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ARTICLES

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Hypersensitive dual-function luminescence switching of a silver-chalcogenolate cluster-based metal–organic framework

Ren-Wu Huang[1†], Yong-Sheng Wei[1†], Xi-Yan Dong[1], Xiao-Hui Wu[1], Chen-Xia Du[1], Shuang-Quan Zang[1*] and Thomas C. W. Mak[1,2]

[1]*College of Chemistry and Molecular Engineering, Zhengzhou University, Zhengzhou 450001, China*

[2]*Department of Chemistry and Center of Novel Functional Molecules, The Chinese University of Hong Kong, Shatin, New Territories, Hong Kong SAR. China*

Md Bodiuzzaman
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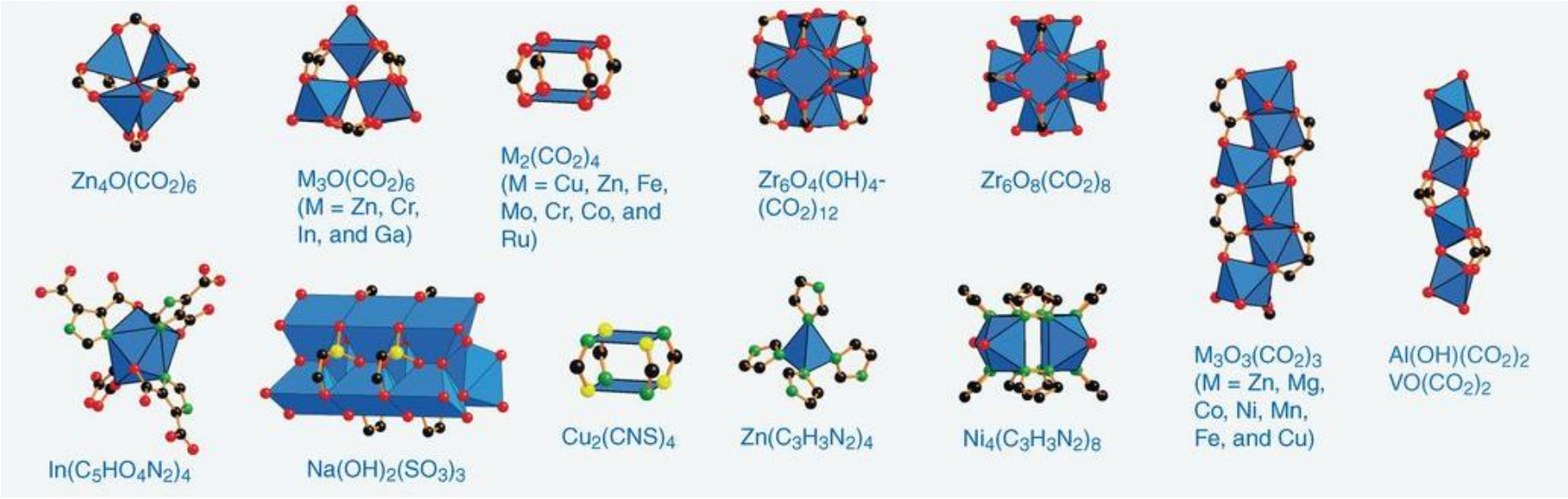
Metal–organic frameworks (MOFs) or porous coordination polymers (PCPs), in which organic ligands connect metal ion via coordination bonds, have become a prominent class of crystalline materials in separation, storage, catalysis, chemical sensing and luminescent signalling devices.

MOFS are constructed by joining metal-containing units [secondary building units (SBUs)] with organic linkers, using strong bonds to create open crystalline frameworks with permanent porosity.

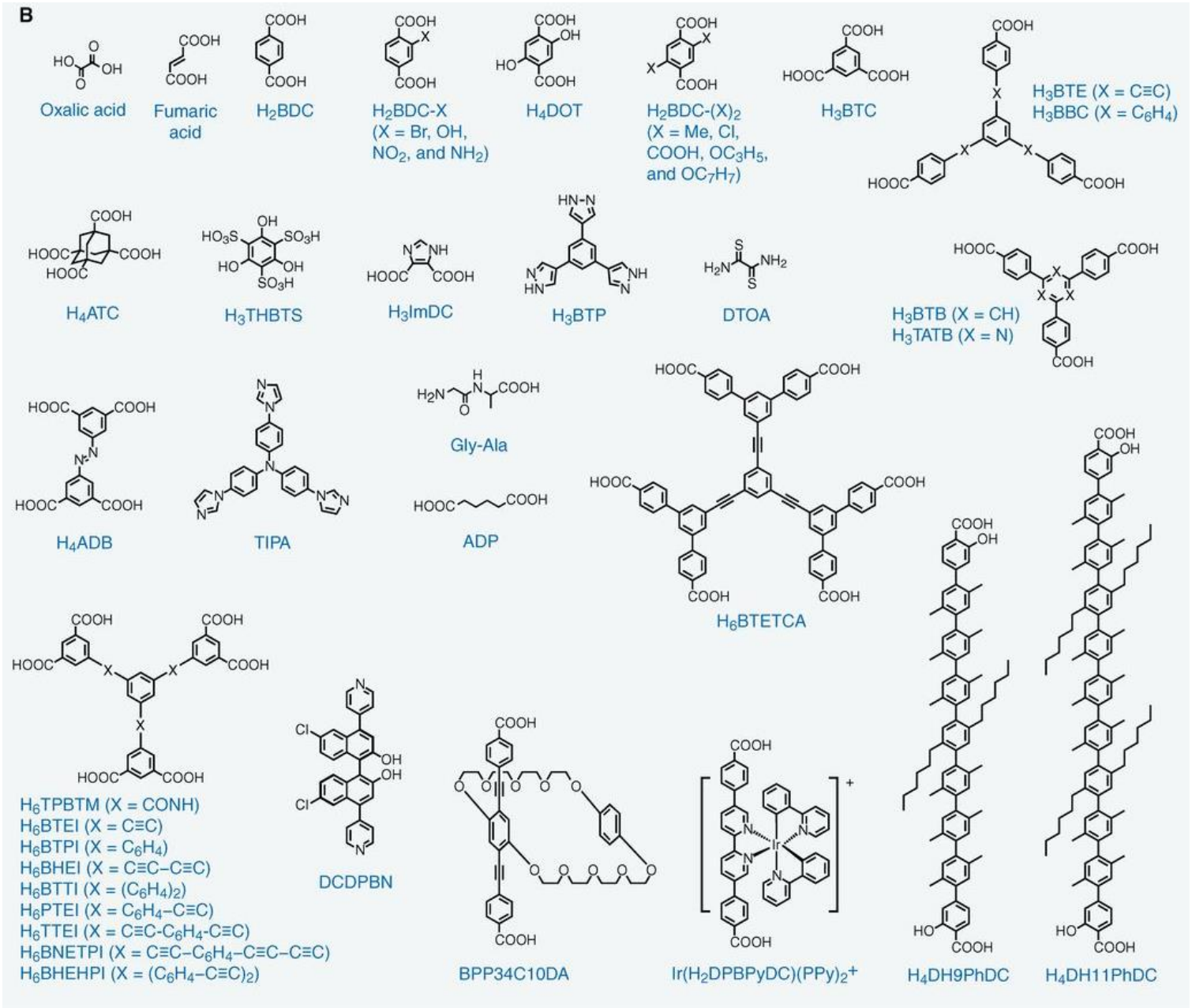
The flexibility with which the constituents' geometry, size, and functionality can be varied has led to more than 20,000 different MOFs being reported and studied within the past decade.

