2)#3	113.37(14)
O(1)-Al(2)-O(14)	107.11(13)	O(10)#2-Al(2)-O(6)	112.66(14)
O(6)#5-Al(2)-O(14)	110.17(14)	O(12)-Al(2)-O(6)	108.37(13)
O(4)#6-Al(3)-O(12)	110.07(16)	O(2)#3-Al(2)-O(6)	105.08(13)
O(4)#6-Al(3)-O(15)	115.07(16)	O(13)-Al(3)-O(4)#4	110.06(14)
O(12)-Al(3)-O(15)	106.19(14)	O(13)-Al(3)-O(5)#2	110.74(13)
O(4)#6-Al(3)-O(7)#5	107.05(19)	O(4)#4-Al(3)-O(5)#2	107.38(13)
O(12)-Al(3)-O(7)#5	109.92(15)	O(13)-Al(3)-O(14)#5	105.56(15)
O(15)-Al(3)-O(7)#5	108.50(14)	O(4)#4-Al(3)-O(14)#5	113.26(14)
O(11)#1-Mg(1)-O(3)#6	100.42(16)	O(5)#2-Al(3)-O(14)#5	109.87(14)
O(11)#1-Mg(1)-O(5)	103.84(13)	O(9)-Mg(1)-O(1)#1	111.83(13)
O(3)#6-Mg(1)-O(5)	155.36(17)	O(9)-Mg(1)-O(15)#6	107.91(13)
O(11)#1-Mg(1)-O(16)	98.89(12)	O(9)-Mg(1)-O(7)	114.67(12)
O(3)#6-Mg(1)-O(16)	94.51(13)	O(1)#1-Mg(1)-O(7)	119.17(13)

O(5)-Mg(1)-O(16)	86.05(12)	O(15)#6-Mg(1)-O(7)	95.83(13)
O(11)#1-Mg(1)-O(17)	94.18(13)		
O(3)#6-Mg(1)-O(17)	84.99(13)		
O(5)-Mg(1)-O(17)	88.94(12)		
O(16)-Mg(1)-O(17)	166.78(13)		
O(11)#1-Mg(1)-O(18)	172.13(18)		
O(3)#6-Mg(1)-O(18)	72.4(2)		
O(5)-Mg(1)-O(18)	83.15(19)		
O(16)-Mg(1)-O(18)	85.06(17)		
O(17)-Mg(1)-O(18)	82.20(18)		

For JU92: Symmetry transformations used to generate equivalent atoms: #1 -x,-y+1,-z+3 #2 -x-1,-y+1,-z+3 #3 x,y,z+1 #4 x-1/2,-y+1/2,z-1/2 #5 -x-1/2,y-1/2,-z+5/2 #6 x-1/2,-y+1/2,z+1/2 #7 x,y,z-1 #8 x+1/2,-y+1/2,z-1/2 #9 -x-1/2,y+1/2,-z+5/2 #10 x+1/2,-y+1/2,z+1/2 #11 -x-1,-y+1,-z+2

For JU92-300: Symmetry transformations used to generate equivalent atoms: #1 -x+2,-y+1,-z+1 #2 x,-y+3/2,z-1/2 #3 x-1,-y+3/2,z-1/2 #4 x+1,y,z #5 -x+2,y-1/2,-z+1/2 #6 -x+1,y-1/2,-z+1/2 #7 x+1,-y+3/2,z+1/2 #8 x-1,y,z #9 x,-y+3/2,z+1/2 #10 -x+2,y+1/2,-z+1/2 #11 -x+1,y+1/2,-z+1/2 #12 -x+1,-y+2,-z+1

