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A temperature-sensitive luminescent Ag_{20} nanocluster template by carbonate *in situ* generated from atmospheric CO_2 fixation

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(1) Experiment details

All the reagents and solvents employed were commercially available and used as received without further purification. Photoluminescence spectra were measured on a Hitachi F-7000 Fluorescence Spectrophotometer equipped with dewar flask with a Suprasil quartz cold finger. TG curve was measured from 30 to 600 ^{o}C on a SDT Q600 instrument at a heating rate 10 ^{o}C/min under the N_2 atmosphere (100 mL/min). X-ray powder diffractions were measured on a Panalytical X-Pert pro diffractometer with Cu-Kα radiation. C, N, and H analyses were performed on an EA1110 CHNS-0 CE 65 elemental analyzer. IR (KBr pellet) spectra were recorded on a Nicolet Magna750FT-IR spectrometer.

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(2) X-ray Crystallography

Single crystals of the complex **1** with appropriate dimensions were chosen under an optical microscope and quickly coated with high vacuum grease (Dow Corning Corporation) before being mounted on a Nylon loop for data collection. Data for **1** were collected on a Bruker-AXS CCD single-crystal diffractometer with graphite-monochromated Mo Kα radiation source (λ = 0.71073 Å). A preliminary orientation matrix and unit cell parameters were determined from 3 runs of 12 frames each, each frame corresponds to a 0.3° scan in 5 s, followed by spot integration and least-squares refinement. Data were measured using ω scans of 0.3° per frame for 20 s until a complete hemisphere had been collected. Cell parameters were retrieved using SMART software and refined with SAINT on all observed reflections.[1] Data reduction was performed with the SAINT software and corrected for Lorentz and polarization effects. Absorption corrections were applied with the program SADABS.[1] In all cases, the highest possible space group was chosen. All structures were solved by direct methods using SHELXS-97[2] and refined on F^2 by full-matrix least-squares procedures with SHELXL-97.[3] Atoms were located from iterative examination of difference *F*-maps following least squares refinements of the earlier models. Hydrogen atoms were placed in calculated positions and included as riding atoms with isotropic displacement parameters 1.2-1.5 times U_{eq} of the attached C atoms. All structures were examined using the Addsym subroutine of PLATON[4] to assure that no additional symmetry could be applied to the models.

Two of the tert-butyl groups (C10-C12 and C18-C20) show rotational disorder, and was refined with equal occupancies. The carbonate ion (O13, O14, O15) was disordered with equal occupancies related to the inversion centre. The Ag9 atom was disordered and refined with splitting mode. The occupancy factor of the disordered Ag atoms is Ag9:Ag9a 0.60:0.40.

(1) Bruker. *SMART, SAINT and SADABS.* Bruker AXS Inc., Madison, Wisconsin, USA, 1998.

(2) G. M. Sheldrick, *SHELXS-97, Program for X-ray Crystal Structure Determination*, University of Gottingen, Germany, 1997.

(3) Sheldrick, G. M. *SHELXL-97, Program for X-ray Crystal Structure Refinement*, University of Gottingen, Germany, 1997.

(4) A. L. Spek, *Implemented as the PLATON Procedure, a Multipurpose Crystallographic Tool*, Utrecht University, Utrecht, The Netherlands, 1998.

(3) Synthesis of complex 1

Complex **1** was synthesized by the room temperature reaction of 0.02 mmol [AgSBu^t]$_n$ precursor with 0.1 mmol $AgNO_3$ in 4 mL methanol–ethanol–DMF (v : v : v = 1 : 1 : 1). The mixture was treated under ultrasonic condition until clear solution is obtained. The resultant solution was allowed to evaporate slowly in darkness at room temperature for three days to give colorless crystals (yield: 73 %). Elemental analysis calcd (%) for $C_{59}H_{132}Ag_{20}N_{14}O_{33}S_{10}$: C 17.52, H 3.29, N 4.85; Found (%) C 17.22, H 3.02, N 4.66. Selected IR peaks (cm^{-1}): 1667 (s), 1485 (m), 1462 (s), 1434 (s), 1350 (m), 1098 (s), 780 (m), 742 (s), 691 (m), 621 (m), 514 (m), 476 (m).