Inorganic secondary building units

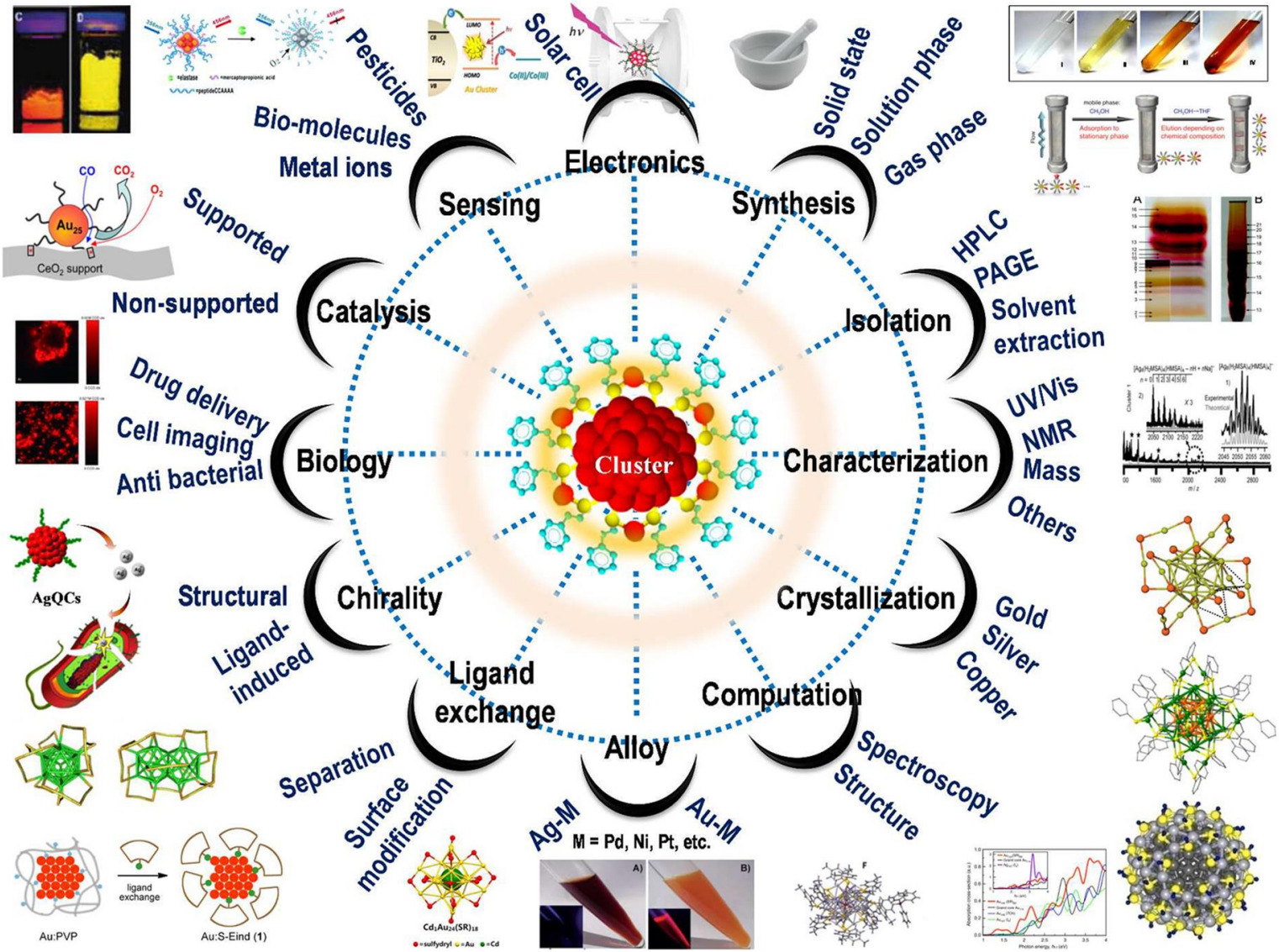


Color code: black, C; red, O; green, N; yellow, S; purple, P; light green, Cl; blue polyhedra, metal ions.

Organic linkers



The Chemistry and Applications of Metal-Organic Frameworks. Hiroyasu Furukawa, Kyle E. Cordova, Michael O'Keeffe, Omar M. Yagh, *Science*, 2013



Atomically Precise Clusters of Noble Metals: Emerging Link between Atoms and Nanoparticles. Indranath Chakraborty and Thalappil Pradeep , *Chem. Rev* 2017

Cluster is no more only cluster, it has become material. Clusters are new materials for future.

The composite properties of noble metal nanoclusters and MOFS.

Gram-scale production and ultrahigh thermal and photo stability.

Easy to crystallize.

In the present study, a luminescent dodecanuclear SCC $[(Ag_{12}(S^tBu)_6(CF_3COO)_6(CH_3CN)_6]\cdot CH_3CN$ was first prepared.

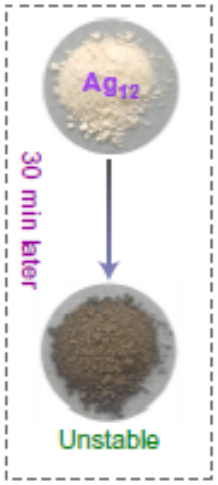
The linear bridging ligand 4,4′-bipyridine (bpy) was used to replace the coordinated CH_3CN ligands of Ag_{12} to construct the rigid SCC-based MOF $[(Ag_{12}(S^tBu)_8(CF_3COO)_4(bpy)_4)]_n$
(Ag_{12}bpy), in which the secondary building units (SBUs) are transformed quasi-isomers of Ag_{12} generated by induction of incoming bpy ligands.

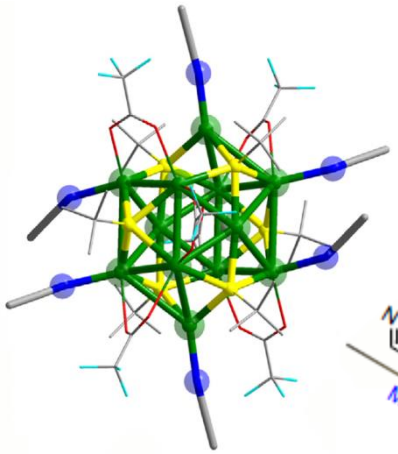
Markedly enhanced stability (from minutes to one year) under ambient conditions and an ~60-fold increase in the RT luminescence quantum yield (QY from 0.2 to 12.1%) were observed from Ag_{12} to Ag_{12}bpy.

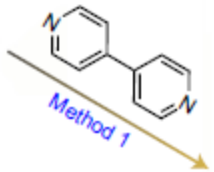
Its adaptable electronic properties (responsible for emission) and rigid open channels endow Ag_{12}bpy with ultrafast dual-function luminescent switching, which is rare among reported MOFs, with ‘turn-off” switching by O_2 and multicolour ‘turn-on’ switching by VOCs.

Its switching mechanism was elucidated by analysing the single-crystal structures of the crystalline inclusion complexes Ag_{12}bpy·O_2 and Ag_{12}bpy·VOCs.