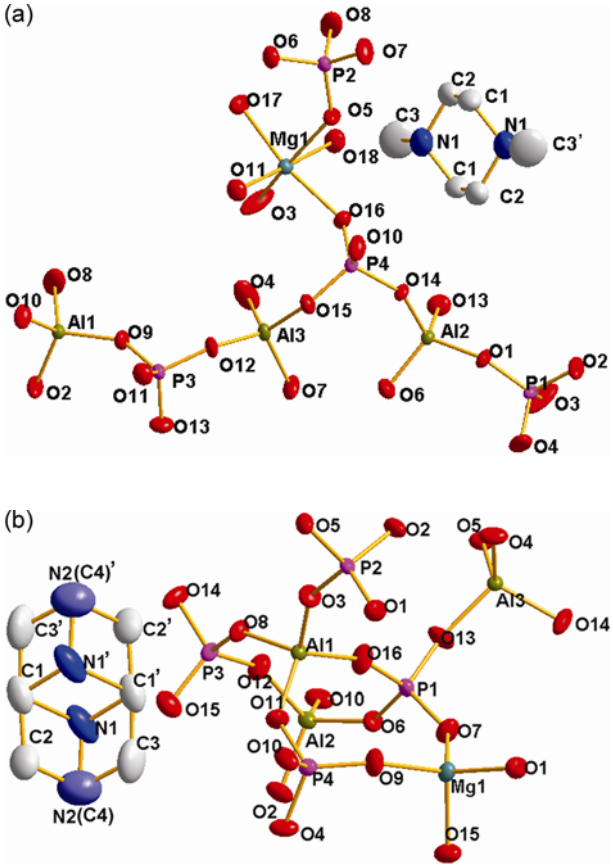


Figure S1. Thermal ellipsoids of (a) JU92 and (b) JU92-300 given at 50% probability, showing the atomic labelling scheme.

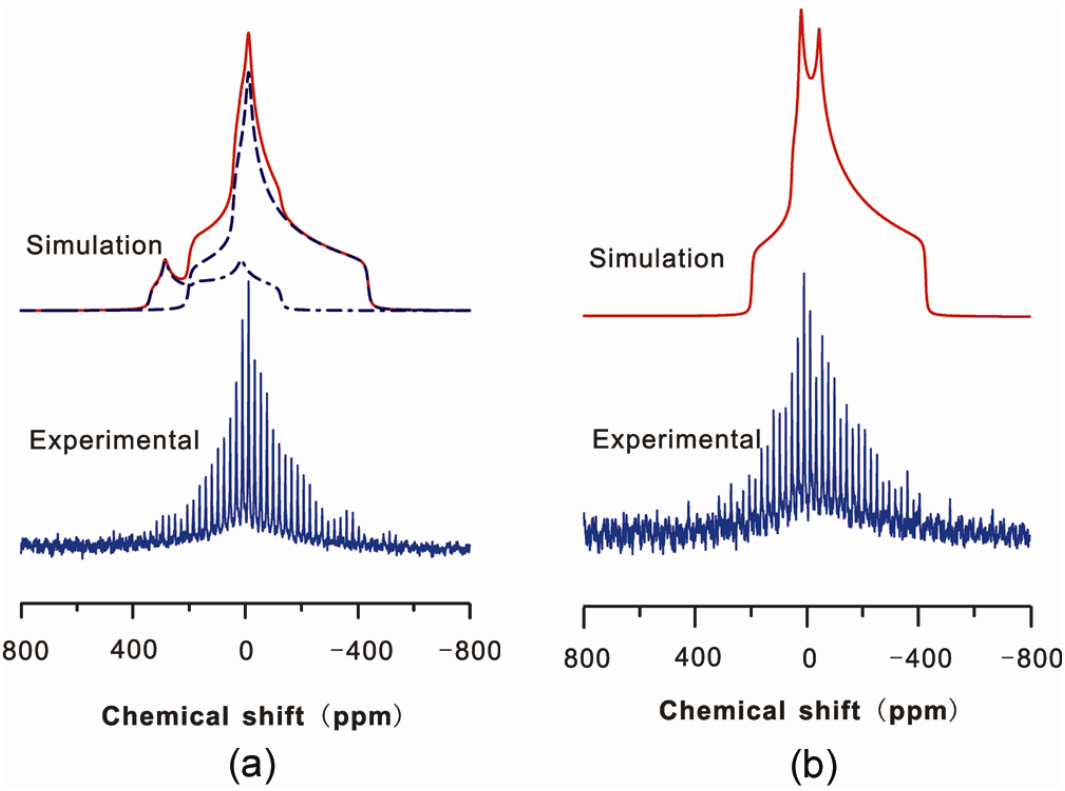


Figure S2 Experimental (down) and simulated (up) ^{25}Mg static DFS-QCPMG spectra of (a) JU92 and (b) JU92-470.