(4) Table S1 Selected bond distances (Å) and angles (°) for 1

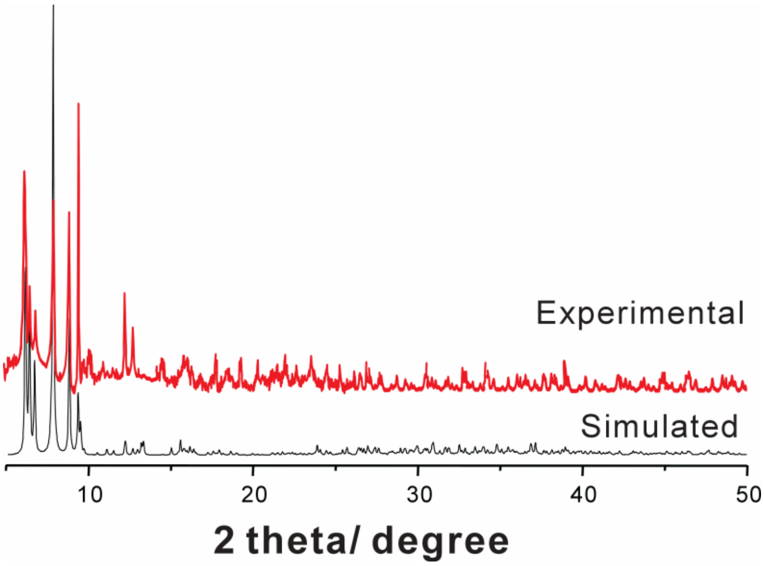
Ag1—Ag2	3.047(2)	Ag4—S5	2.434(5)
Ag1—Ag4	3.057(2)	Ag5—S1	2.584(6)
Ag1—Ag5	3.079(2)	Ag5—S4	2.541(6)
Ag1—Ag6	3.060(2)	Ag6—S3	2.432(5)
Ag2—Ag3	3.088(2)	Ag6—S4	2.435(5)
Ag2—Ag4	3.018(2)	Ag7—S2	2.436(5)
Ag2—Ag7	2.995(3)	Ag7—S3	2.434(5)
Ag3—Ag7	3.136(3)	Ag8—S2	2.563(6)
Ag3—Ag8	3.266(3)	Ag8—S4^{i}	2.517(6)
Ag3—Ag9^{i}	2.991(4)	Ag9—S4	2.400(7)
Ag5—Ag6	2.958(2)	Ag9—S5^{i}	2.334(7)
Ag5—Ag8^{i}	3.102(2)	Ag10—S1	2.389(5)
Ag5—Ag10	2.957(3)	Ag10—S2^{i}	2.388(5)
Ag6—Ag9	3.224(5)	Ag1—O5	2.338(17)
Ag7—Ag10^{i}	3.179(3)	Ag1—O12	2.548(18)
Ag8—Ag10^{i}	3.289(3)	Ag2—O4	2.452(17)
Ag1—S1	2.502(5)	Ag2—O10	2.426(14)
Ag1—S3	2.487(5)	Ag4—O13	2.46(2)
Ag2—S3	2.531(5)	Ag4—O14	2.56(3)
Ag2—S5	2.516(5)	Ag5—O7	2.346(14)
Ag3—S2	2.487(5)	Ag6—O14	2.52(3)
Ag3—S5	2.478(5)	Ag7—O13	2.49(2)
Ag4—S1	2.440(5)	Ag8—O11	2.287(17)
S3—Ag1—S1	124.86(17)	S5—Ag4—O13	86.3(6)
S3—Ag1—O12	110.4(5)	S5—Ag4—O14	112.6(6)
O5—Ag1—S1	101.2(5)	O13—Ag4—O14	26.6(7)
O5—Ag1—S3	120.8(4)	S4—Ag5—S1	129.71(18)
O5—Ag1—O12	94.3(7)	O7—Ag5—S1	113.4(5)
S5—Ag2—S3	126.97(17)	O7—Ag5—S4	112.5(5)
O4—Ag2—S3	105.8(5)	S3—Ag6—S4	162.45(19)
O4—Ag2—S5	117.9(6)	S3—Ag6—O14	83.8(7)
O10—Ag2—S3	111.0(5)	S4—Ag6—O14	108.1(7)
O10—Ag2—S5	103.7(5)	S2—Ag7—O13	108.0(8)
O10—Ag2—O4	82.0(7)	S3—Ag7—S2	160.03(18)
S5—Ag3—S2	126.18(17)	S3—Ag7—O13	84.2(7)
O2—Ag3—S2	111.2(4)	S4^{i}—Ag8—S2	113.21(17)
O2—Ag3—S5	122.2(4)	O11—Ag8—S2	128.2(5)
S1—Ag4—O13	108.0(7)	O11—Ag8—S4^{i}	118.6(5)