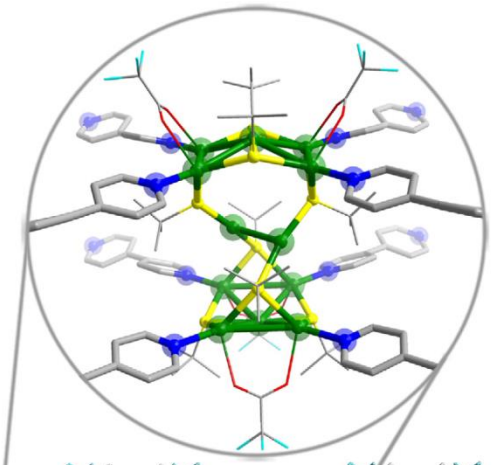
Synthesis and crystal structure of Ag_{12}bpy and observation of its microporosity

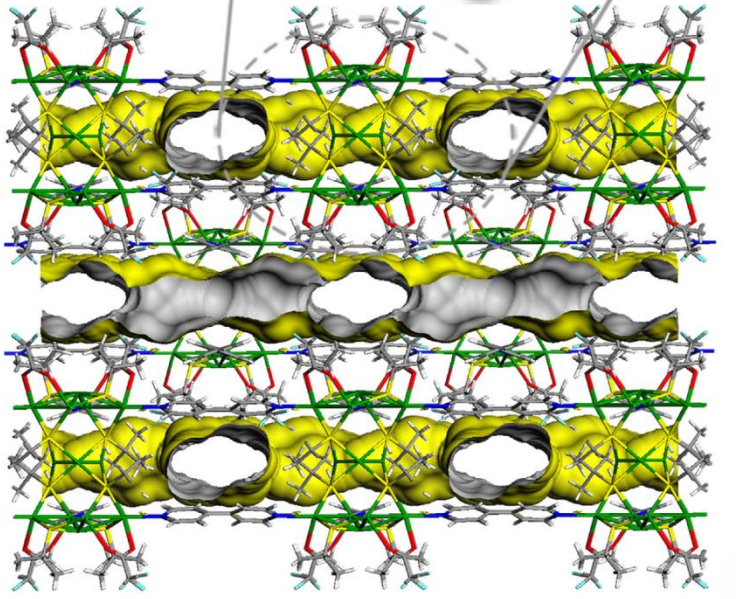


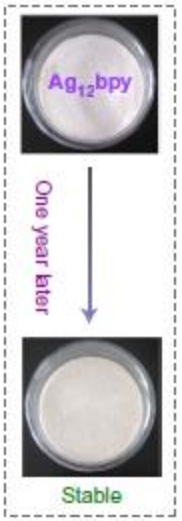


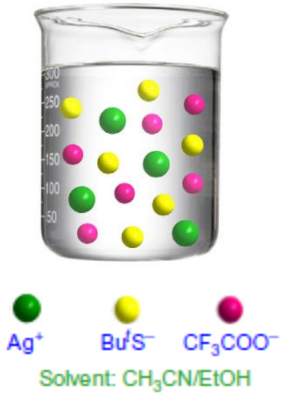


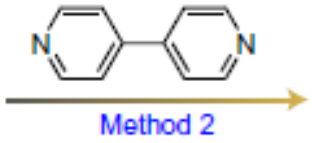
$[(Ag_{12}(S^tBu)_6(CF_3COO)_6(CH_3CN)_6]\cdot CH_3CN$