The simulation of ^{25}Mg static NMR spectrum of JU92 gives two resonances with different second-order quadrupolar coupling broadening (δ_{iso} = -11.24 ppm, C_Q = 3.79 MHz, η_Q = 1; and δ_{iso} = 180 ppm, C_Q = 3.99 MHz, η_Q = 0.3), suggesting the existence of two kinds of coordination modes of Mg atoms in JU92. As for JU92-470, only one single resonance with second-order quadrupolar coupling broadening (δ_{iso} = -10.38 ppm, C_Q = 3.859 MHz, η_Q = 0.85) is observed, which is corresponding to the 4-coordinated Mg in the framework.

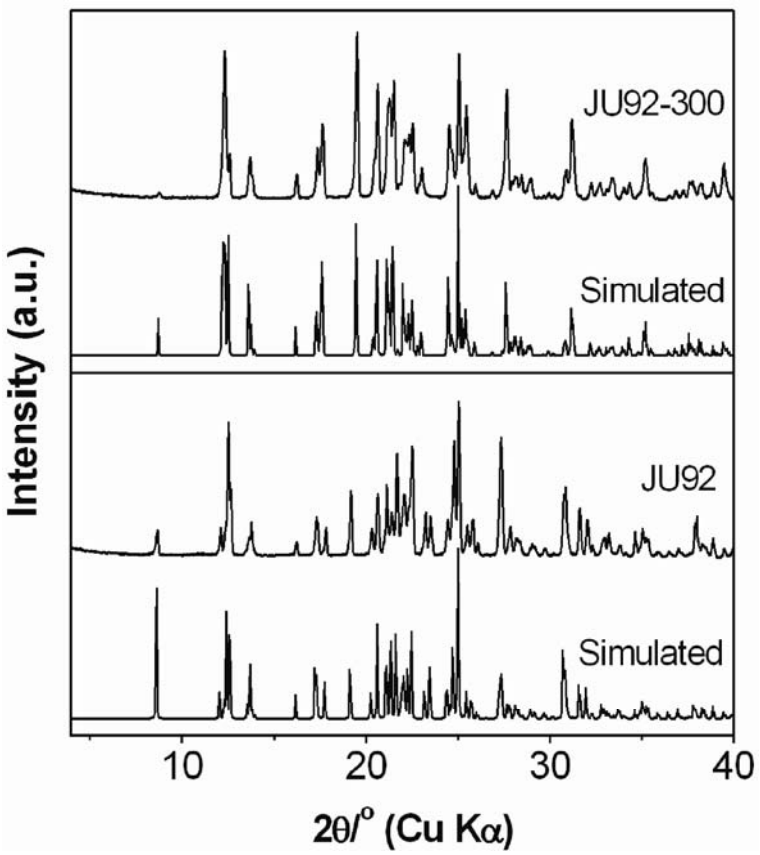


Figure S3. Experimental and simulated PXRD patterns of JU92 and JU92-300.