Symmetry codes: (i) 2-*x*,1-*y*,1-*z*

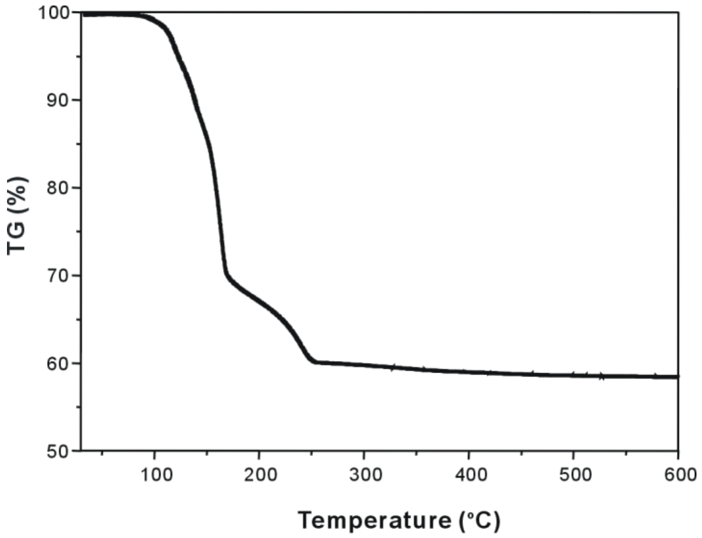
(5) Table S2: Crystal data for 1

Empirical formula	$C_{59}H_{132}Ag_{20}N_{14}O_{33}S_{10}$
Formula weight	4043.79
Temperature/K	120(2)
Crystal system	monoclinic
Space group	$P2_1/n$
a/Å	16.9534(18)
b/Å	12.6293(13)
c/Å	26.729(3)
α/°	90.00
β/°	92.474(2)
γ/°	90.00
Volume/Å^3	5717.5(10)
Z	2
ρ_{calc}mg/mm^3	2.349
μ/mm^{-1}	3.590
F(000)	3896.0
Crystal size/mm^3	0.12 × 0.10 × 0.08
Index ranges	$-20 \leq h \leq 19$, $-8 \leq k \leq 15$, $-31 \leq l \leq 31$
Reflections collected	27333
Independent reflections	10019[R(int) = 0.0815]
Data/parameters	10019/195/692
Goodness-of-fit on F^2	1.001
Final R indexes [I>=2σ (I)]	R_1= 0.0888, wR_2= 0.1933
Final R indexes [all data]	R_1= 0.1661, wR_2= 0.2309
Largest diff. peak/hole / e Å^{-3}	2.21/-1.56

(6) Fig. S1: PXRD patterns for (a) simulated 1, (b) as-synthesize



(7) Fig. S2: The TGA curves of 1



(8) Fig. S3: The IR spectrum of 1