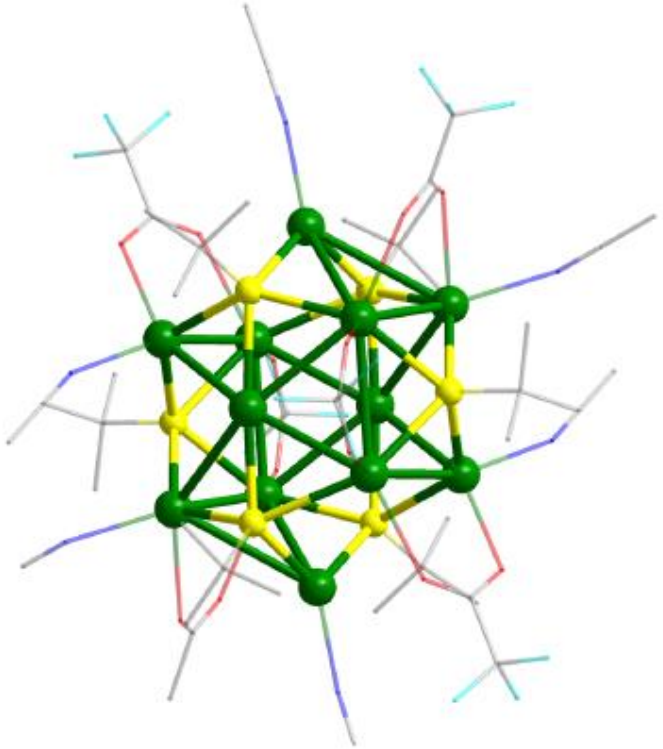


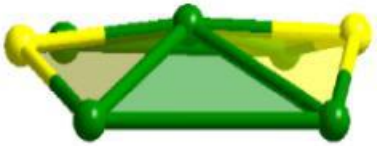




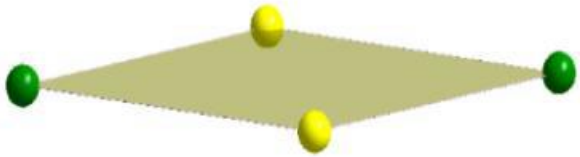






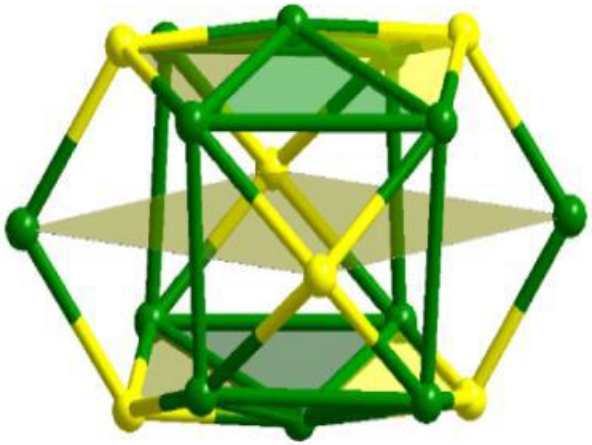


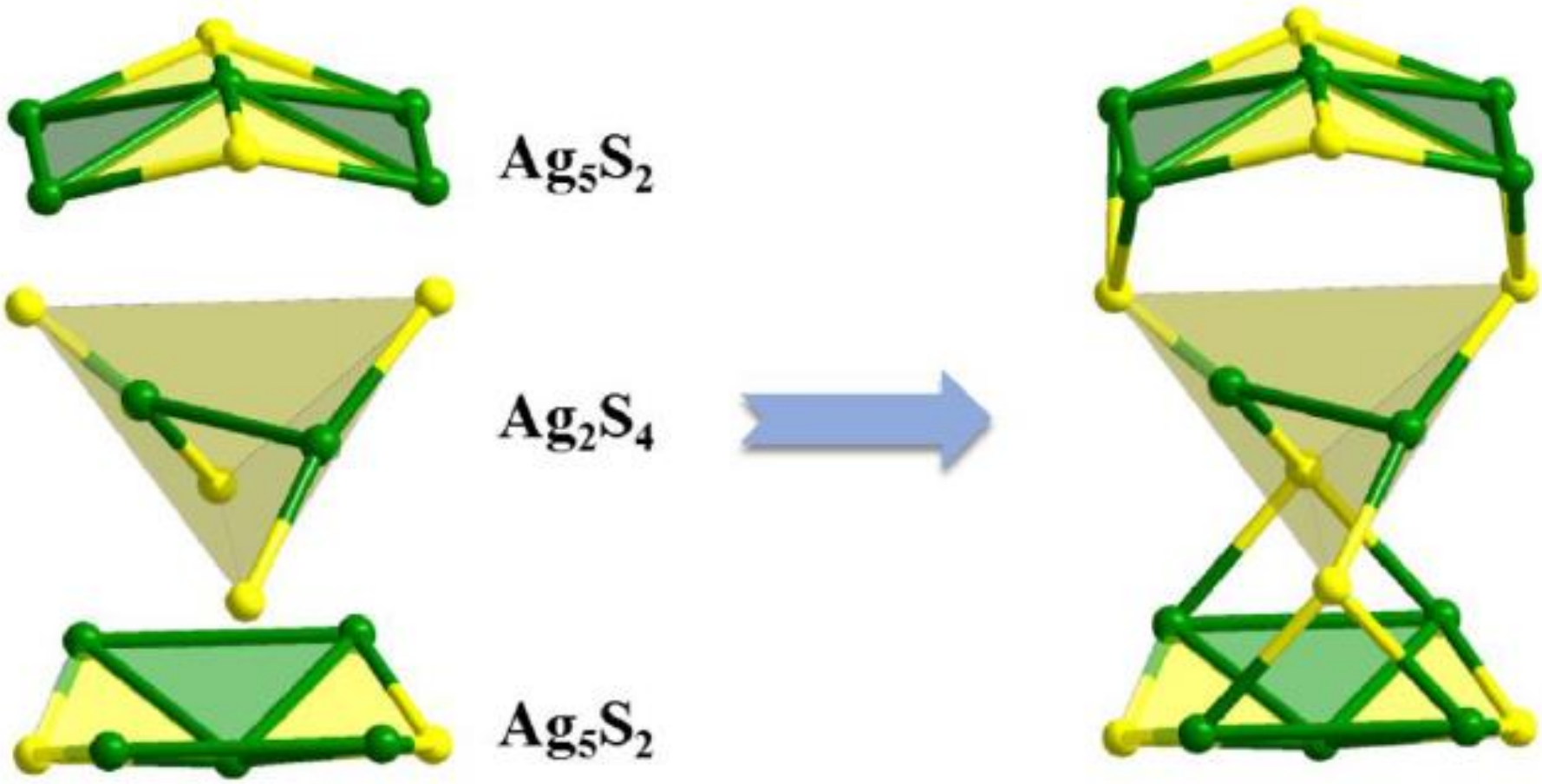
Ag_5S_2



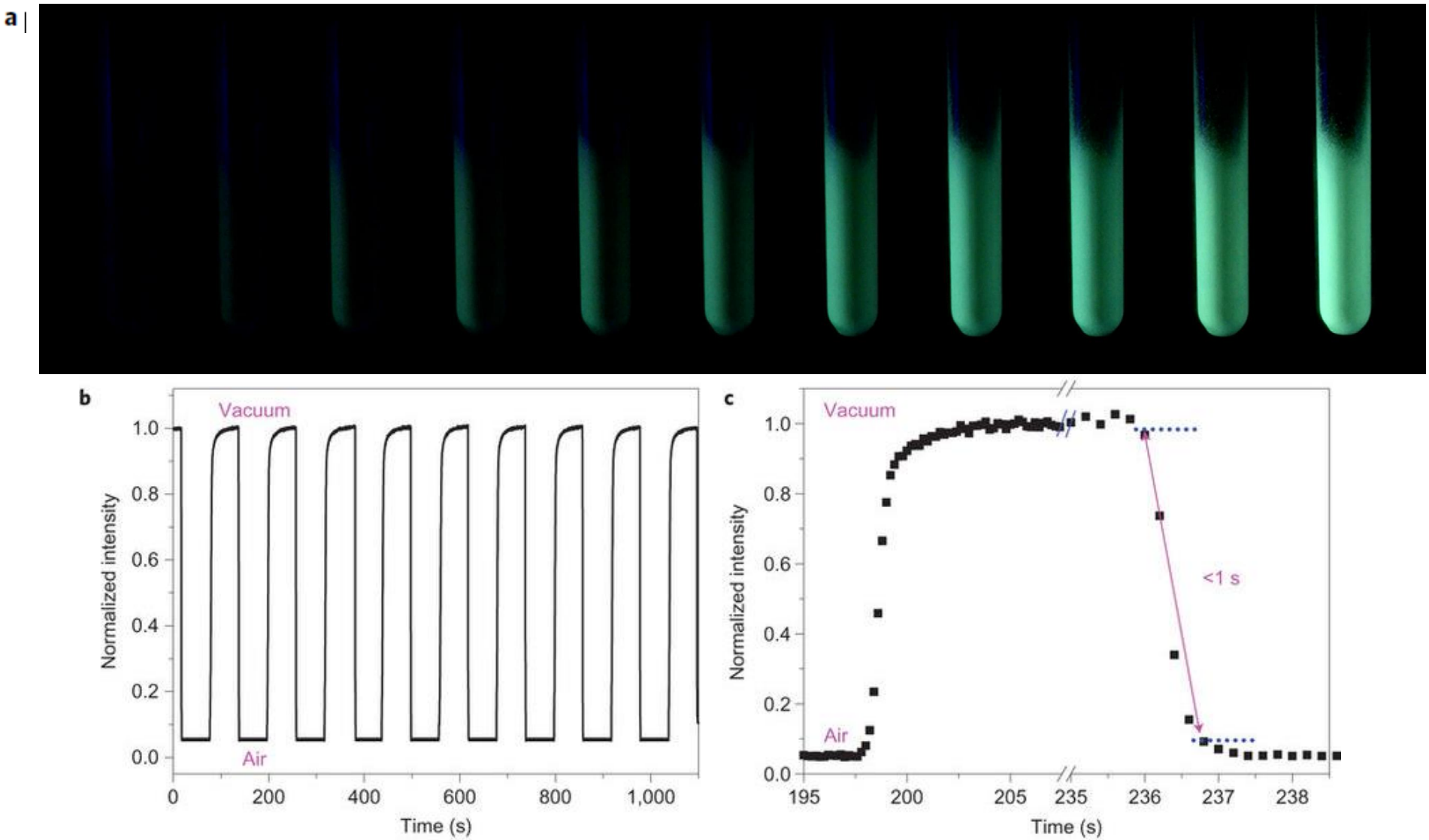
Ag_2S_2

Ag_5S_2

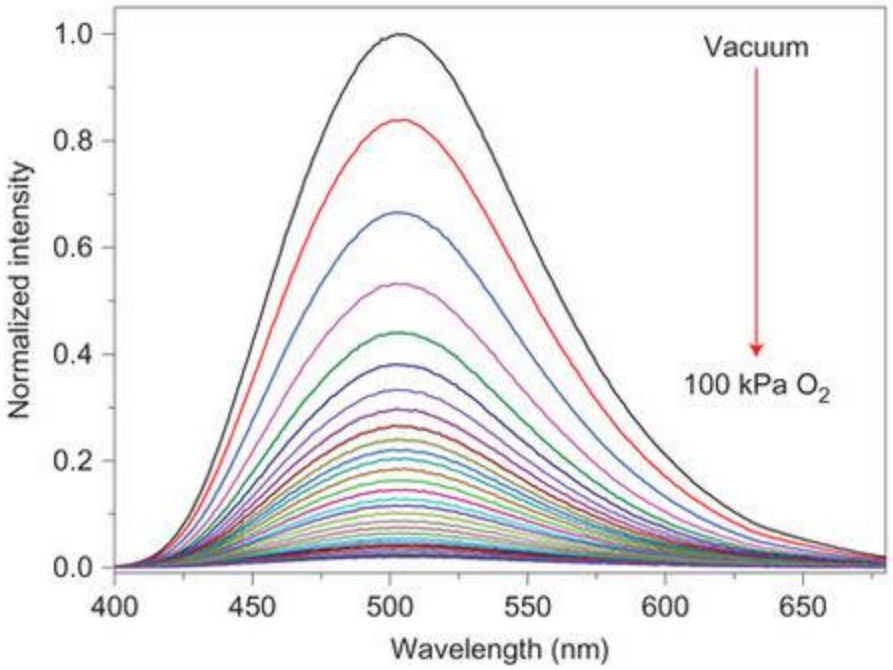


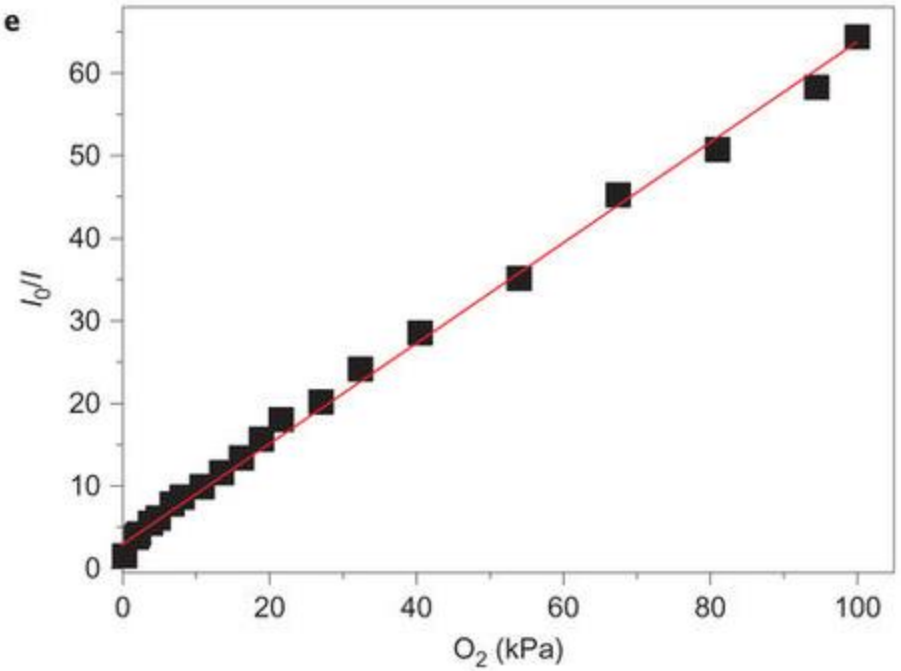

Ag_5S_2
Ag_2S_4
Ag_5S_2

Luminescent quenching response to O_2



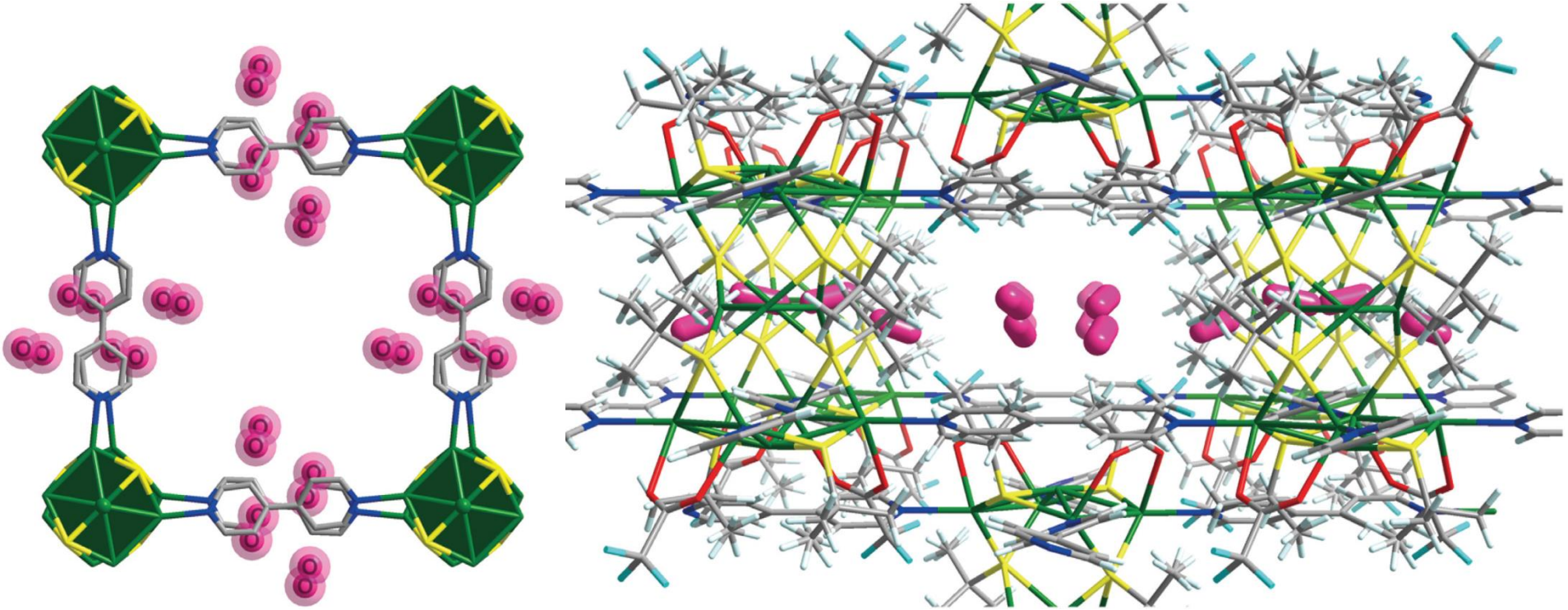