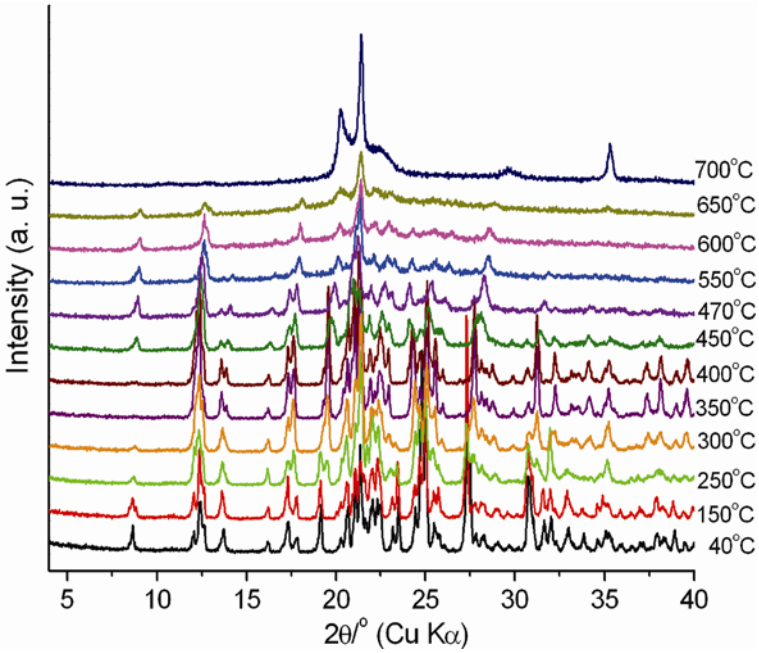


Figure S4. HT-PXRD patterns of JU92 with a heating rate of 10 °C min^{-1} from room temperature to 700 °C.

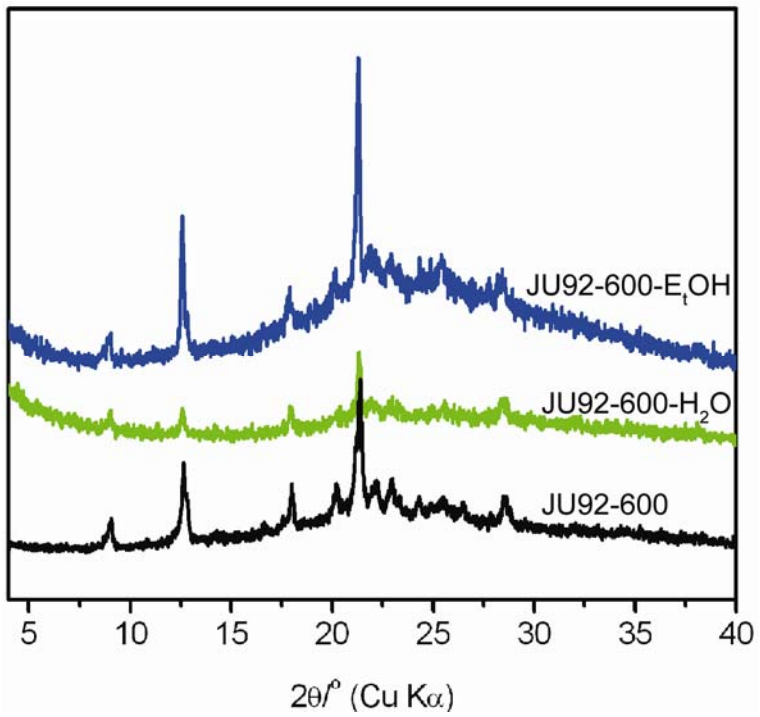


Figure S5. PXRD patterns of JU92-600 and JU92-600 samples immersed in water (JU92-600-H_2O) or ethanol (JU92-600-E_tOH) for 24 hours and dried at room temperature.

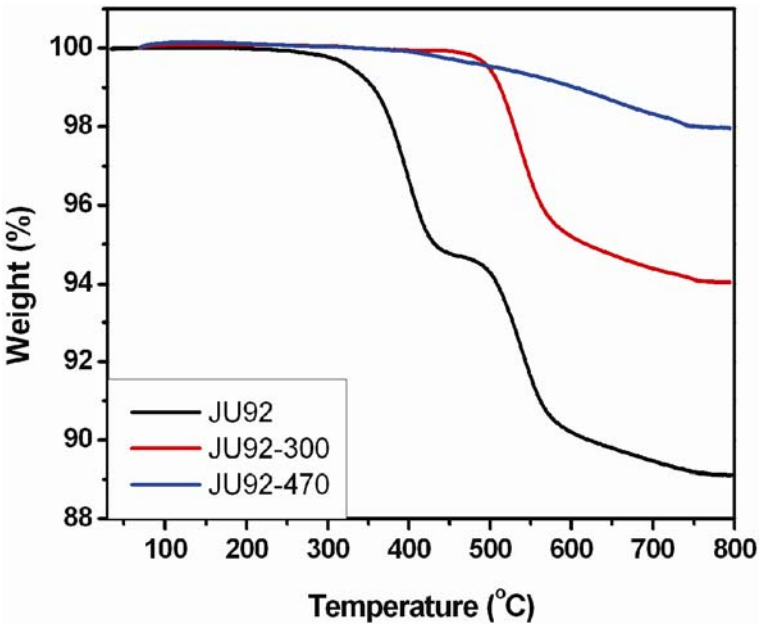


Figure S6. TGA curves of as-synthesized JU92 and calcined JU-92-tem (tem=300, 470).