a, Photographs of Ag_{12}bpy excited by 365 nm light in a glass tube from vacuum to air. b, Reversible luminescence on–off cycles under alternating exposure to air/vacuum for Ag_{12}bpy. c, Enlargement of the response transient curves of Ag_{12}bpy with air. The air-quenching response time was less than 1 s (the response time is defined as that corresponding to a 90% decrease in emission intensity when the gas phase is changed from vacuum to air.





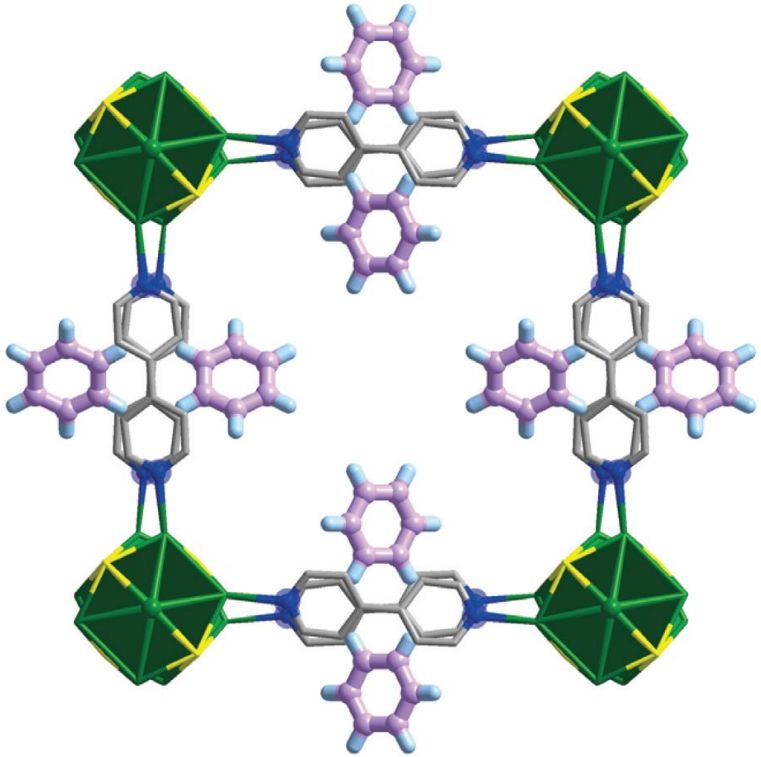
d, Emission spectra at different O2 pressures (excited at 365 nm) from vacuum to 100 kPa O2. e, Representative Stern–Volmer plot of O2.

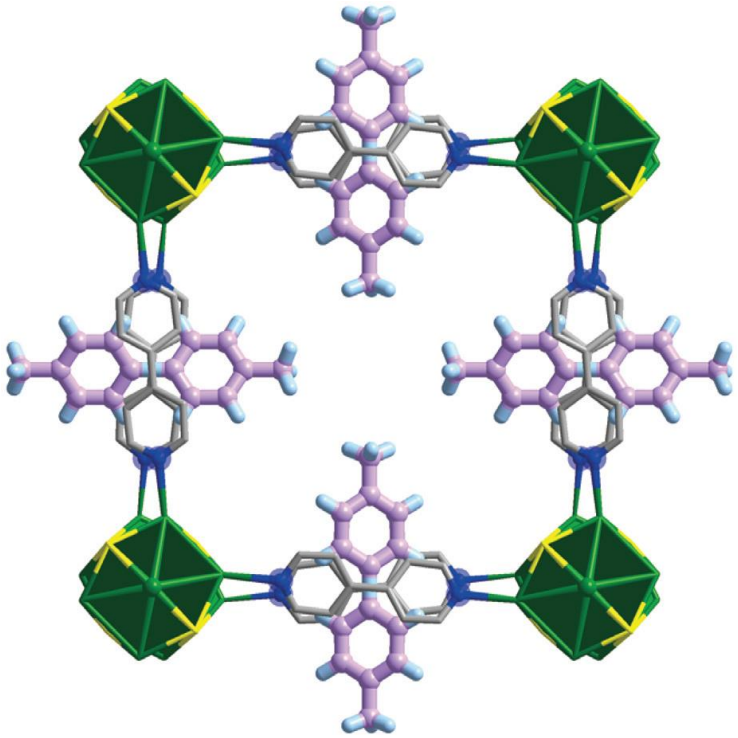
Sites of guests in the cavity of $Ag_{12}bpy$

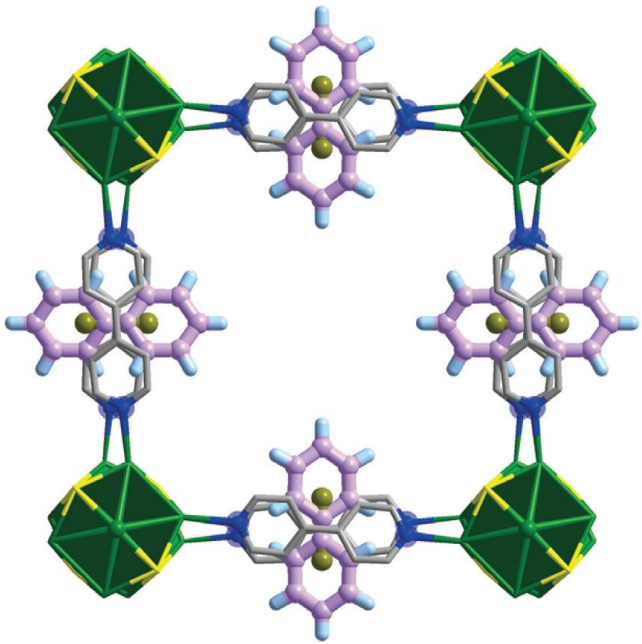


Molecular O_2 interacts more readily with the bpy linkers that correlate with its LUMO (lowest unoccupied molecular orbital), transfers the triplet energy and quenches its emission

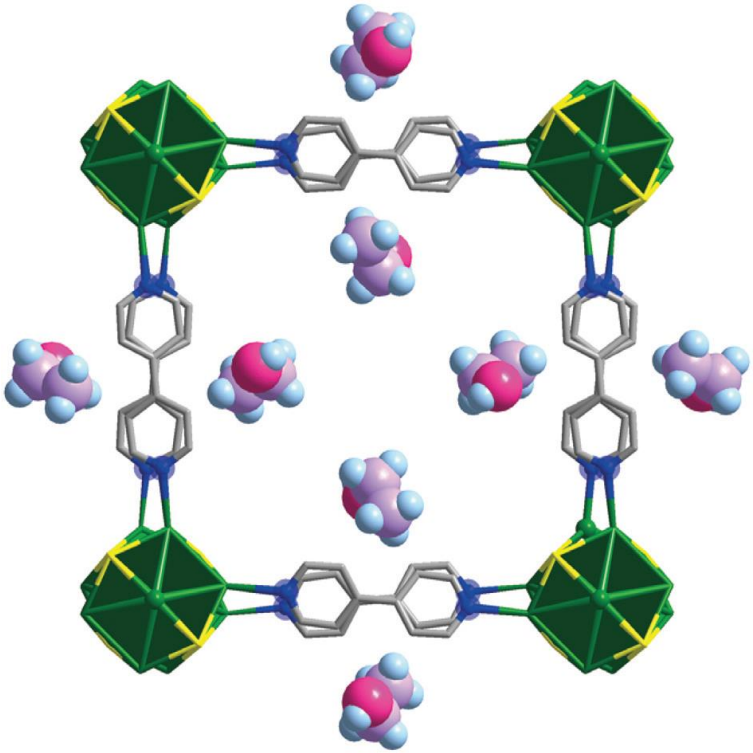
View of $Ag_{12}bpy{\cdot}O2$ structure along the c and a directions, respectively.