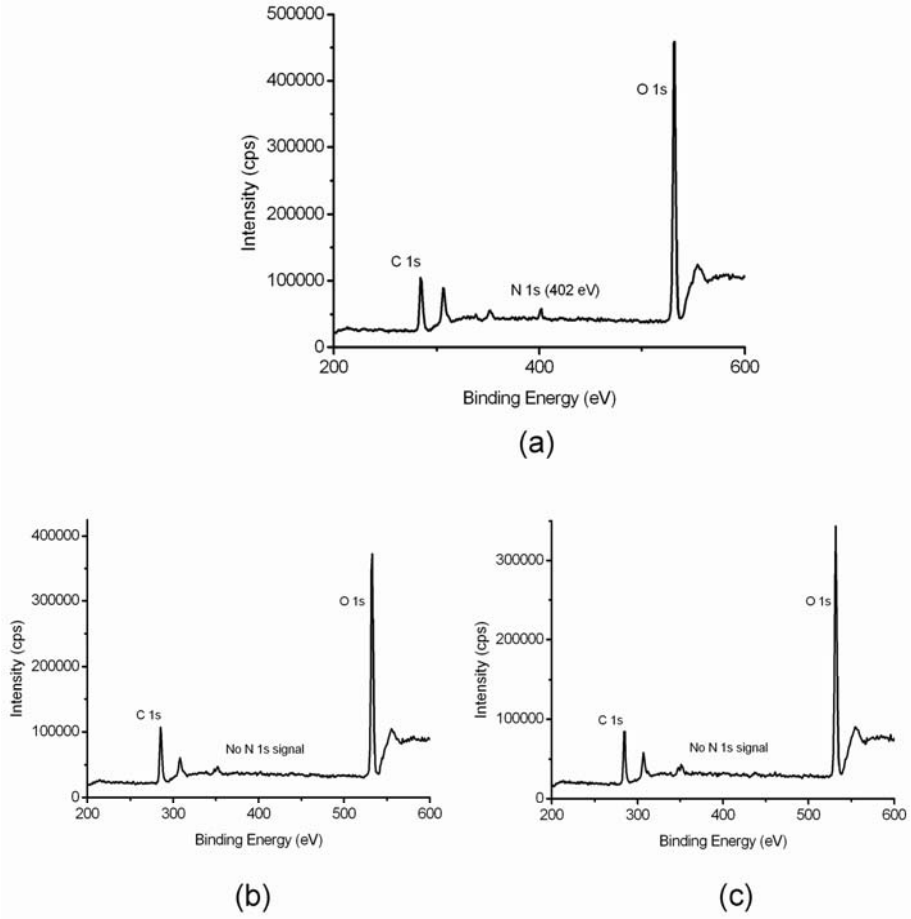


Figure S7. XPS spectra for (a) JU92-300; (b) JU92-470; (c) JU92-550.

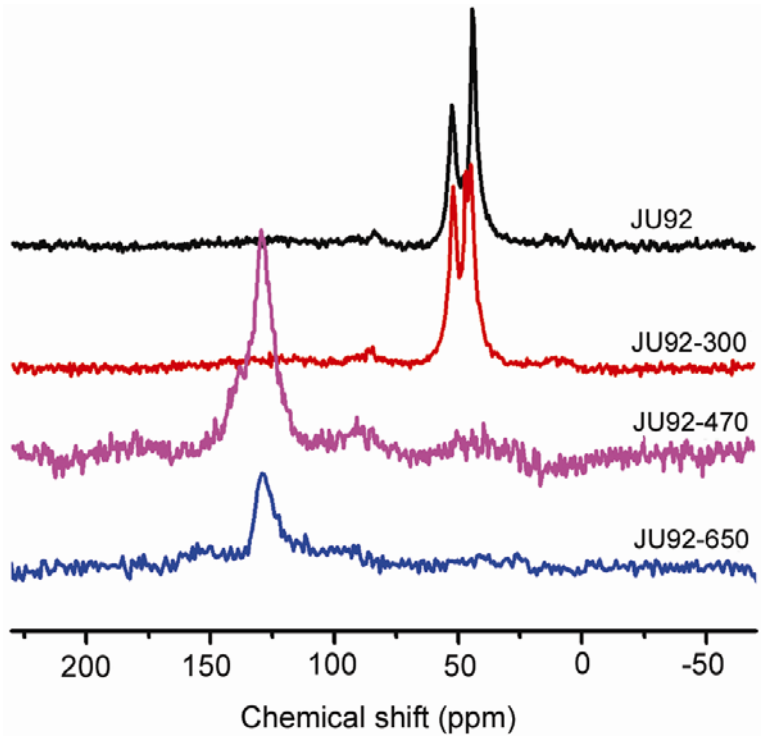


Figure S8. ^{13}C MAS NMR spectra of JU92 and JU92-tem (tem = 300, 470, 650).

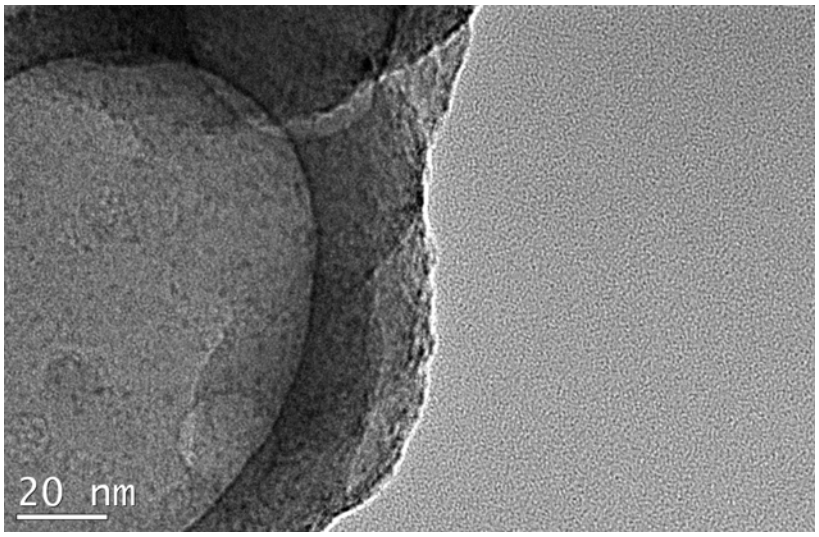
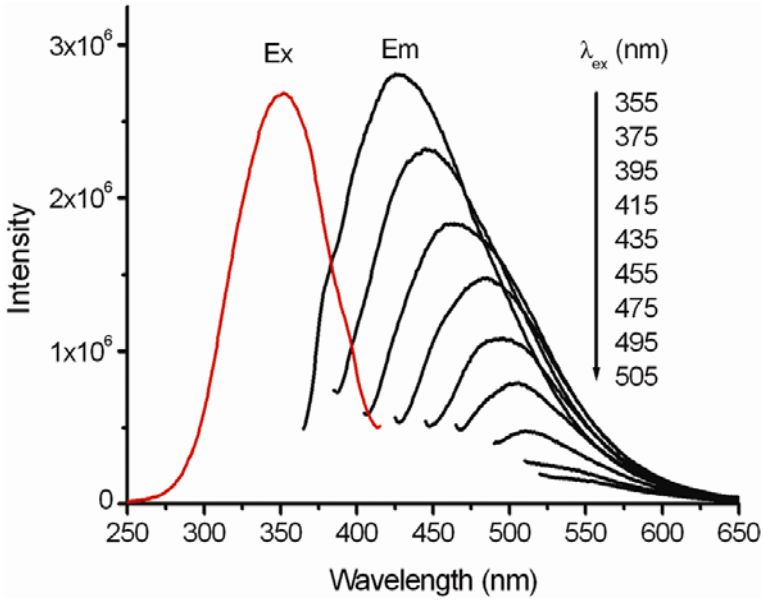
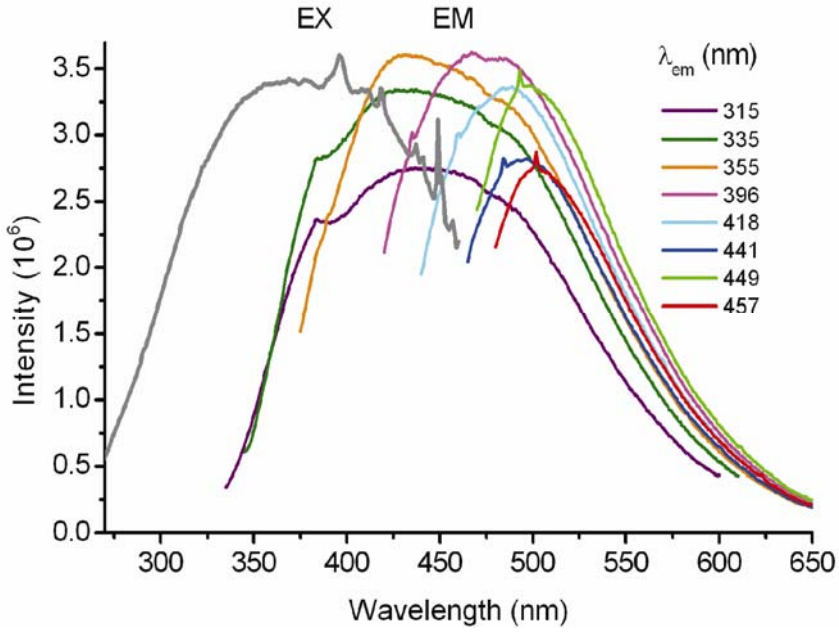