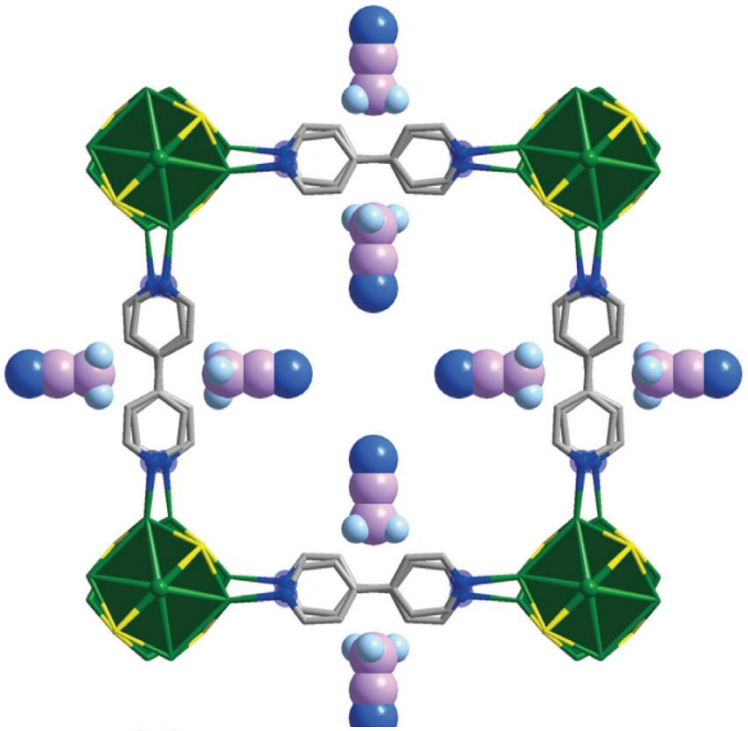


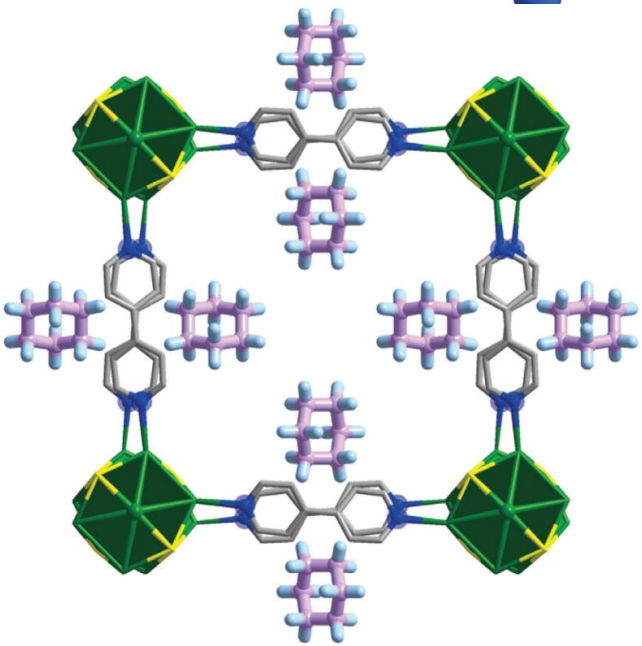




View of Ag_{12}bpy·VOCs(benzene, toluene, bromobenzene).

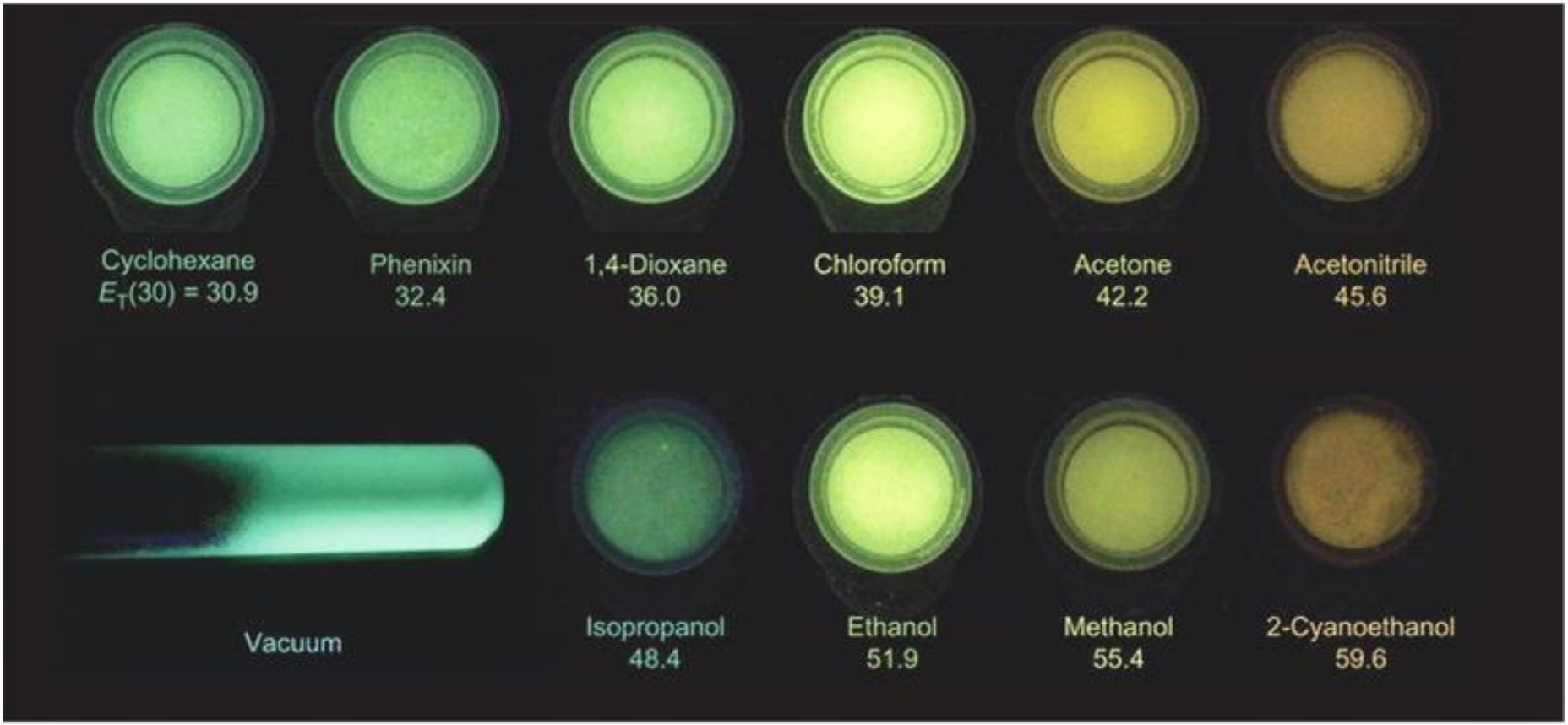






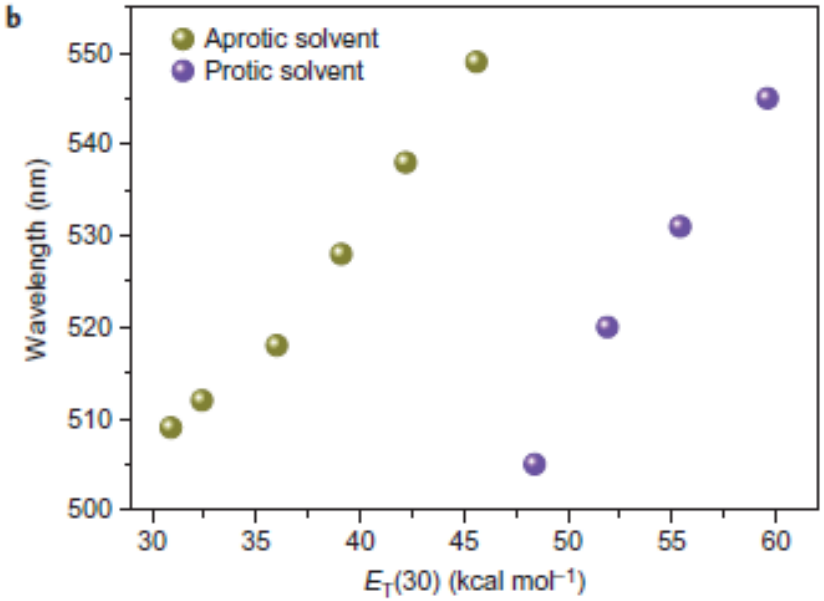
View of Ag_{12}bpy·VOCs (ethanol, acetonitrile, cyclohexane).

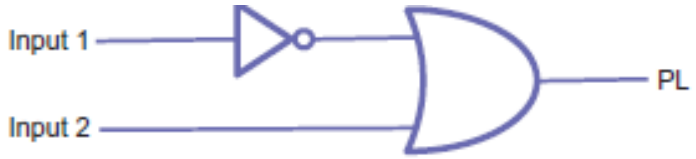
Vapochromic responses of Ag_{12}bpy and logic gate



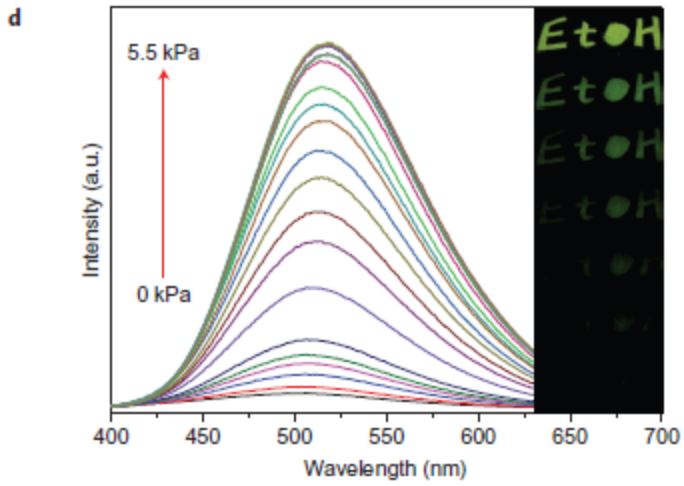
The intercalation of VOCs occupies the channels and impedes contact of O_2 with the host framework, which consequently turns on the emission of Ag_{12}bpy.