Figure S9. TEM image of JU92-550.

The C-dots with dimensions of 0.7 to 1.5 nm can be observed even though the crystal lattice of magnesium aluminophosphate zeolite is difficult to see in the TEM.



(a)



(b)

Figure S10. (a) Excitation and emission spectra of isolated C-dots aqueous solution (the excitation and emission slit widths are 3.0 nm); (b) excitation and emission spectra of JU92-550 calcined for 24 hours (the excitation and emission slit widths are 1.0 nm).

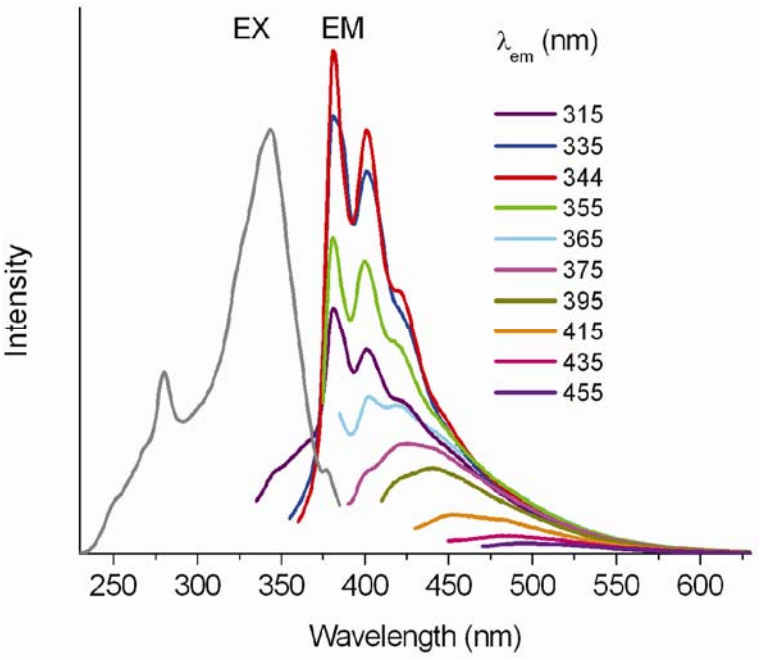


Figure S11. The excitation and emission spectra of isolated C-dots aqueous solution from JU92-700 with excitation wavelengths varied from 315 nm to 455 nm (the excitation and emission slit widths are 4.0 nm).