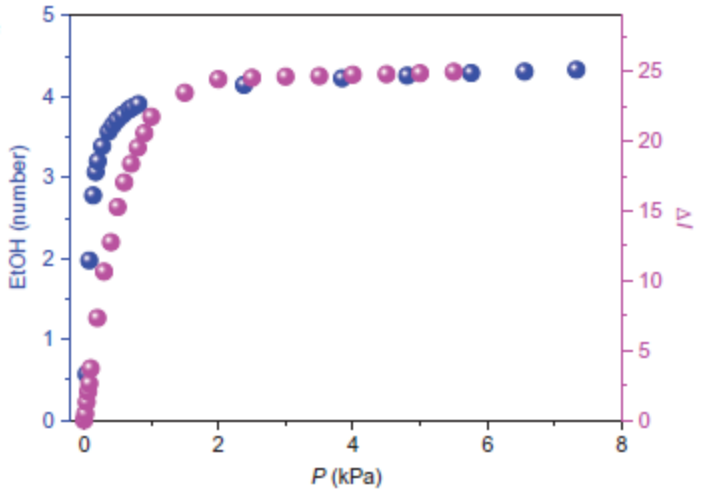
Photographs of luminescence responses of Ag_{12}bpy·VOCs under an ultraviolet lamp (365 nm).



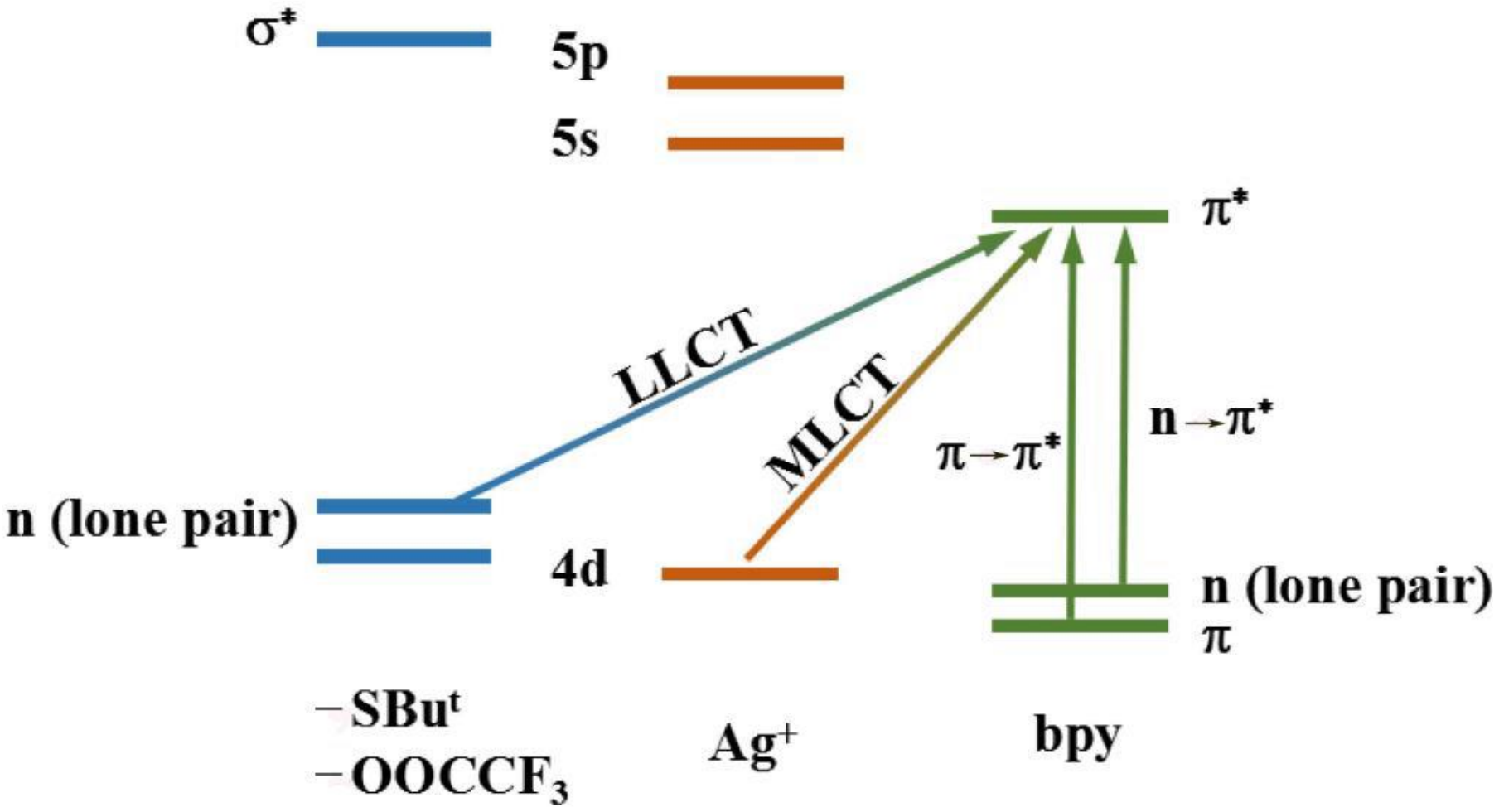


Input 1	Input 2	Output
O_2	VOCs	PL
1	0	0 (off)
1	1	1 (on)
0	1	1 (on)
0	0	1 (on)





b, Maximum emission against the solvent ET(30) values. c, A two-input IMPLICATION (a combination of NOT and OR logic functions) logic gate and truth table. Input 1: O_2; Input 2: VOCs. Output: photoluminescence (PL). d, Emission spectra of Ag_{12}bpy at different EtOH partial pressures (excitation at 365 nm) in the air mixture. Inset: tracking photographic record of the escape of EtOH in air in 1 min. e, Adsorption isotherm for EtOH and relative change in emission intensity [ΔI = (Iethanol − Iair)/Iair)] as a function of ethanol vapour pressure at 298 K.



Energy and transition diagram of Ag_{12}bpy. The orbitals of bpy are clearly related to the emissive excited state in Ag_{12}bpy. The excited-state responsible for luminescence is assigned to a metal-to-ligand (MLCT) and ligand-to-ligand (LLCT) charge transfer.

In summary, this work explored silver(I) chalcogenide/chalcogenolate clusters as new building blocks to design and synthesize a lightemitting porous metal–organic framework.

This novel SCC-MOF overcomes the problematic instability of SCCs to exhibit remarkably improved luminescence properties.

Its permanent open channel provides a platform for various applications in host–guest chemistry.

Ultrafast dual-functional, turn-off fluorescence switching by O2 and multicoloured turn-on fluorescence switching by VOCs were obtained.

This work successfully demonstrates that the designed construction of SCC-MOFs opens a route to functional metal (Ag, Au, Cu, Pd)-cluster-based MOFs exhibiting enhanced stability and desirable photophysical properties for chemical sensing, catalysis and optoelectronic devices.

Thank you